NIPU
NON-ISOCYANATE POLYURETHANES

TOWARDS GREENER COMPOSITES: ARE POLYHYDROXYURETHANES SUITABLE FOR NATURAL FIBERS COMPOSITES?

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MSCA-ITN-EJD
H2020-EU

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MARIE CURIE ACTIONS

Polyurethanes, commodity polymers…

Thermoset (TS)

Foams 66%

Polyurethanes (PUs) Applications

TS + some TP

Adhesives 6%

Coatings 7%

TS

TS & TP (25%)

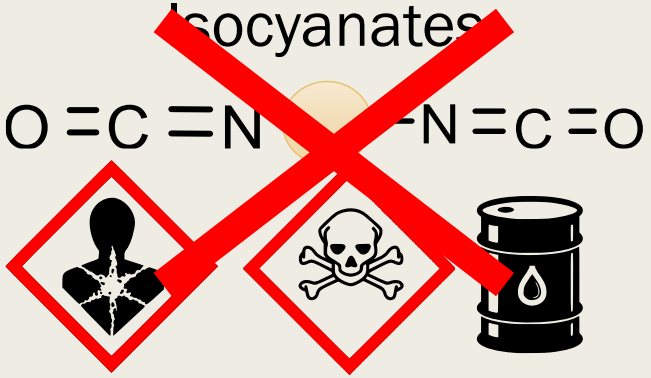
Elastomers & Other (21%)

GLOBAL MARKET :

- 50 billion USD (2021)
  → 82 billion USD (2028)
- 25 million tons (2021)
  → 6th more produced polymer
- Mostly Thermoset

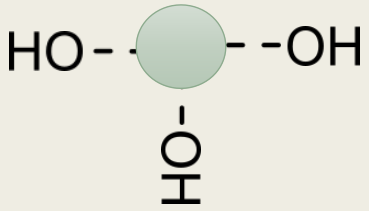
(Market&Market,2022)

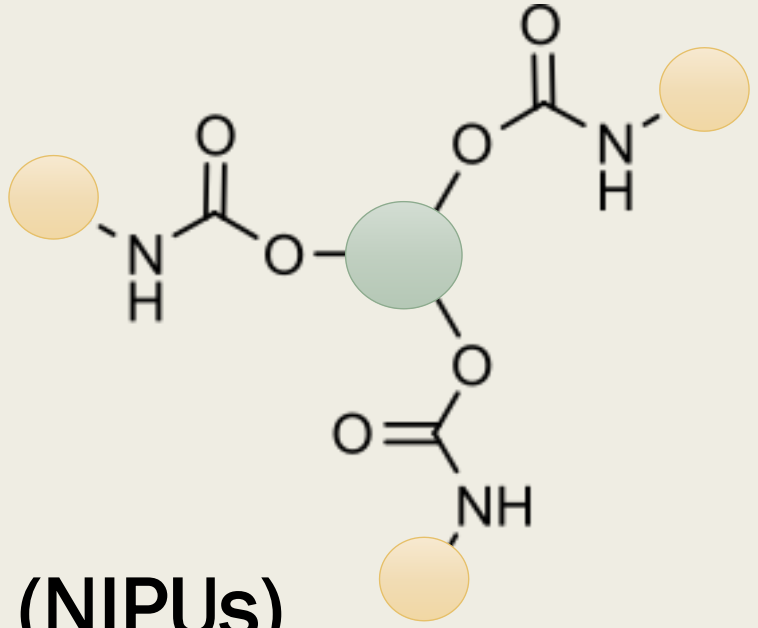
...To replace



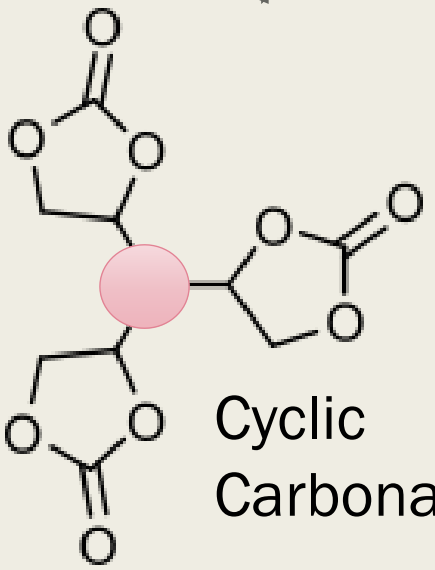
+

Polyols



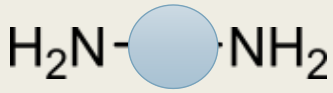


Non-Isocyanate Polyurethanes (NIPUs)

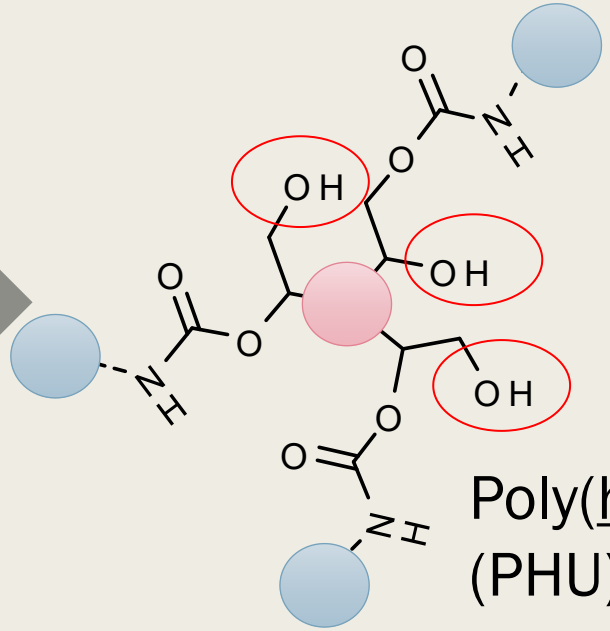


Cyclic Carbonates

+

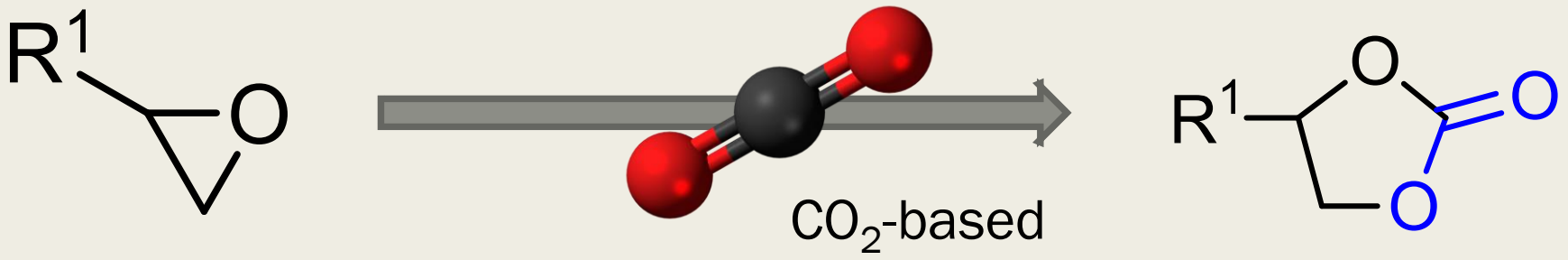


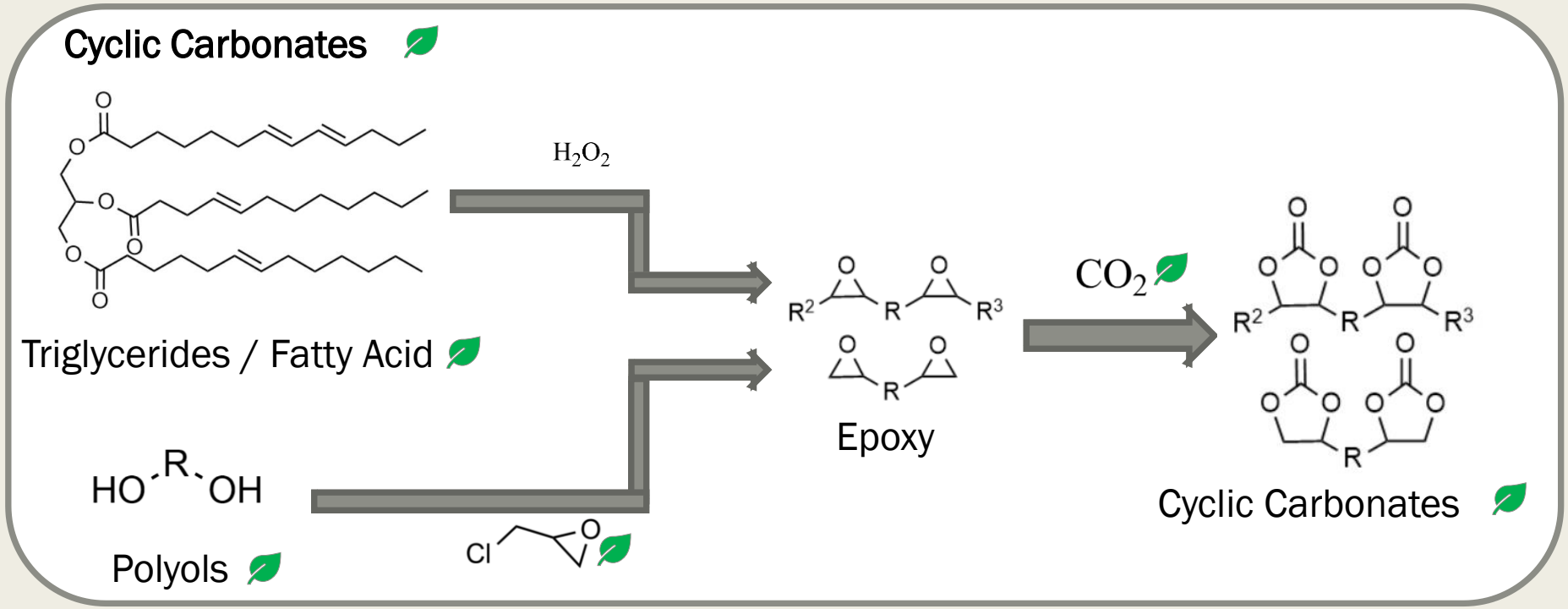
Primary Amines



Poly(hydroxyurethane) (PHU)

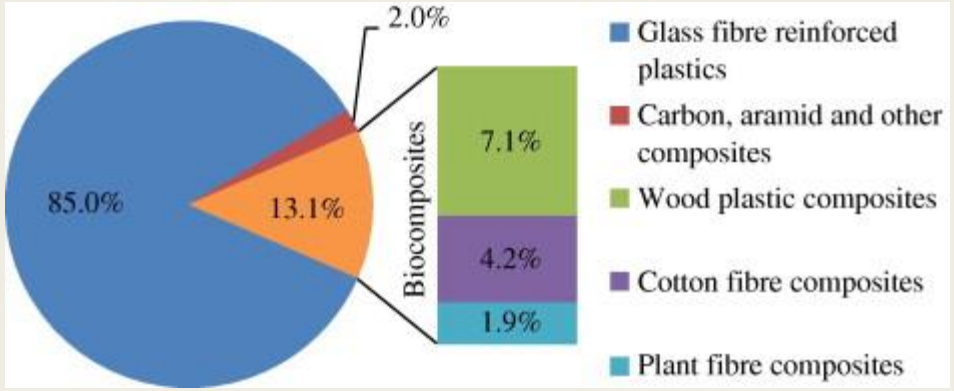
Poly(hydroxyurethane) (PHU), a sustainable NIPU





Potentially biobased or biobased

Natural fibers – Sustainable & Strong composite reinforcement



M.Carus, Bio-composites: Technologies, applications and markets,2010

	E (GPa)	σ (MPa)	ε (%)	E/ρ	σ/ρ	ρ (g/cm3)
E-Glass	70	2000-3000	2.5	28.3	866	2.5
Flax	37-75	600-1500	1.2-3.6	**27-80**	**230–1220**	**1.5**
Hemp	15-45	300-900	0.8-3.3	**20-40**	**300-800**	**1.4**

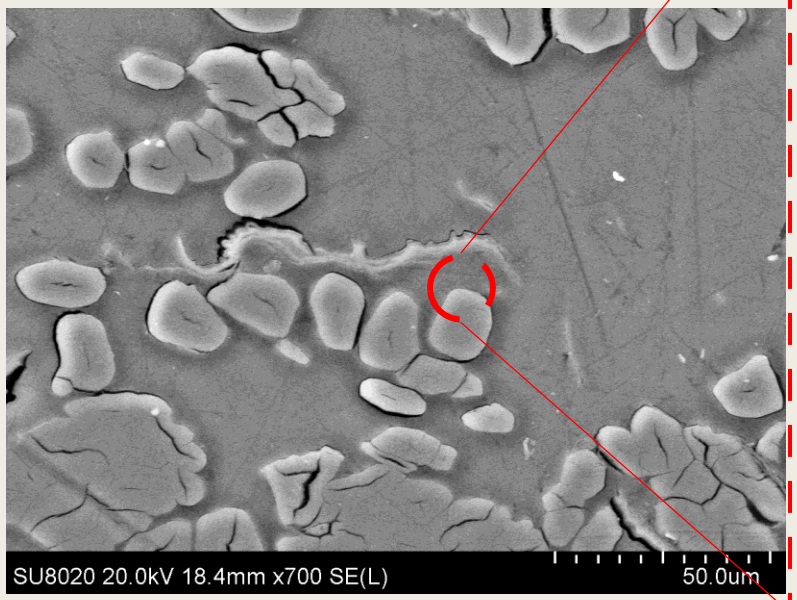
(Pickering et al., 2016), (Bourmaud et al., 2018) (Shah, 2013)

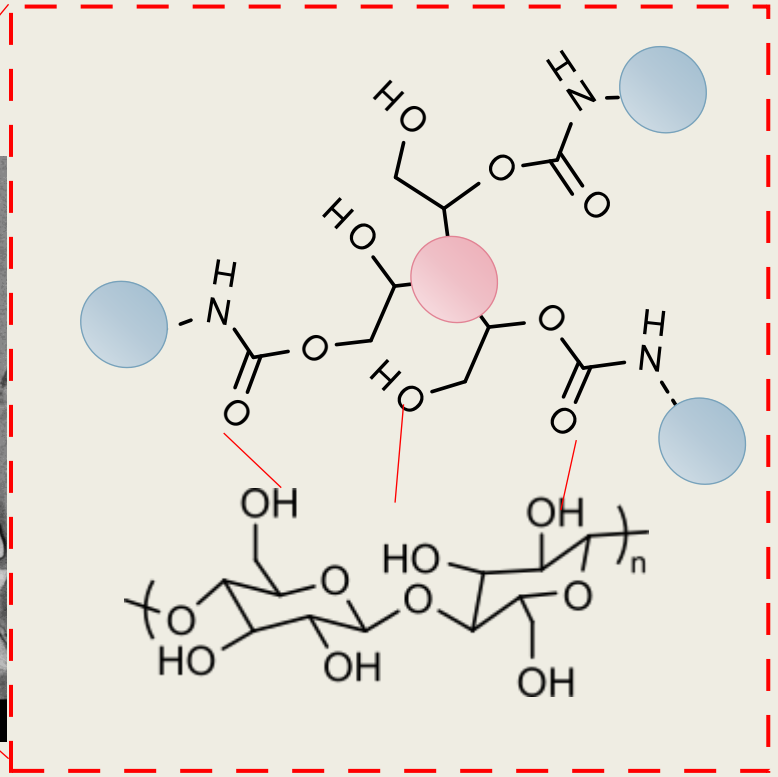
VanEcko/NPSP
(Hemp Scooter)

GreenBoats/BCOMP
(Flax Café Racer Boat)

Replacing glass fibers with flax, but what about the matrix ?

Why Flax & PHU ?





Better affinity?

Stronger interface?

Enhanced properties?

Is PHU chemistry a promising platform for Natural Fiber Composites ?

- Neat Polyhydroxyurethanes

  Abilities, properties, and advantages

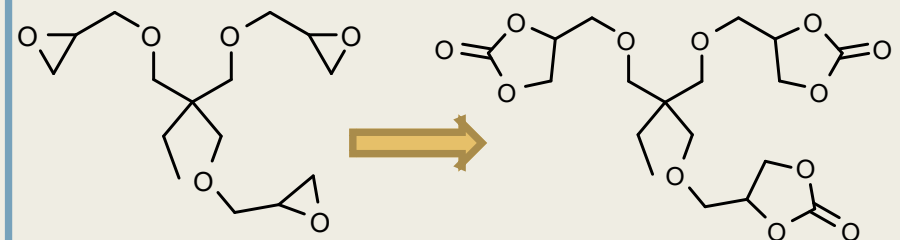
- PHU-based Laminates

  Towards high-performance flax composites?

- Specific features of PHUS

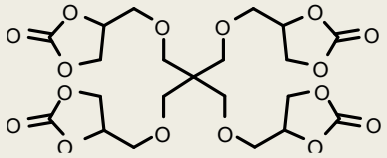
- Perspectives & Challenges

Cyclic Carbonates, an easy synthesis

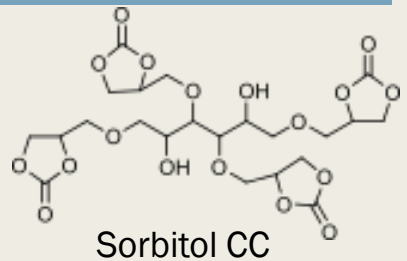


Trimethylol Propane TriGlycidyl Ether (TMPTGE)

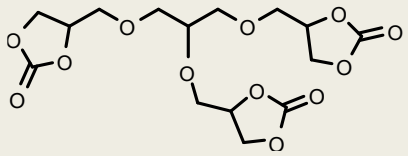
Short, biobased, LIQUID and reactive molecules



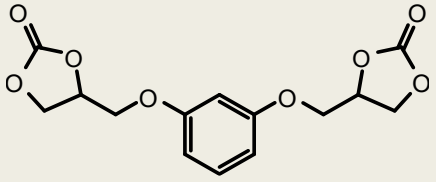
PentaErythritol CC



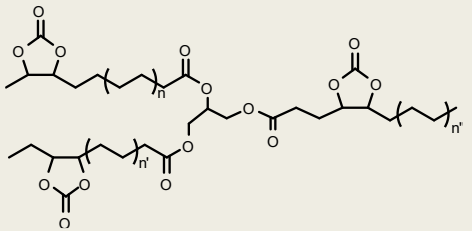
Sorbitol CC



Glycerol CC



Resorcinol CC

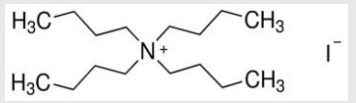


Epoxidized SoyBean Oil

General synthesis of carbonates

Stainless steel HP reactor

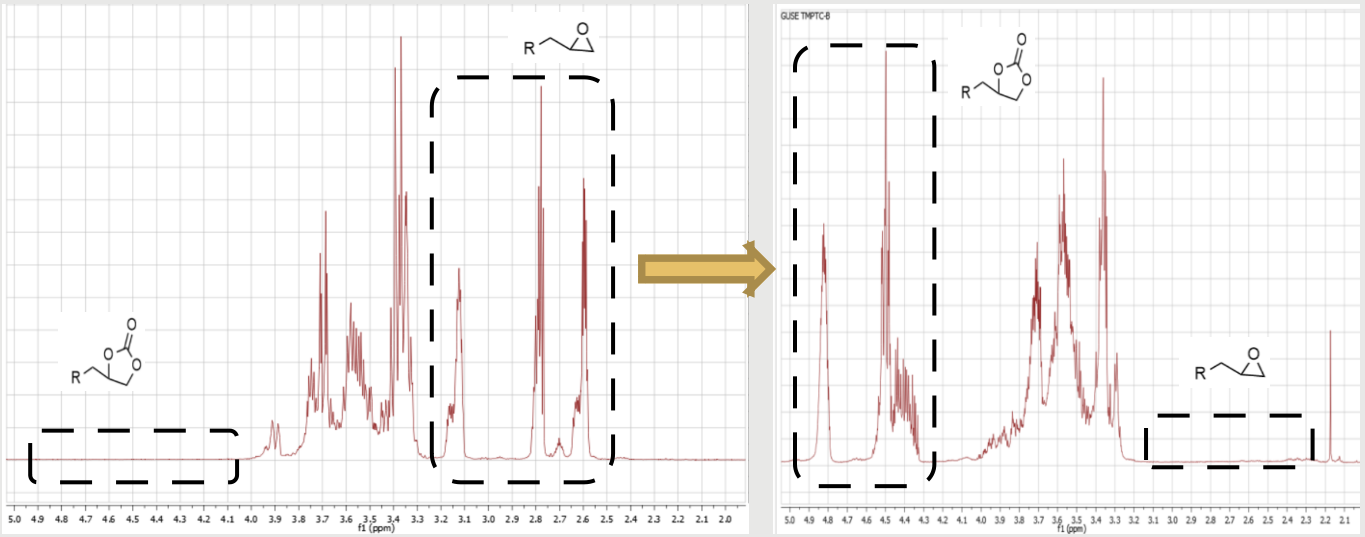
Catalyst : TBAI (2.5 mol%)



$scCO_2$

80-100 °C - 110 bar - 24 h - 350 rpm

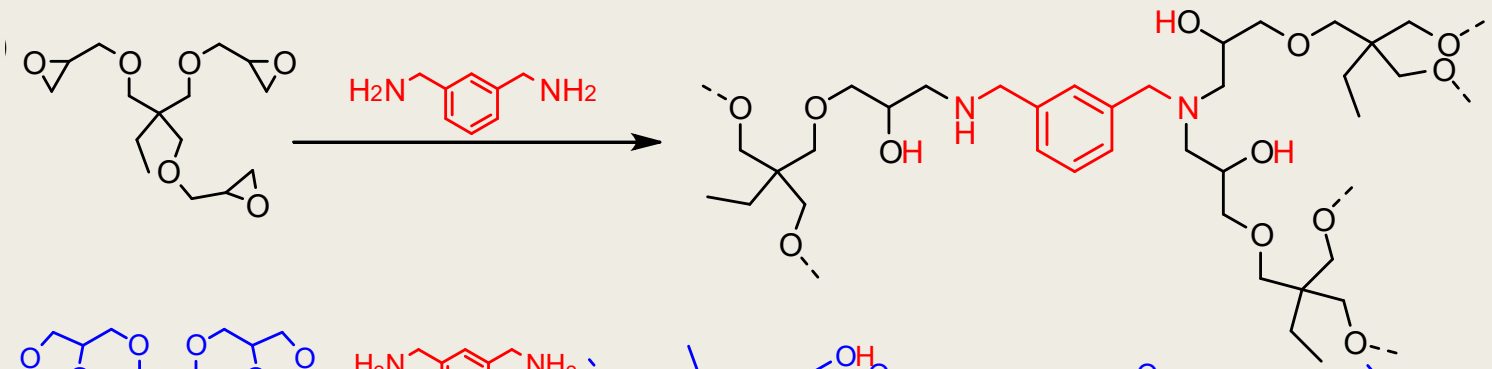
Full conversion assessed by ^{1}H-NMR



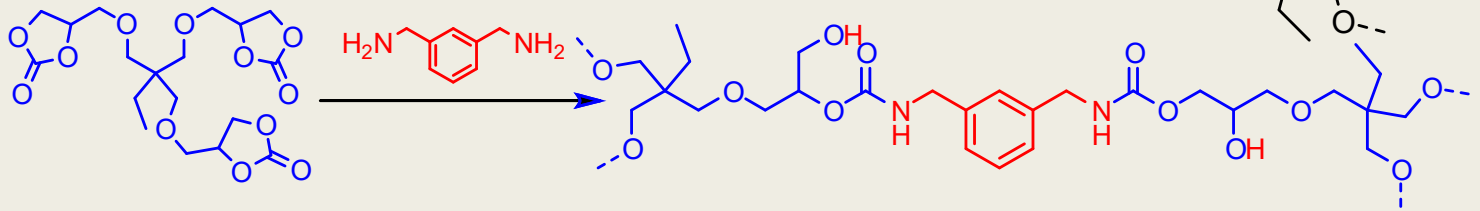
- ✓ Versatile
- ✓ Easy conversion
- ✓ Quantitative yield
- ✓ Solvent-free
- ✓ No purification step
- ✓ Fully scalable

Comparison between PHU and Epoxyde
Similar macromolecular structure

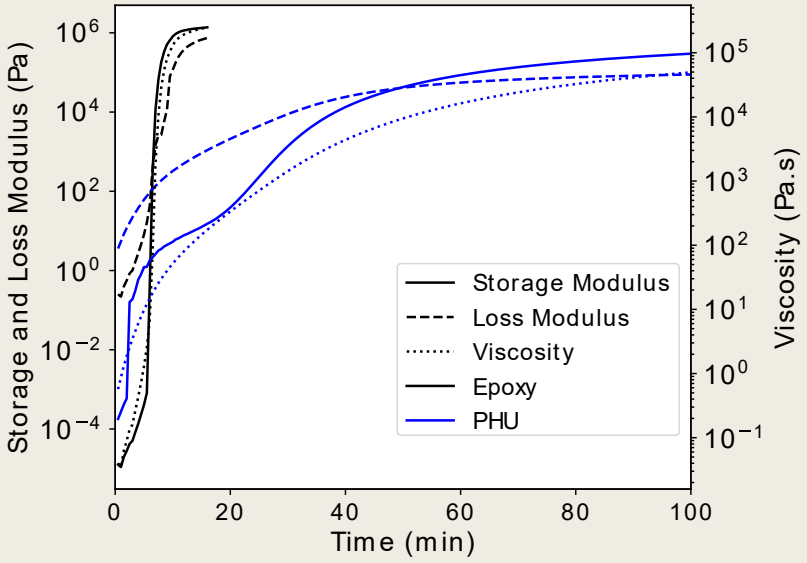
EPOXY



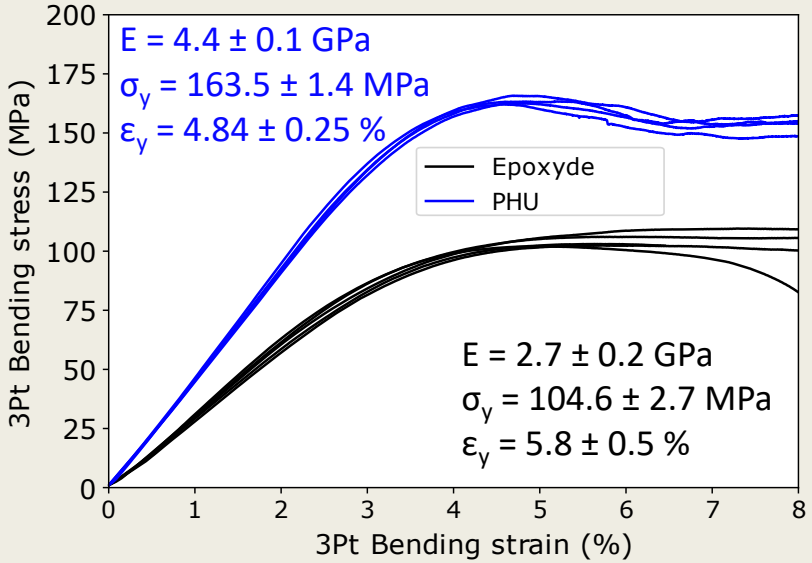
PHU



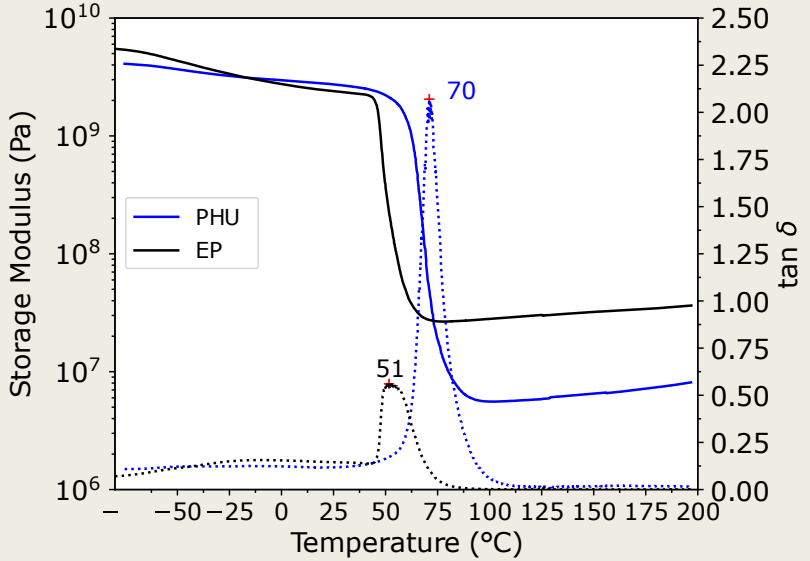
Curing Rheology



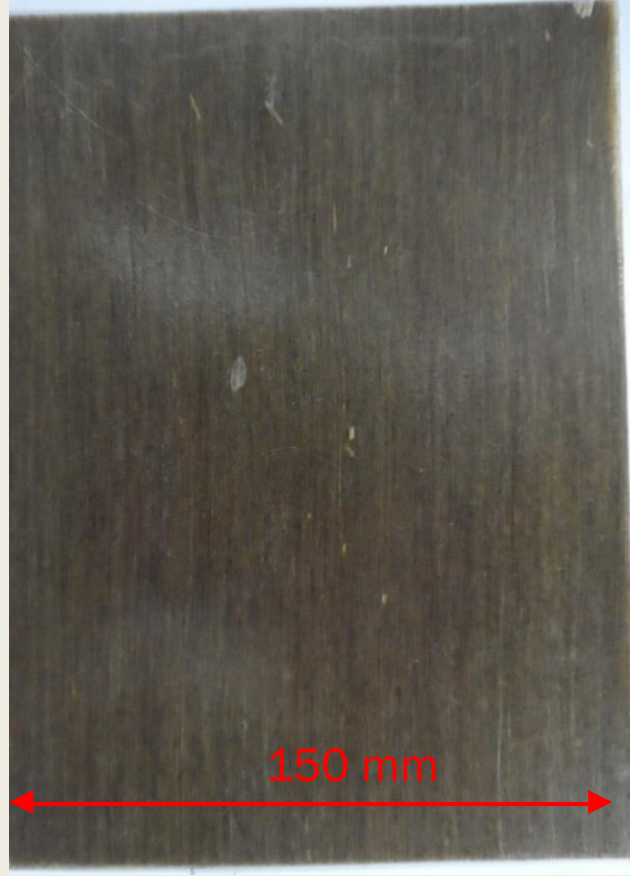
3Pt Bending



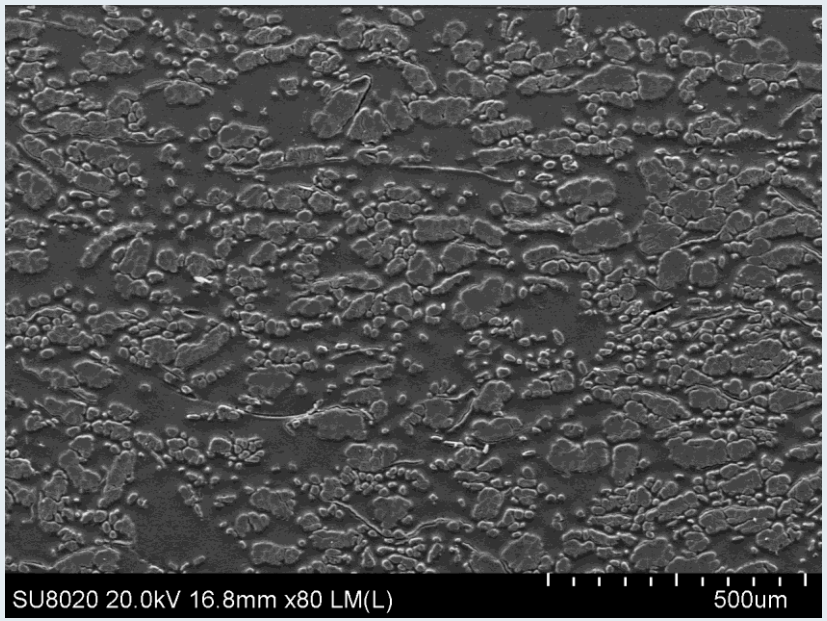
DMA



PHUS, STRONGER THAN EQUIVALENT EPOXIDES, BUT HARDER TO PROCESS

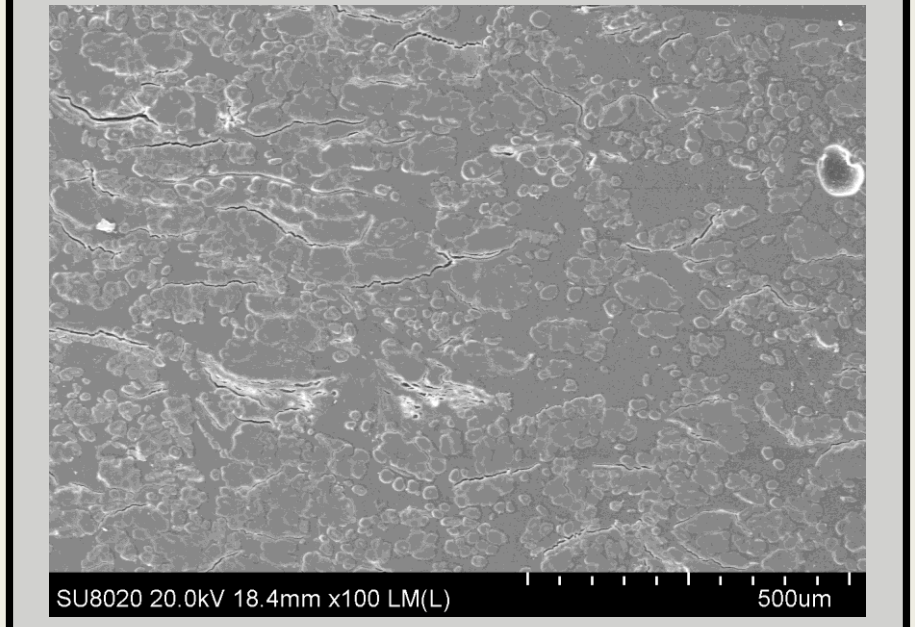


ABOUT FLAX/PHU LAMINATES

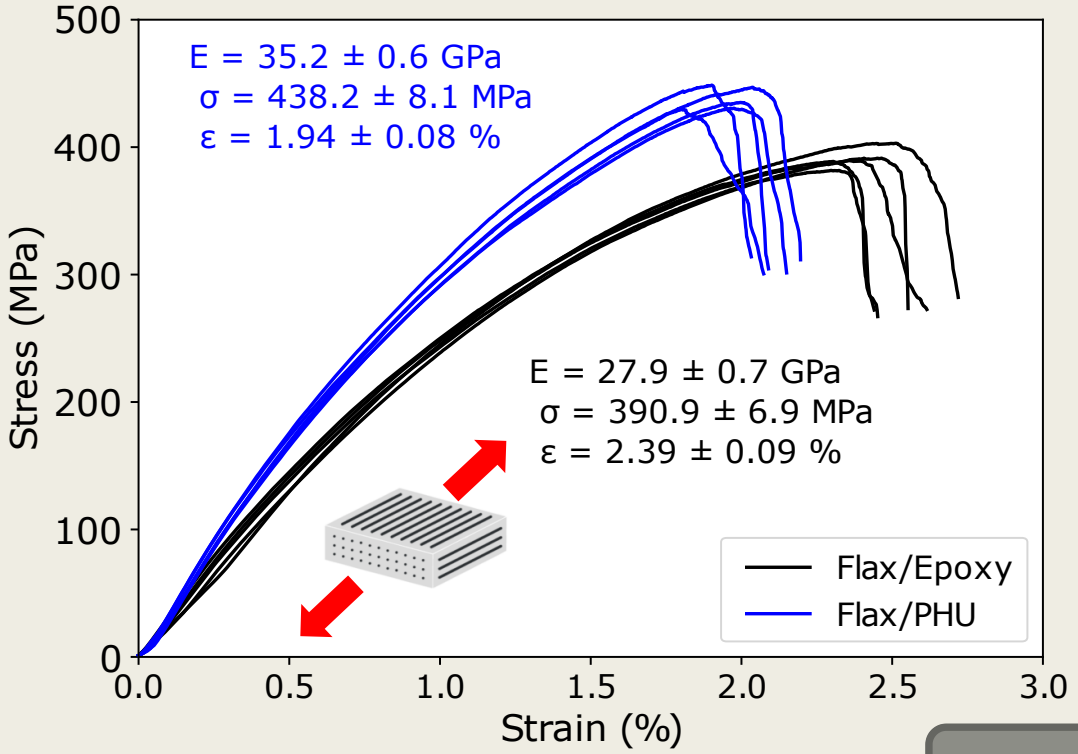


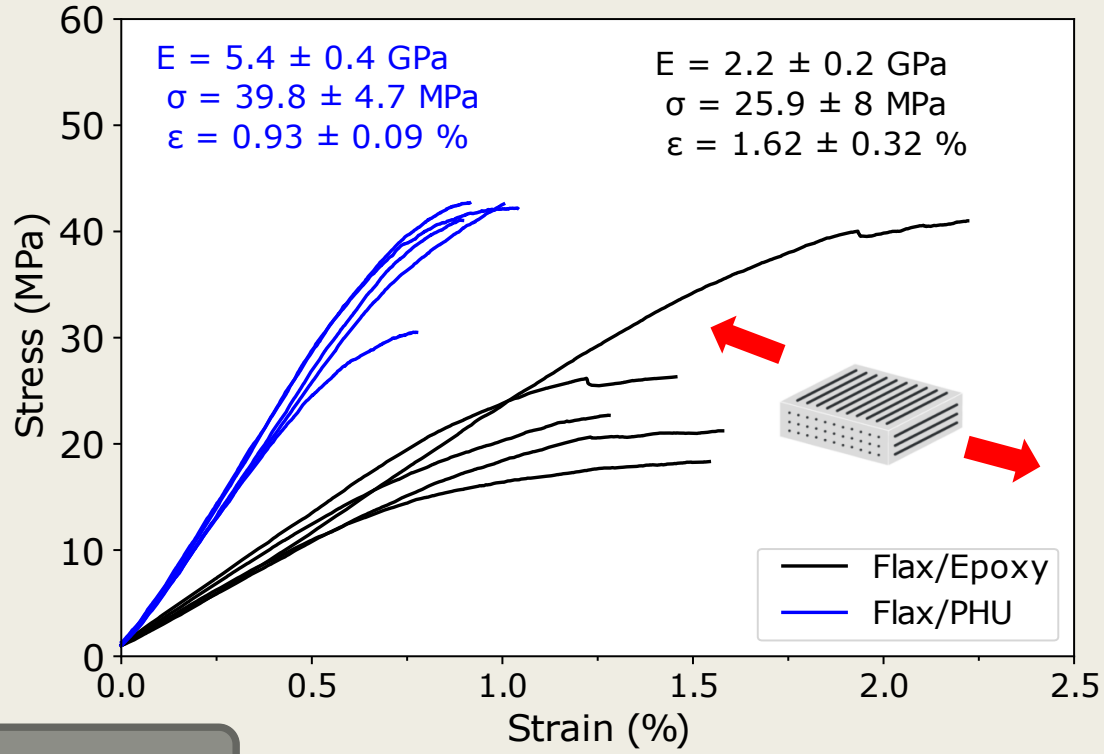
FLAX/PHU
$[0]_6$
V_f = 48%
V_P = 5%

FLAX/Epoxy
$[0]_6$
V_f = 46%
V_P = 3%



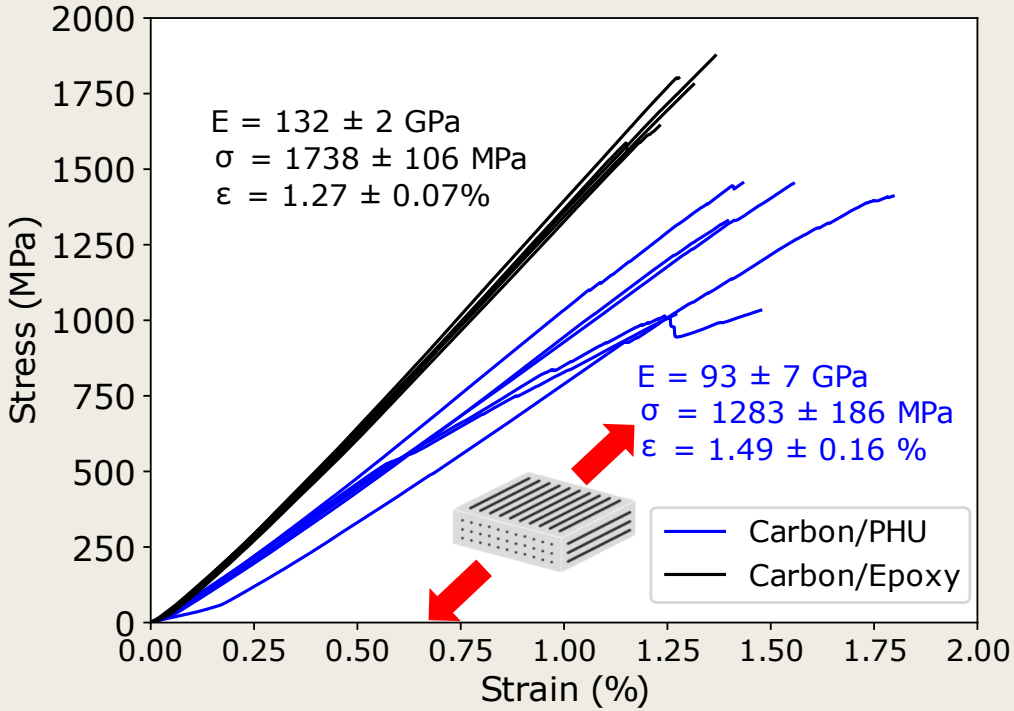
DESPITE HIGH VISCOSITY, HIGH V_F / LOW V_P CAN BE OBTAINED

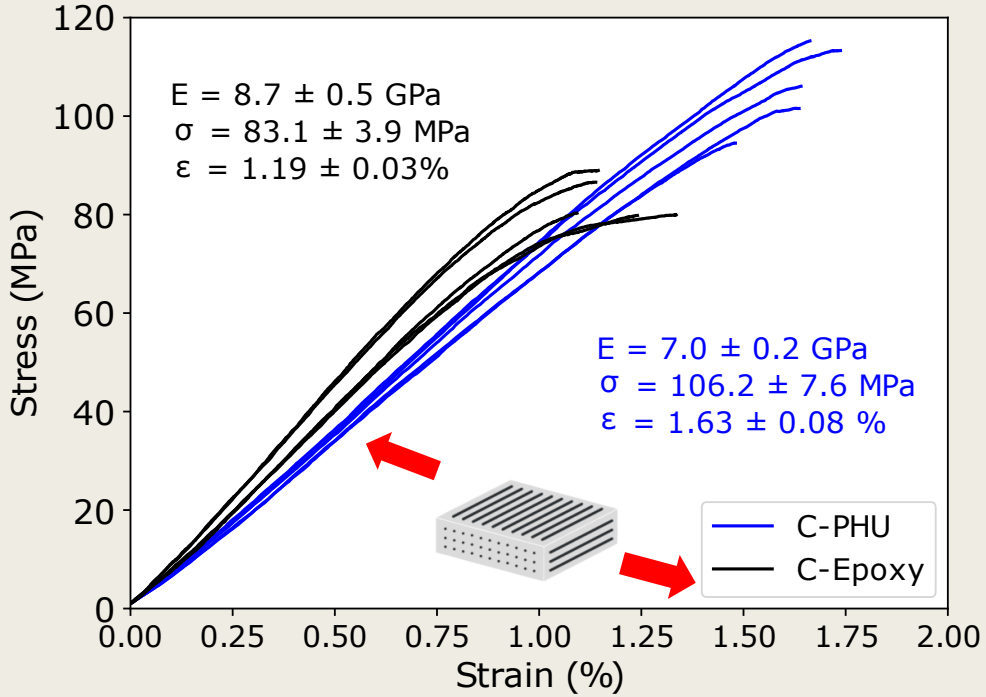




Three-point Bending

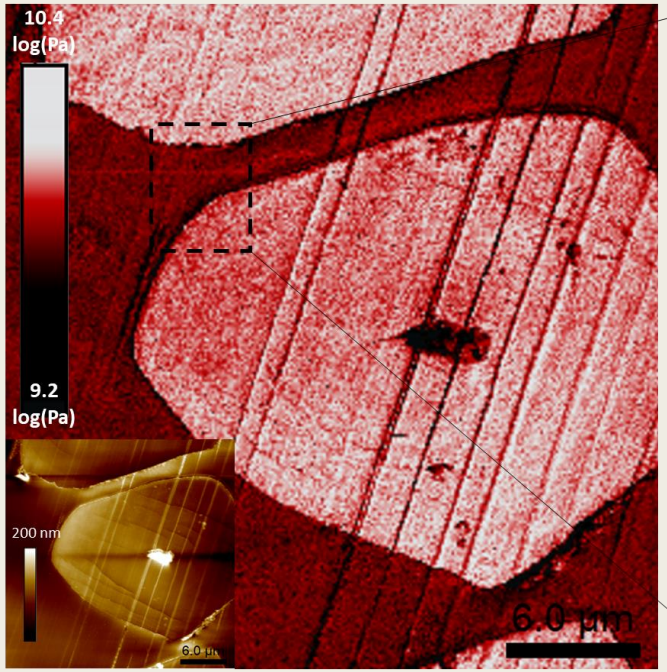
SIGNIFICANTLY HIGHER MECHANICAL PROPERTIES IN BOTH 0° & 90° DIRECTIONS (≈ 30-50% INCREASE)

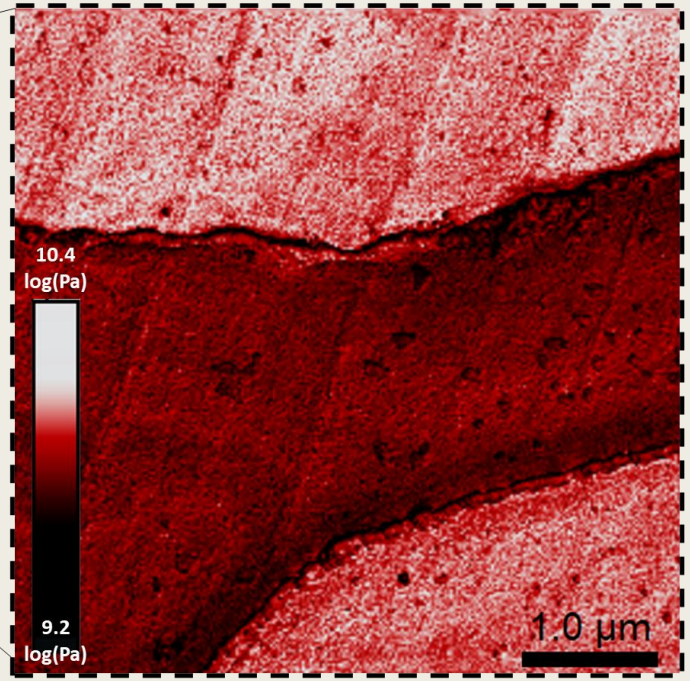




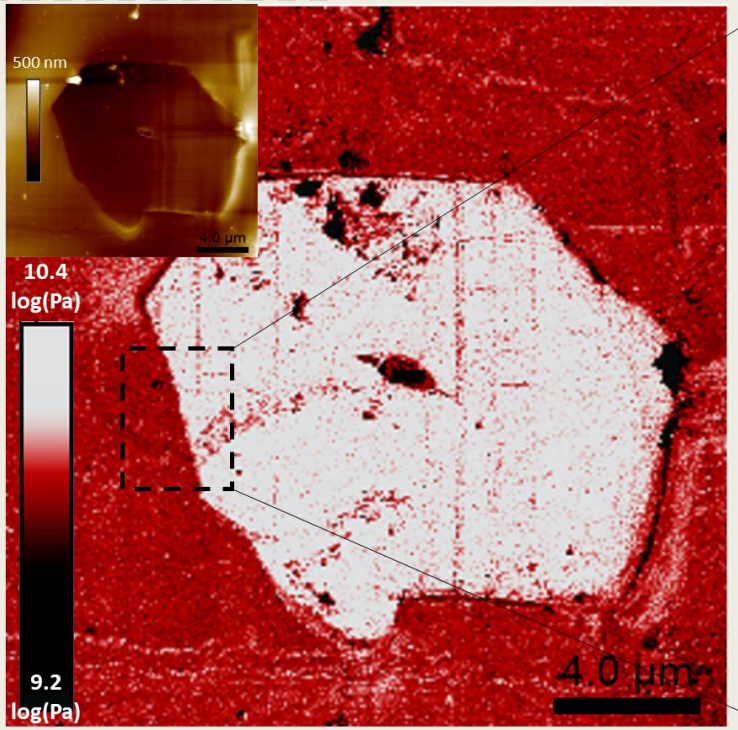
WITH CARBON FIBERS, EPOXY-BASED LAMINATES EXHIBIT BETTER PROPERTIES

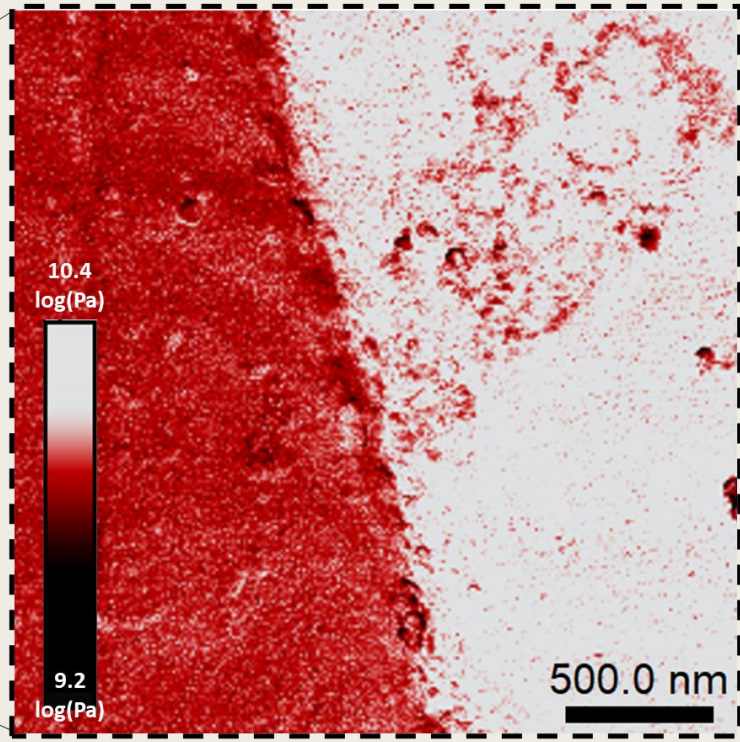
AFM
STRONG ADHESION
FLAX/PHU





EPOXY





PHU

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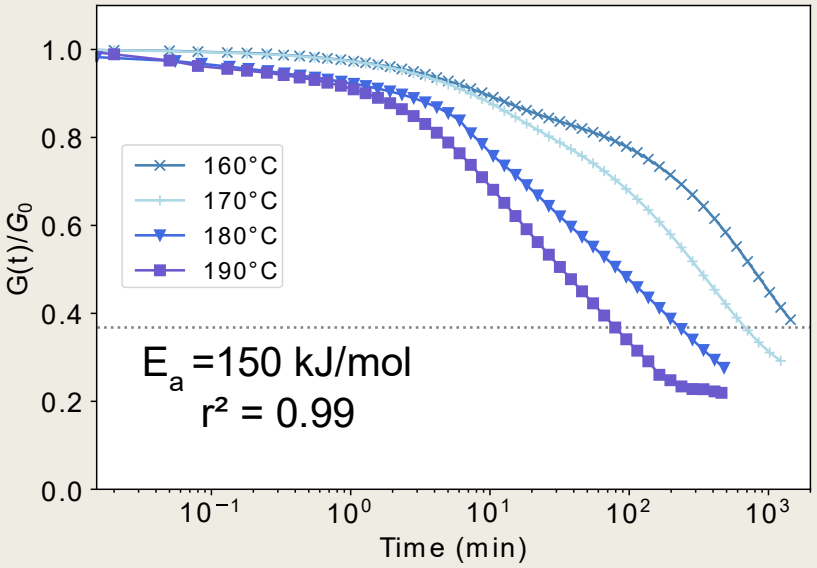
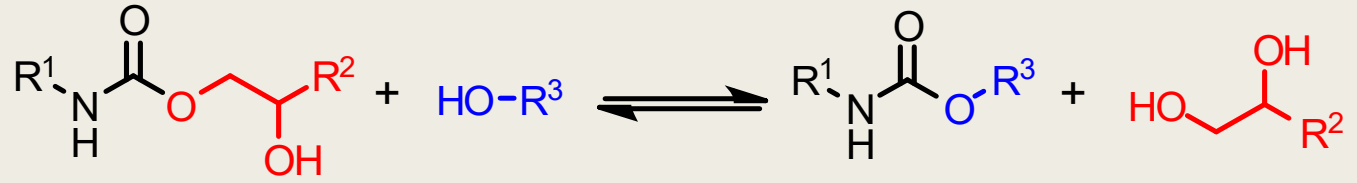
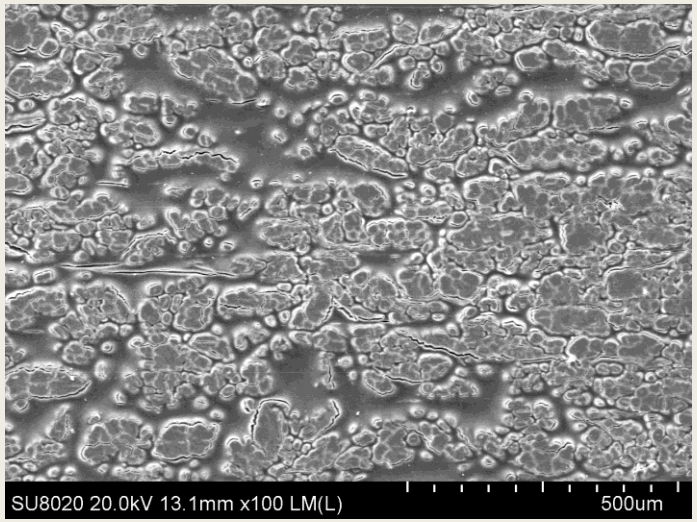
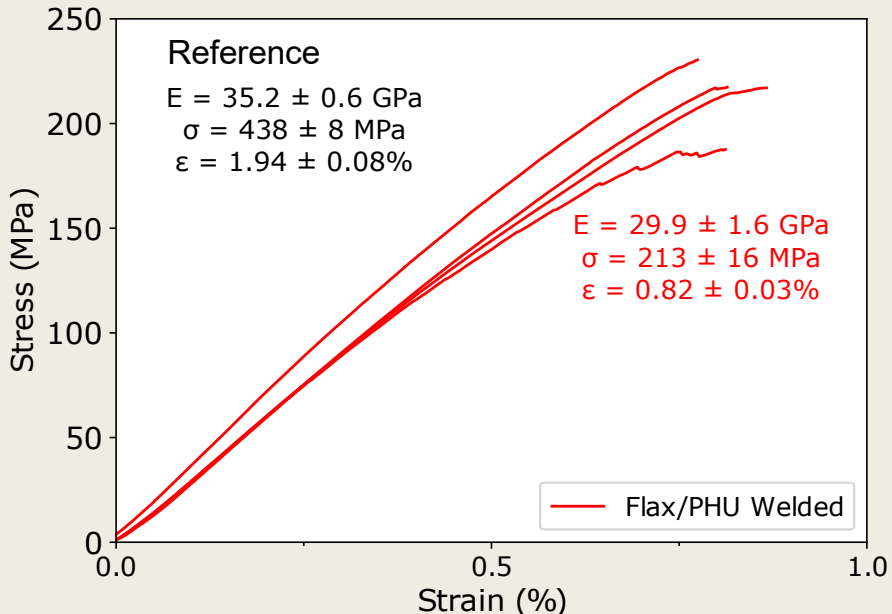
PHUs reprocessable thermoset!









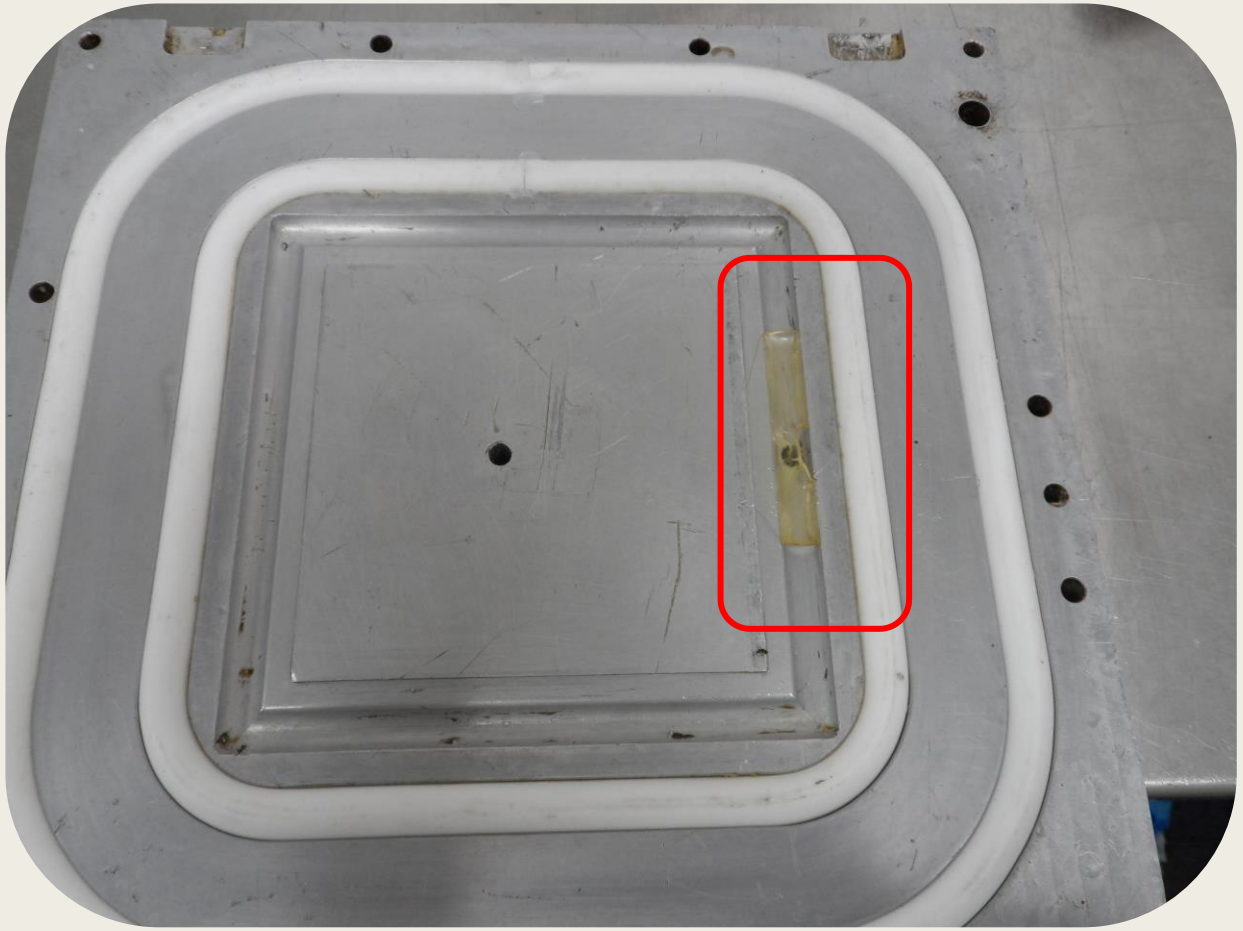
✓ Catalyst-free

BUT HARSH CONDITIONS…

160°C
15 hours
6 MPa

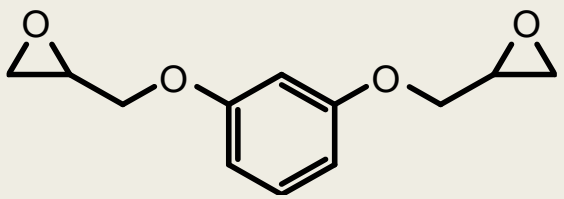
Can we upscale it to industrial process like RTM?

So far....

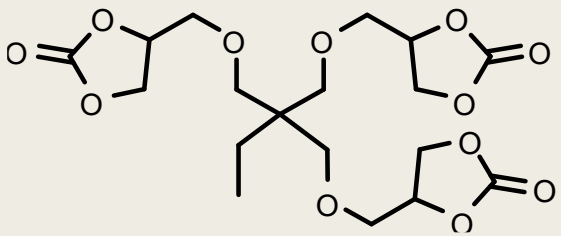


NO !

A simple solution: epoxy/PHU hybrid

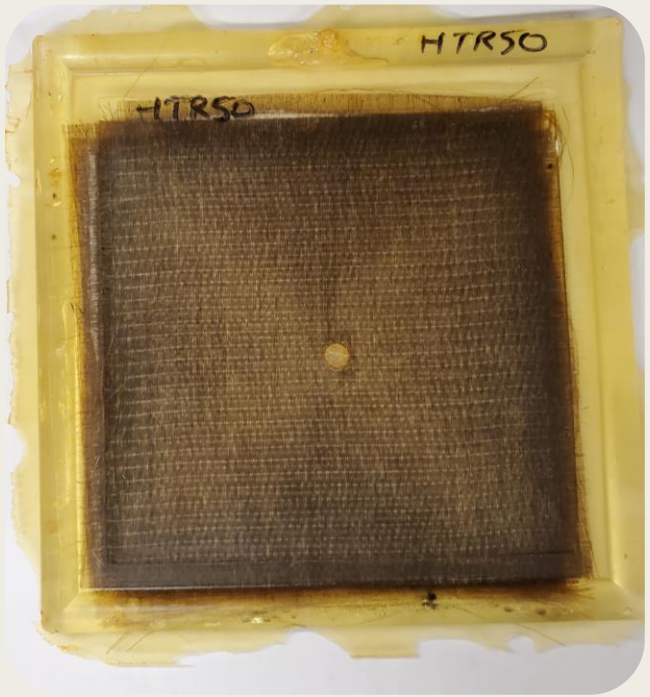


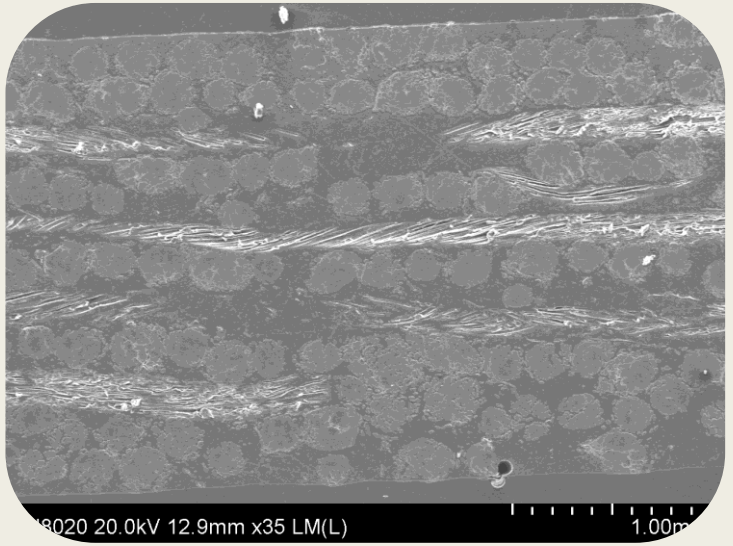
50%



50%

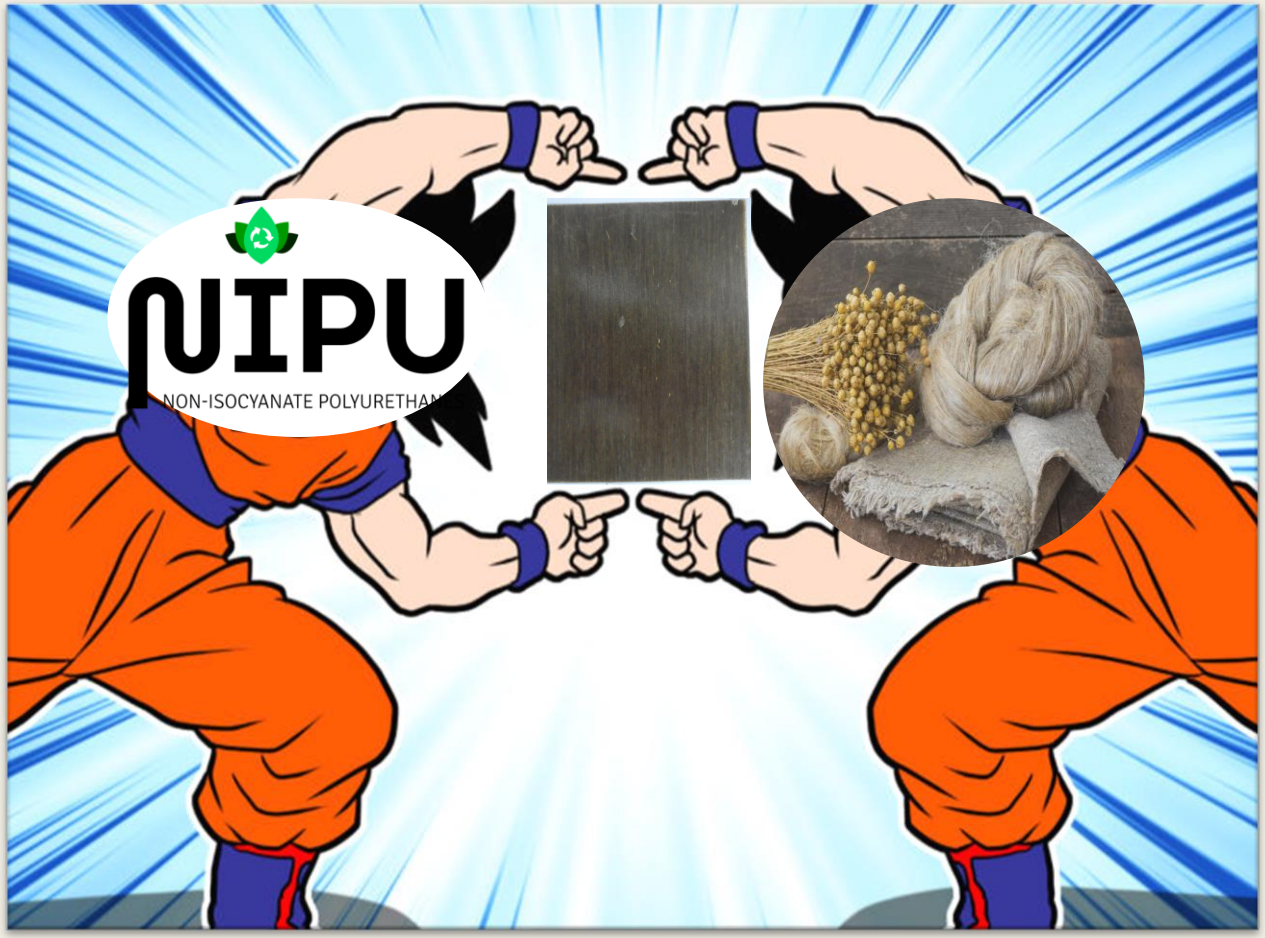
- ✓ Better processability
- ✓ Faster curing
- ✓ Enhanced thermo-mechanical properties
- ✓ Improved impregnation
- ✓ Maintain PHU-added values





TO BRING HOME

Polyhydroxyurethanes emerging sustainable matrices for natural fiber composites



- Sustainable
- Can replace epoxy
- Scalable
- CO_2 –based
- High performances
- Reprocessable
- Strong adhesion with natural fibers

Still at the very beginning (low TRL): a lot of work remains to better understand, improve and implement this very promising chemistry

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H2020-EU

Thanks for your attention!
Feel free to ask any questions!

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Wants to know more?