Aristotle University of Thessaloniki
Department of Chemistry
Laboratory of Chemical and Environmental Chemistry

Utilization of Kraft and Organosolv lignin towards bio-based epoxy polymer composites

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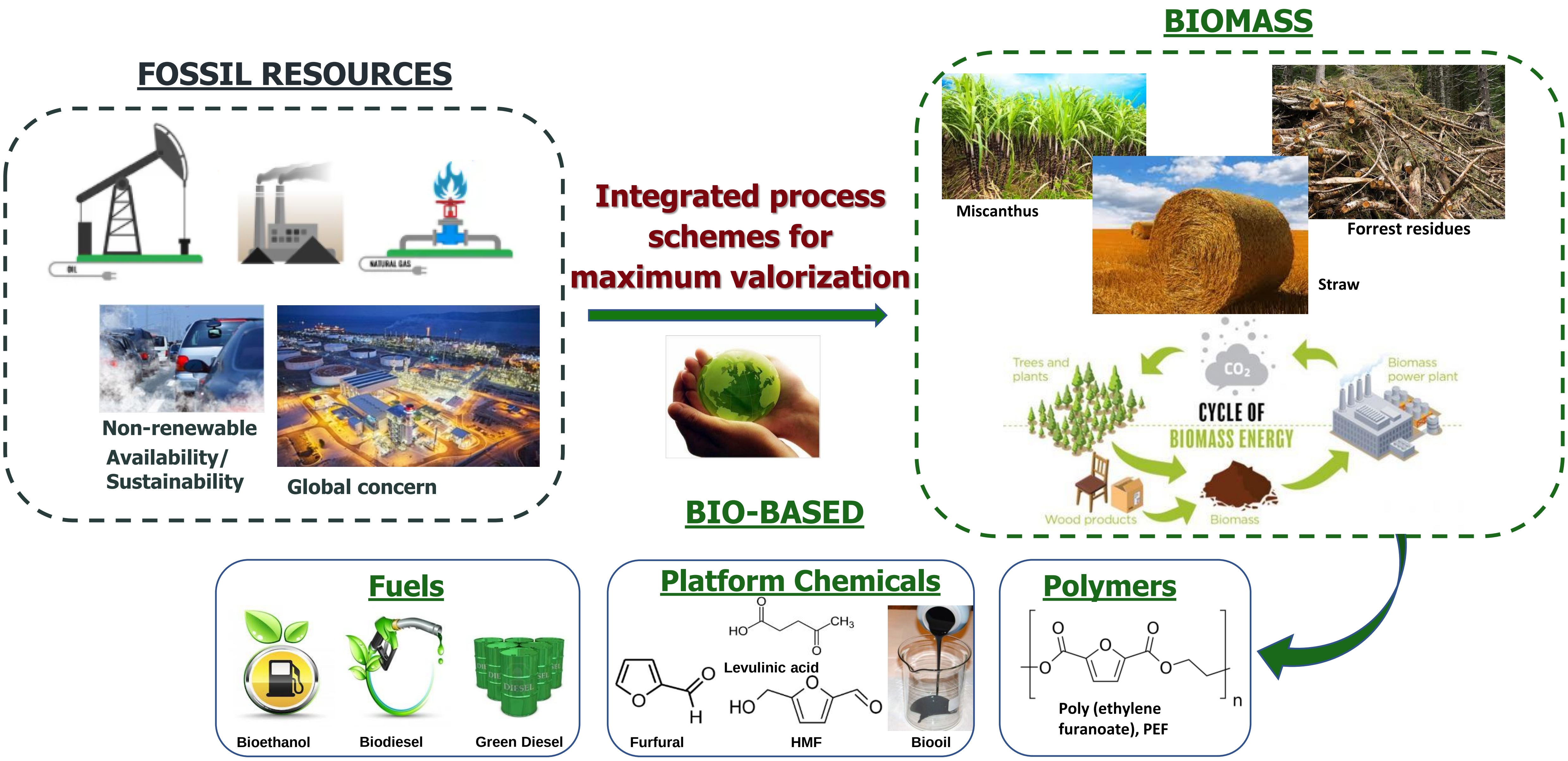
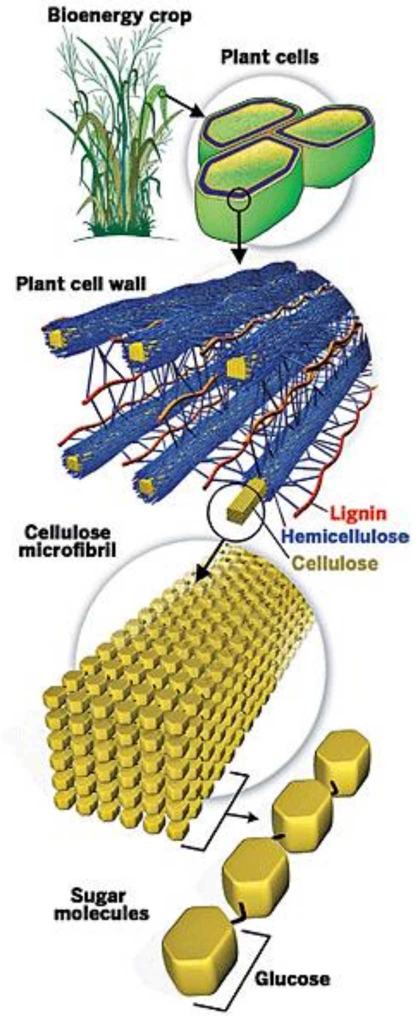
Utilization of Biomass



Lignocellulosic Biomass – Structure and Composition

Structure

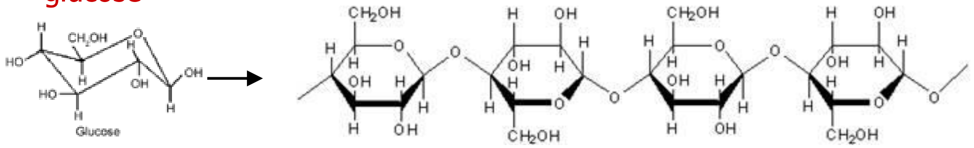


Source: Ritter S.K., Lignocellulose: A Complex Biomaterial, Plant Biochemistry, 86(49) (2008) 15

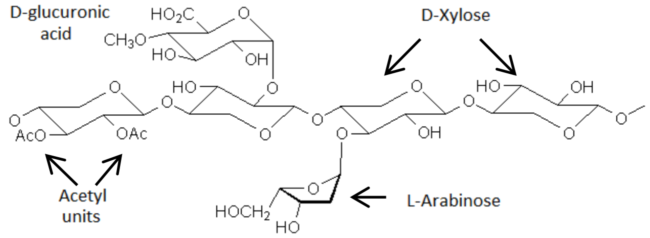
Composition

- **Cellulose:** general formula $(C_6H_{10}O_5)_n$, MW: 300.000-500.000

glucose

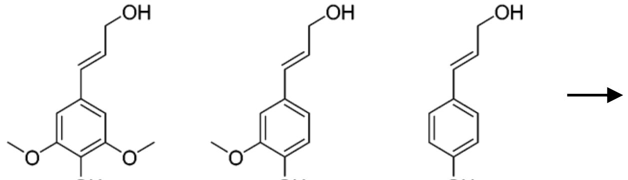


- **Hemicellulose:** general formula$(C_5H_8O_4)_n$



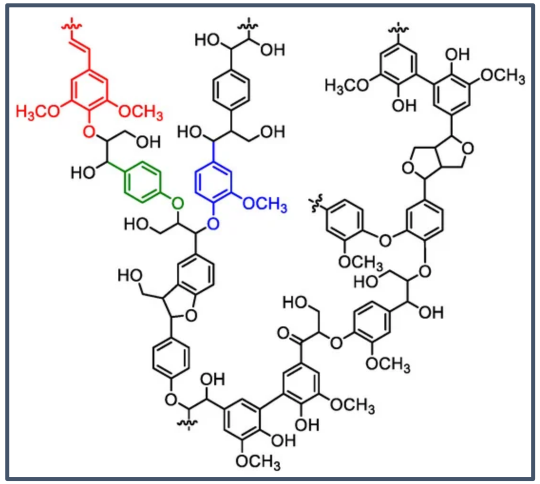
C_5 & C_6 sugars, uronic acids, acetyl units

- **Lignin:**



sinapyl alcohol coniferyl alcohol p-coumaryl alcohol

Phenolic monomers



Syringyl (S)

Guaiacyl (G)

p-Hydroxyphenyl (H)

Cellulose: 30-50%, Hemicellulose: 20-40%, Lignin: 15-25%
Others, 5-35% - Ash 3-10% (Si,Al,Ca,Mg,K.Na), Extractives: Resins, Phenols, Sterols, etc

Biomass Fractionation and Lignin Extraction Processes

Kenaf

Beechwood

Vine prunings

Olive prunings

Almond shells

Hydrothermal, steam-explosion, Dilute acid pretreatment → **Enzymatic hydrolysis – Fermentation (2-G Bioethanol)** → **Hydrolysis Lignin**

Mild Hydrothermal treatment in the presence of organic solvent (ethanol, butanol, acetone,..) → **Organosolv Lignin**

Alkaline pretreatment usually with aq. NaOH under mild hydrothermal conditions → **Alkali (soda) lignin**

Wood pulping processes - hemicellulose & lignin dissolution (Kraft process using NaOH & Na_2S or Sulfite process using sulfite (SO_3^{2-}) or bisulfite (HSO^{3-}) salts) → **Kraft lignin**

C.K. Nitsos, K.A. Matis, K.S. Triantafyllidis, ChemSusChem 6 (2013) 110−122
C.K. Nitsos, T. Choli-Papadopoulou, K.A. Matis, K.S. Triantafyllidis, ACS Sustainable Chem. Eng. 4 (2016) 4529−4544

Lignin – Use In Polymeric Materials

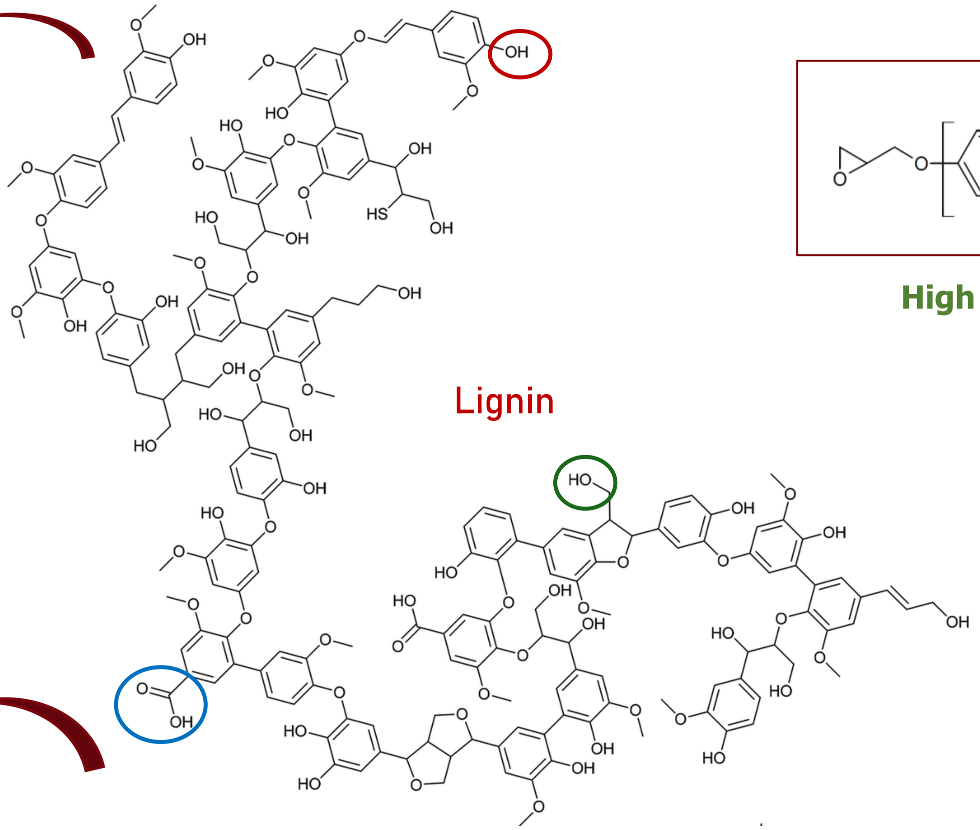
Polymer Additive

- **Thermoplastic** (PS, PET, PP, PVC, PVA, PBS, PE)
- **Thermosetting** (epoxies, phenol-formaldehyde)
- **Rubbers, Foams** (poly-urethanes)

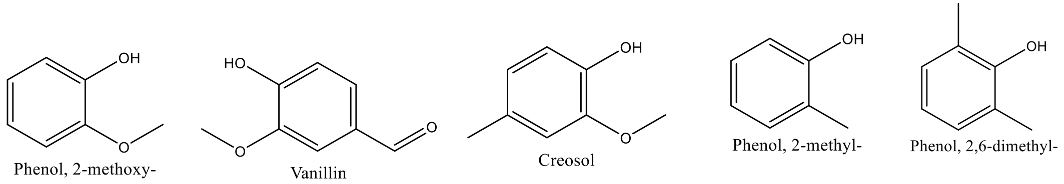
Polymer Blends and Grafted Copolymer

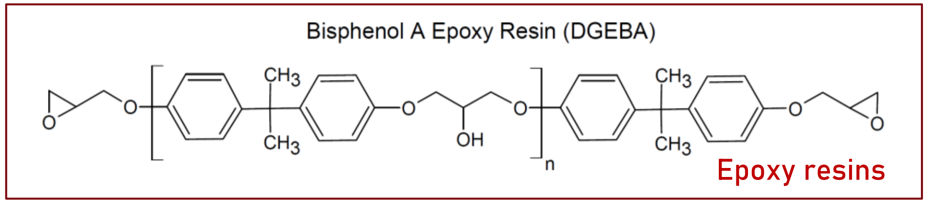
- **PEG, PBS**
- **PP, PE, PS, LD/HD-PE, PVC, PET**
- **PMMA, PLA**
- **PEO, PVA, EVOH**

Highly functional **Phenolic**, **Aliphatic** -OH and **carboxyl** groups



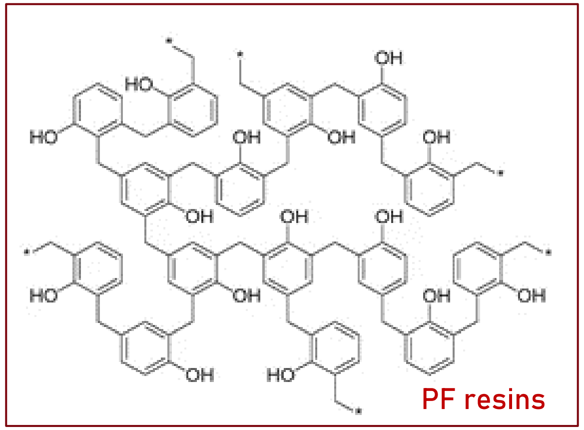
Depolymerization to alkoxy- and alkyl-phenols momomers via solvolysis, hydrogenolysis, fast pyrolysis followed by "re-polymerization"





High chemical similarity & affinity between lignin and phenolic resins

Due to its aromatic/phenolic structure & functional hydroxyls

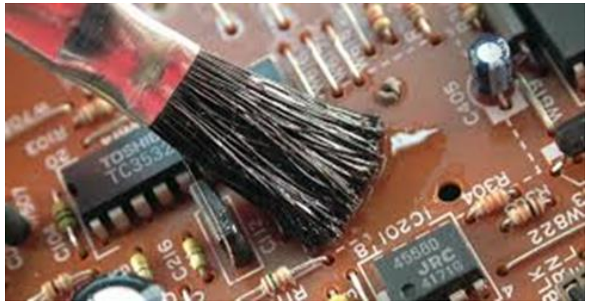


Crestini et al. Green Chem. (2017). 17. 10.1039/C7GC01812F
Argyropoulos et al. Green Chem. (2015). 17. 10.1039/C5GC01066G

Epoxy Polymers

Performance characteristics of epoxy polymers

- Materials with high mechanical strength
- Strong adhesion to a broad range of substrates
- Good electrical insulating characteristics and dielectric properties
- Flame retardancy
- High resistance to a variety of chemicals including caustics, acids, fuels and solvents

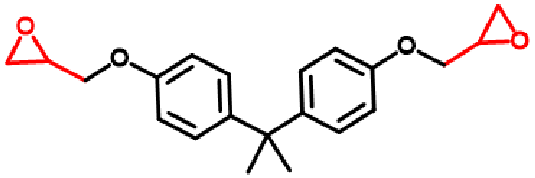



Applications of epoxy polymers

- Paints and coatings
- Adhesives
- Industrial tooling and composites
- Electrical systems and electronics
- Aerospace (spacecraft hardware, flame retardancy and reinforcement of space suits)
- Construction (flooring)
- Lightweight parts for automobiles, rails, bicycle frames, golf clubs, snowboards, racing cars and musical instruments

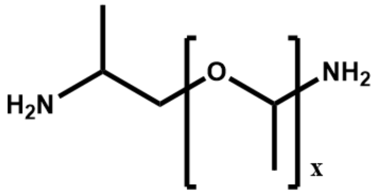
Epoxy Resin and Curing Agents

Epoxy Resin :
Diglycidyl Ether of Bisphenol A (DGEBA)



Mw = <u>340</u> g/mol

Curing agents



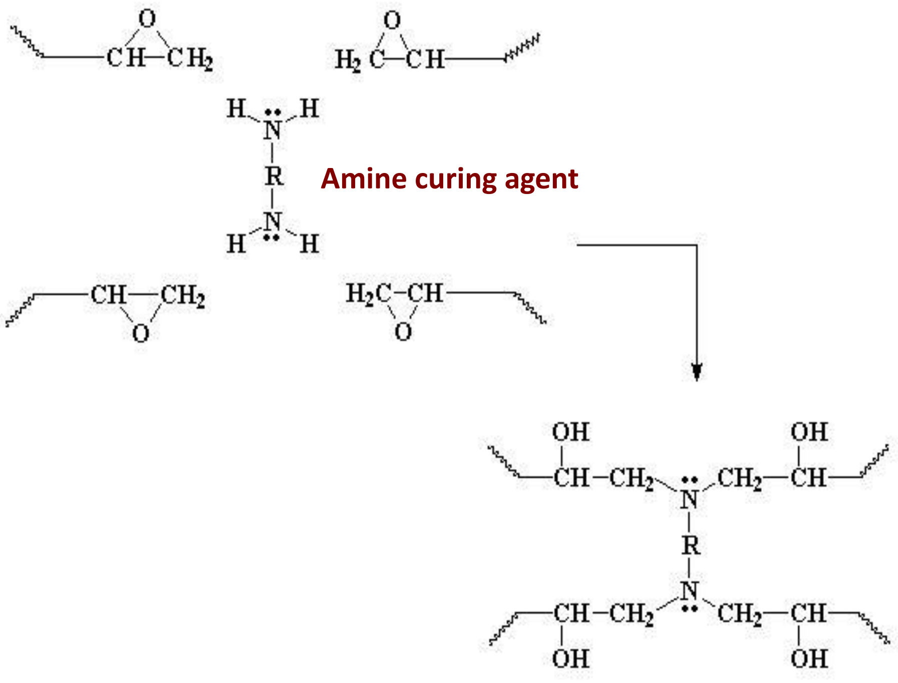
Polyetheramine Jeffamine

Mw = <u>230</u> g/mol, x=3

Mw = <u>2000</u> g/mol, x=33

Cross-linking of epoxy resins with diamines

Epoxy monomers



Cross-linked epoxy polymer

- Highly reactive amine curing agents
- Polymer's properties depend on nature of the curing agent.
  - *R : aromatic, <u>glassy</u> product with high T_g*
  - *R : short carbon chain (R), <u>glassy</u> product with medium T_g*
  - *R : long carbon chain (R), <u>rubbery</u> product with sub-ambient T_g*

Curing Conditions

Curing Agent	1st Step Curing	2nd Step Curing
Jeffamines	3 h at 75 °C	3 h at 125 °C

Experimental: Lignins Used in Epoxy Polymer Composites

Lignin feedstock

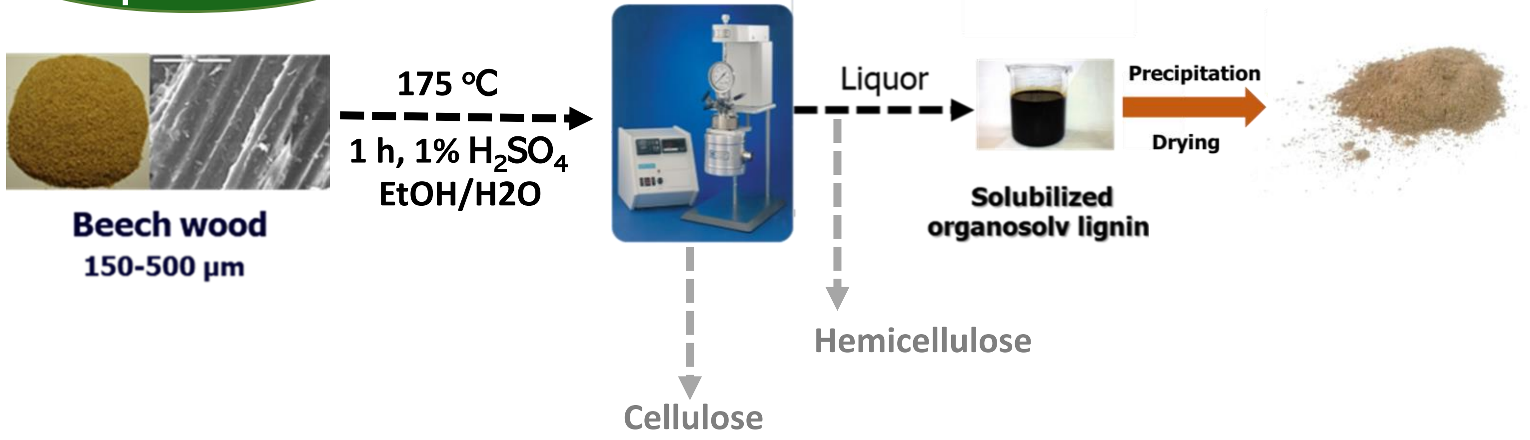
- **Kraft lignin (KL)**
  Spruce, softwood

Treated Kraft Lignins

Glycidylized Lignin (GKL)

Nano-Lignin (NLH)

Organosolv process

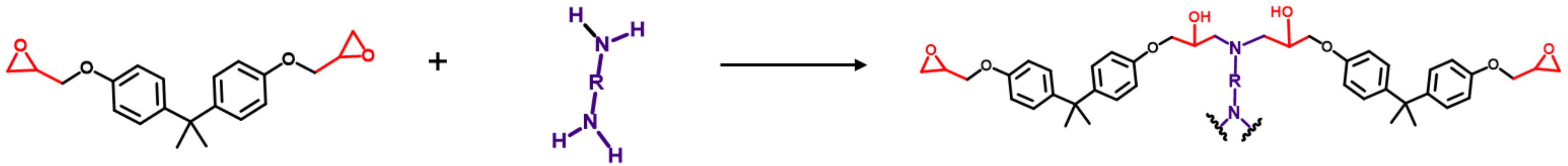


- **Organosolv Lignin (OBs)**
  Beechwood, hardwood

https://www.irnas.csic.es/en/lanzamiento-del-proyecto-woodzymes/

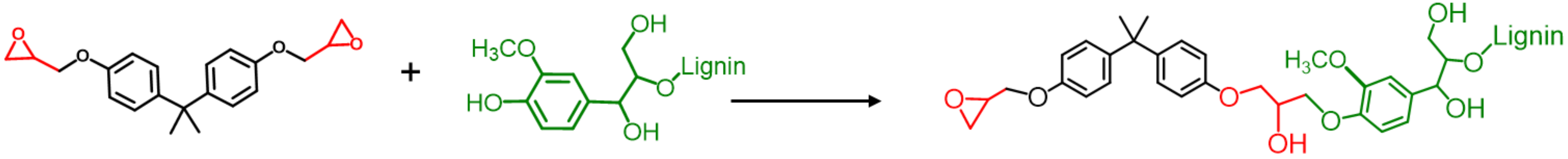
Curing Mechanism of Epoxy Resins and Epoxy – Lignin Composites

a) Crosslinking Mechanism of DGEBA Epoxy Resin with Diamine Curing Agent:



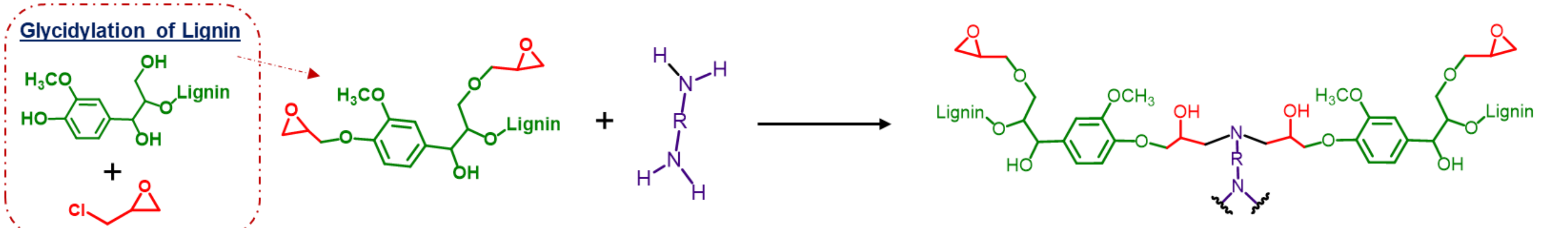
Diglycidyl ether of Bisphenol A (DGEBA) | Amine Curing agent | DGEBA crosslinked with Diamine Curing Agent

b) Crosslinking Mechanism of DGEBA Epoxy Resin with Lignin:



Diglycidyl ether of Bisphenol A (DGEBA) | Lignin | DGEBA crosslinked with –OH of Lignin

c) Crosslinking Mechanism of Glycidylized Lignin with Diamine Curing Agent:



Glycidylized Lignin | Amine Curing agent | Glycidylized Lignin crosslinked with Diamine Curing Agent

Characterization of Kraft Lignin

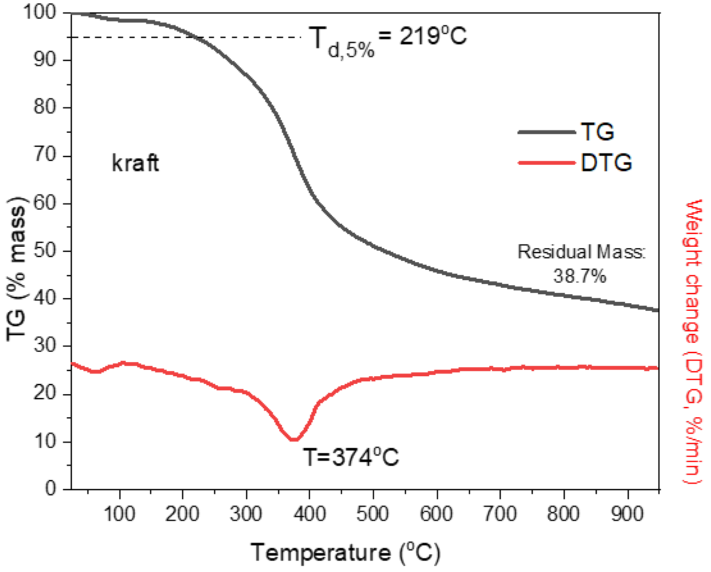
Kraft Lignin (KL)

Lignin	Alip-OH (mmol/gr)	Ph-OH (mmol/gr)	COOH (mmol/gr)	Mw (g/mol)	Mn (g/mol)	PDI	T_g (°C)	Particle Size (μm)
KL	2.25	**3.61**	0.45	4456	856	5.2	143	67

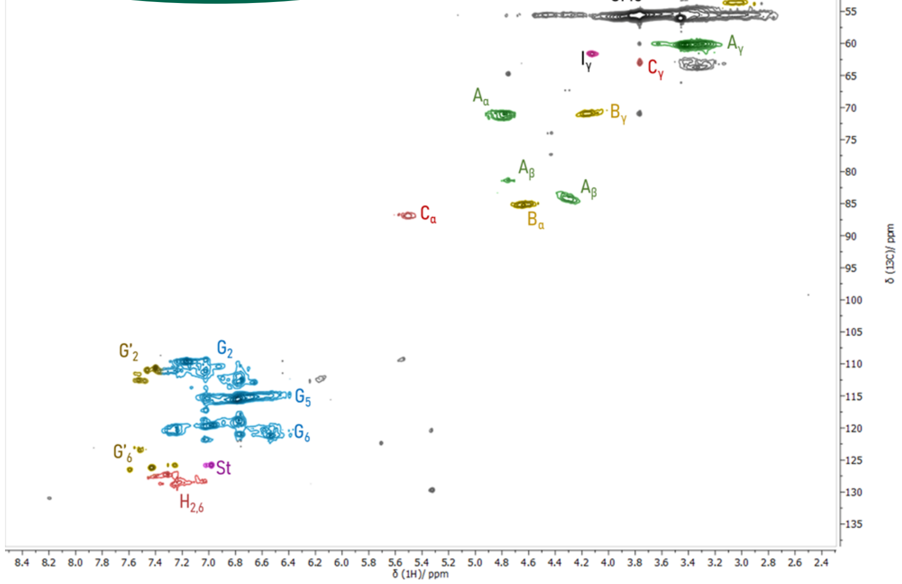
** from ^{31}P-NMR* (Alip-OH, Ph-OH, COOH)

** from GPC* (Mw, Mn, PDI)

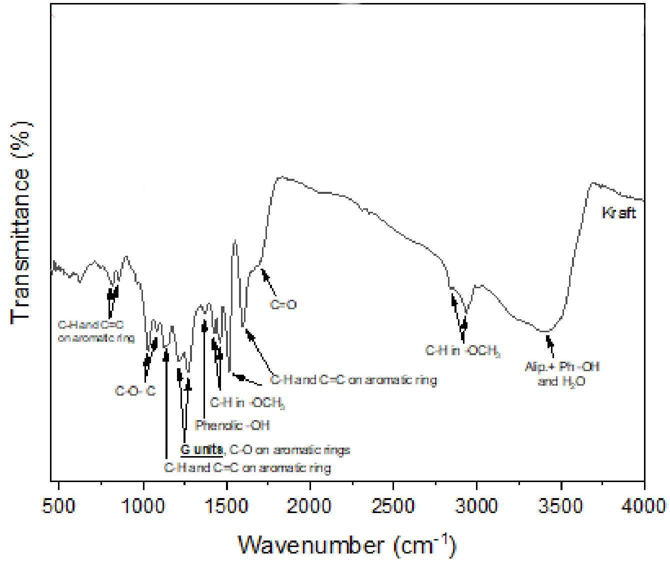
TGA/DTG



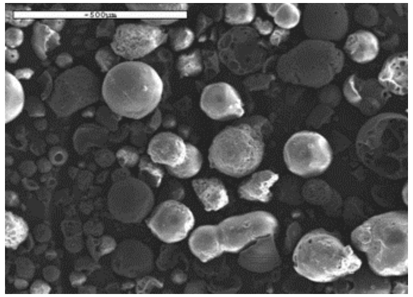
2D HSQC NMR



FTIR



SEM images (~50-200μm)

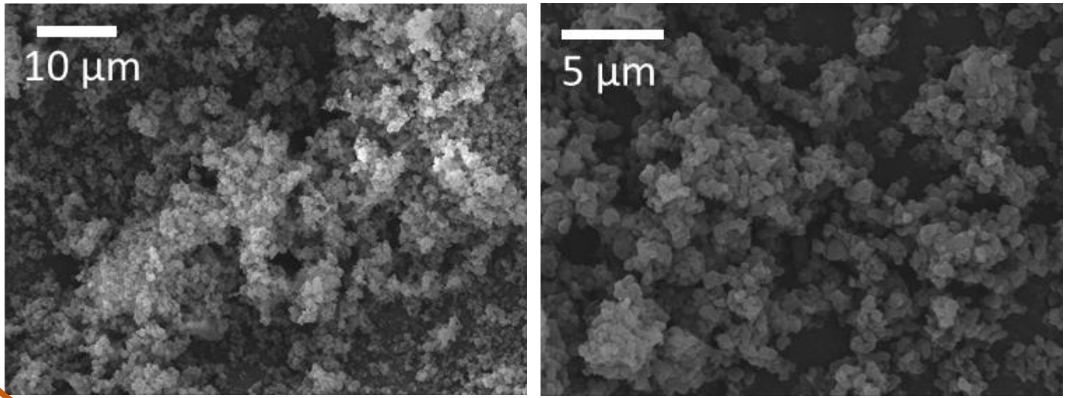


	Arylglycerol-β-aryl ethers (β-*O*-4) *	Pinorecinols (β-β)*	Phenyl coumarin (β-5)*	S/G/H (% content)
KL	22.76	10.92	6.90	0/91.2/8.8

** per 100 Ar*

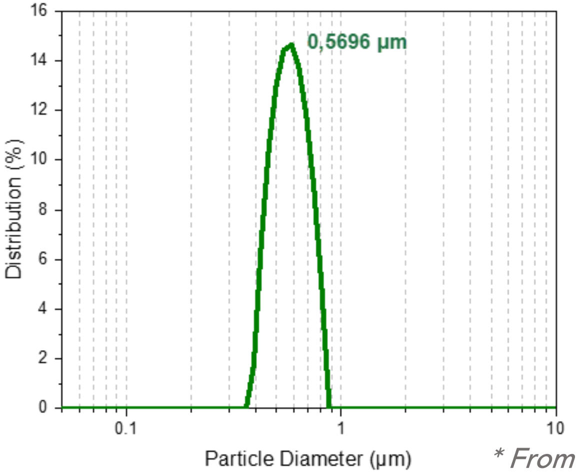
Characterization of Organosolv Lignin (OBs)

SEM IMAGES



ORGANOSOLV LIGNIN (OBs)

PARTICLE DIAMETER: 570 nm

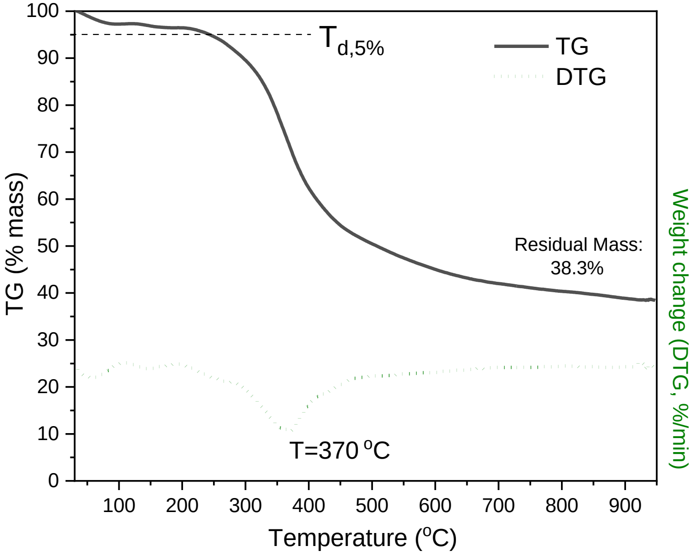


** From DLS*

	$T_{d,5\%}$ (°C) *	DTG_{max} (°C) *	Res. Mass (%)*	Tg (°C) **	Mw (g/mol) ***	Mn (g/mol) ***	PDI ***
OBs	239	370	38.3	114	1810	1070	1.69

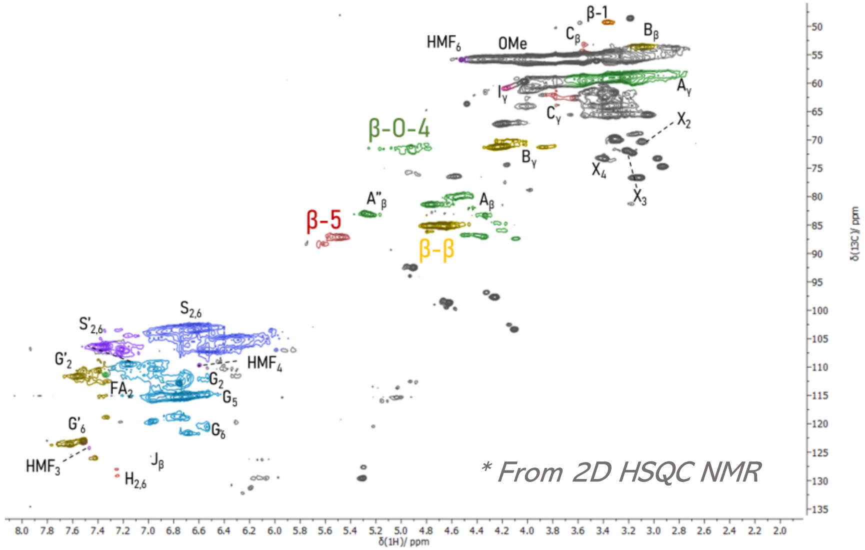
** From TGA, ** From DSC, *** From GPC*

** From TGA*



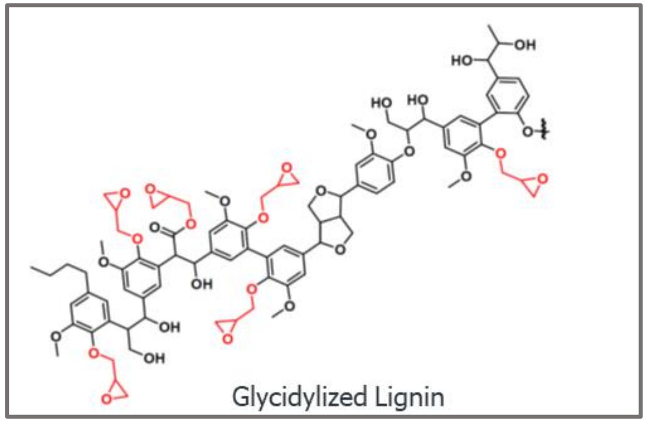
Lignin interunit bonds – Abundance (per 100 Ar) [a]	
Arylglycerol-β-aryl ethers (β-O-4)	9.0
Pinorecinols (β-β)	16.37
Phenyl coumarin (β-5)	7.37
Lignin aromatic units – Abundance (%)	
S/G/H	56.8/42.5/0.7
Lignin functional groups – Abundance (mmol/gr) [b]	
Aliphatic OH	1.33
Condensed	2.40
Non-condensed	1.06
Total PhOH	3.46
COOH	0.08

[a] Ar = aromatic units, [b] = From ^{31}P-NMR

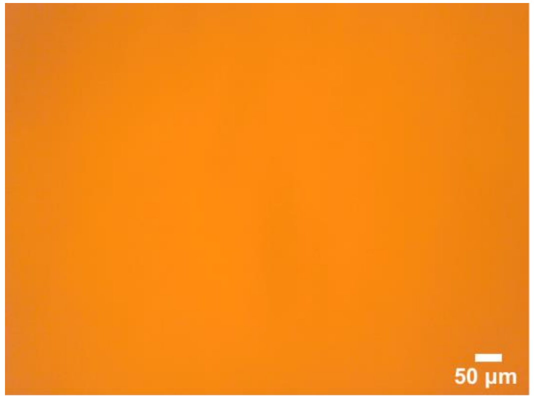


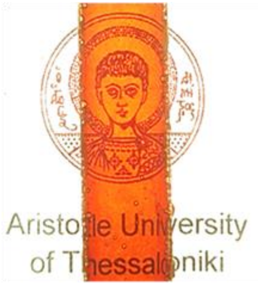
Epoxy / Lignin Composites - Lignin Dispersion

Glycidylized Kraft Lignin (GKL)



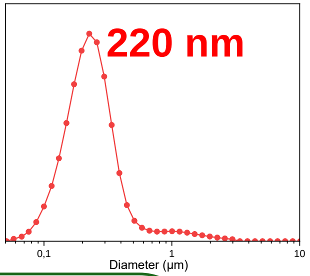
Increased affinity [by the attachment of the epoxy rings to lignin's OH] results in complete transparent lignin/epoxy composites

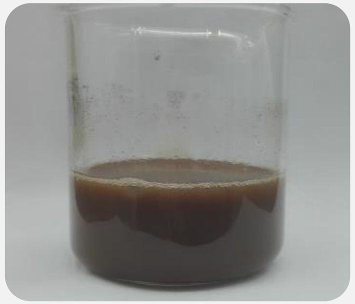




** Optical microscopy*

Nano-Kraft Lignin (NLH)



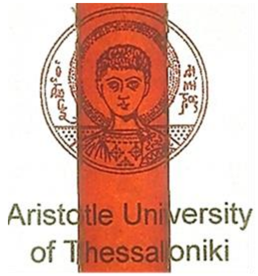


KL in H2O

sonication 2 h

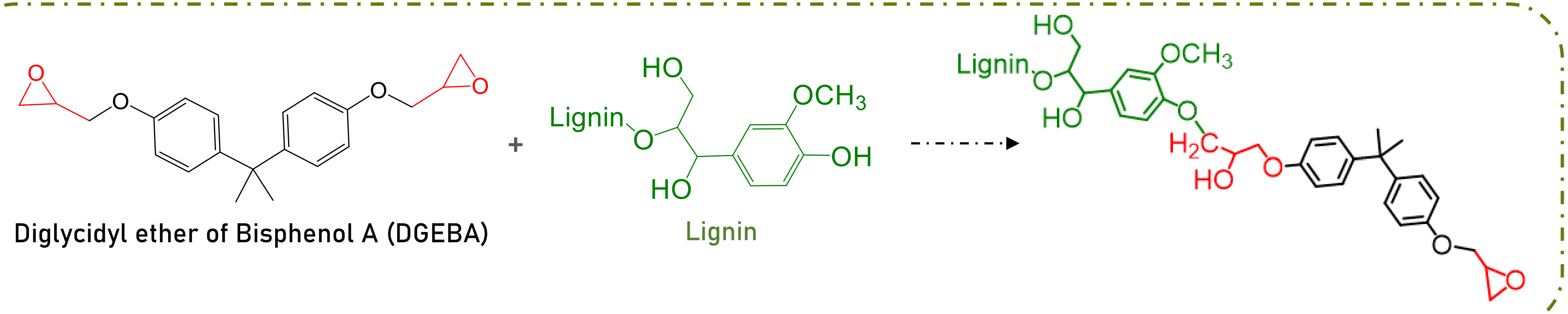
EtOH

Nano-sized lignin was able to dissolve in EtOH completely and result in transparent composites

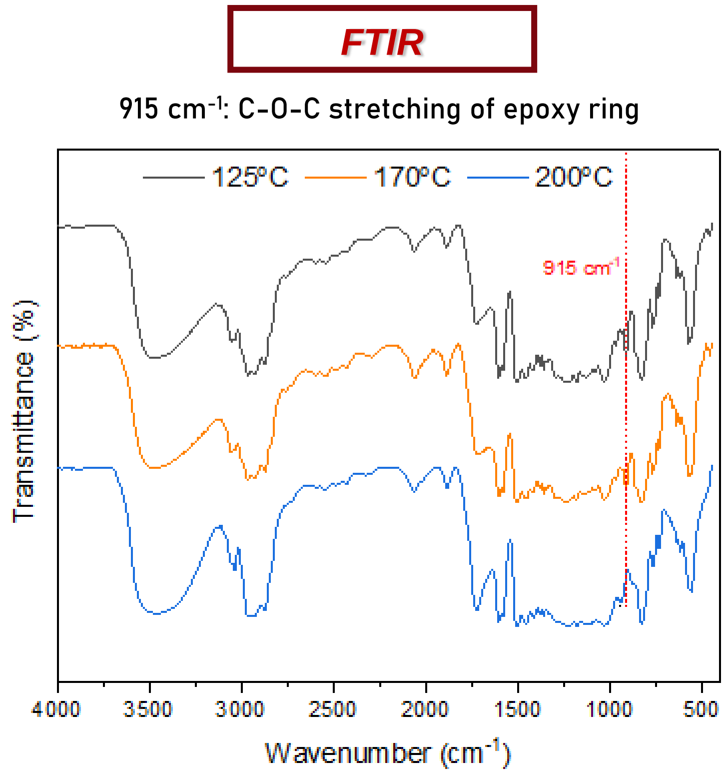


** Optical microscopy*

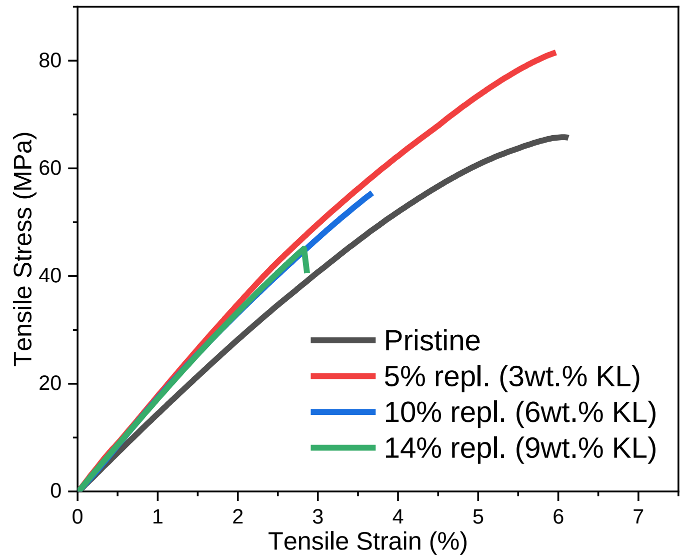
Reactivity/Ring Opening Initiation of Epoxy Polymer by Kraft Lignin



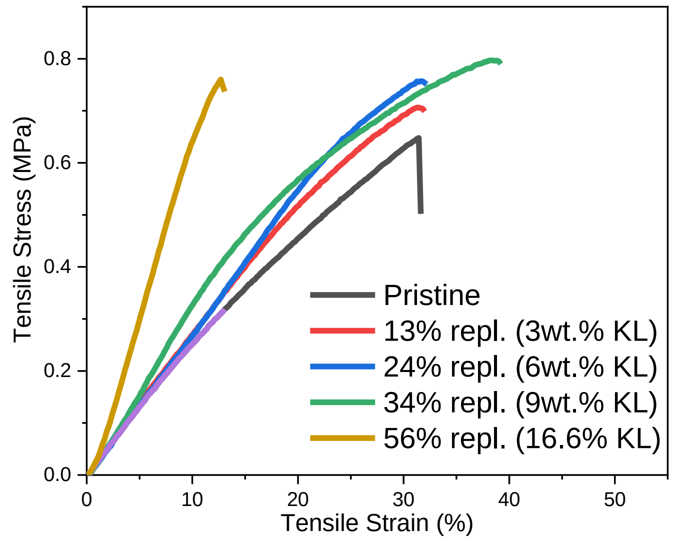
- Initially, Kraft lignin and epoxy resin were mixed in 1:1 molar ratio (oxiranes : phenolic hydroxyls)
- Jeffamine curing agents were progressively replaced by lgnin



Glassy composites

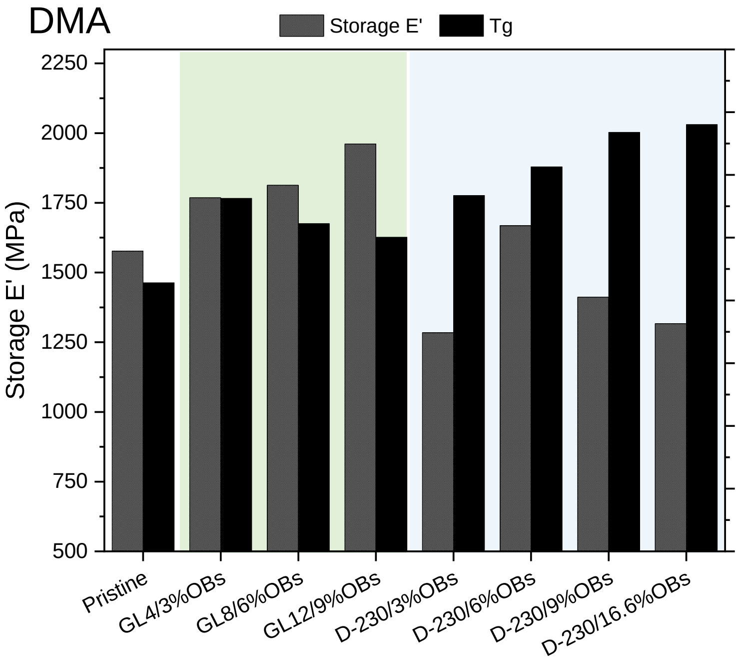


Rubbery composites



- A 5% replacement of curing agent by kraft lignin is achieved in the glassy composites while on the rubbery composites successful replacement can be achieved even up to 34% replacement.
- 3 wt% Kraft lignin content on the glassy composites results in an increase of ~20% in tensile stress.
- 9 wt% Kraft lignin content on the rubbery composites results in an increase of ~20% in tensile stress and ~10% in tensile strain.

Thermo-Mechanical properties of Organosolv (OBs) Epoxy Composites

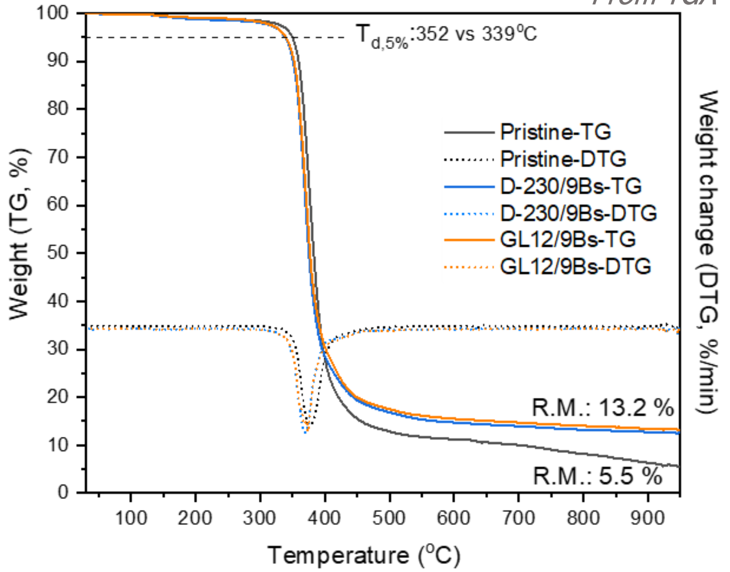


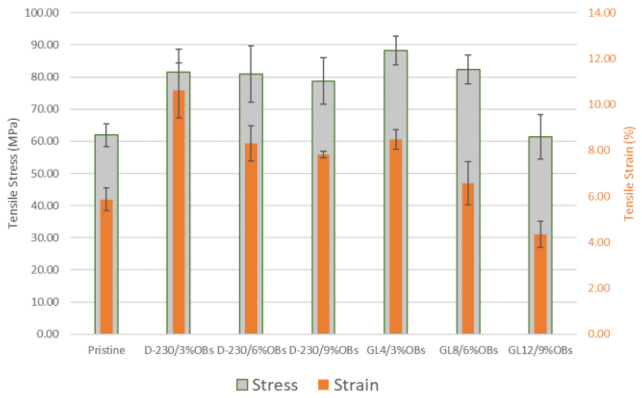
General increase of Tg and E' for OBs composites (especially when OBs is used as crosslinker)

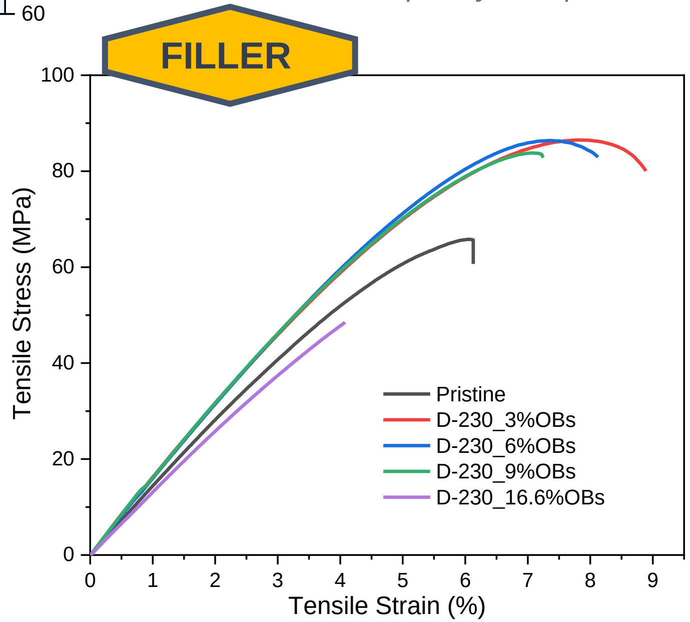
Optical Microscopy - Composites

Completely transparent composites

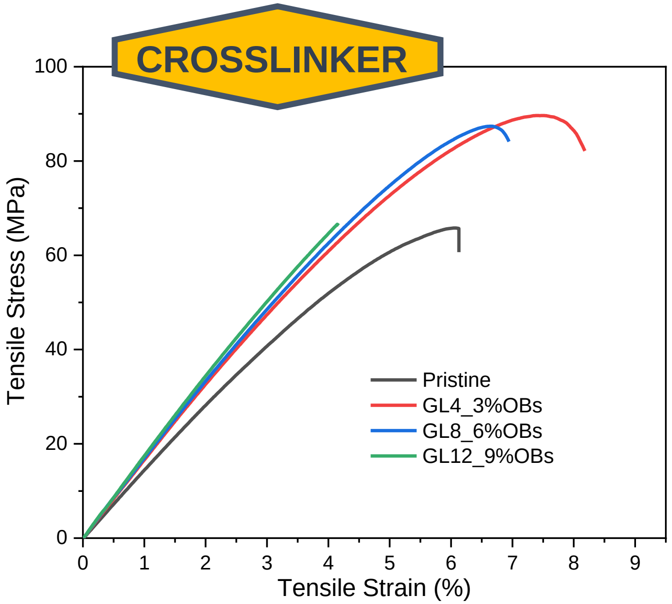
** From TGA*







Substantial increase of both tensile stress and strain of OBs-based composites even at high %.



Successful replacement (increase of mechanical properties) of Jeffamine curing agent up to 6 wt.% by OBs lignin

GL4/3%OBs *GL12/9%OBs*

D-230/3%OBs *D-230/9%OBs*

Conclusions

- **Lignins** (Kraft, Glycidylized, Nano-Kraft and Organosolv), with high functionality were successfully used as **crosslinkers** and **fillers** in glassy and rubbery epoxy composites.
- Effective use of pulp industries byproduct**, Kraft lignin**, as a filler, with loadings ranging from 3 to 45% (in rubbery epoxy polymers) towards the **improvement/tailoring of their mechanical properties**
- A 3 wt.% addition of kraft lignin in glassy/rigid epoxy composite systems resulted in **improvements** similar to those offered by classical inorganic nano-fillers, such as clays and CNTs
- Successful **replacement** of **5 wt.%** of glassy curing agent and **34 wt.%** of rubbery curing agent by Kraft Lignin, that resulted in not only retaining of initial mechanical properties but also in a significant (>10%) improvement.
- **Treated lignins (glycidylized and nano-lignin)** provided greater dispersion in the epoxy polymer and **increase of strain, stiffness and strength**
- **Organosolv Lignin** shows great potential in glassy epoxy resins applications.

Overall,

- Great potential of Kraft and Organosolv lignin towards the production of **"green" lignin/epoxy composites**, reducing the use of petroleum-based chemicals and monomers

Acknowledgments

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Aristotle University of Thessaloniki, Greece

http://ktrianta.webpages.auth.gr/

K. Triantafyllidis Group

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