# Mechanical, Rheological and Thermal Characterization of Lignin based Materials

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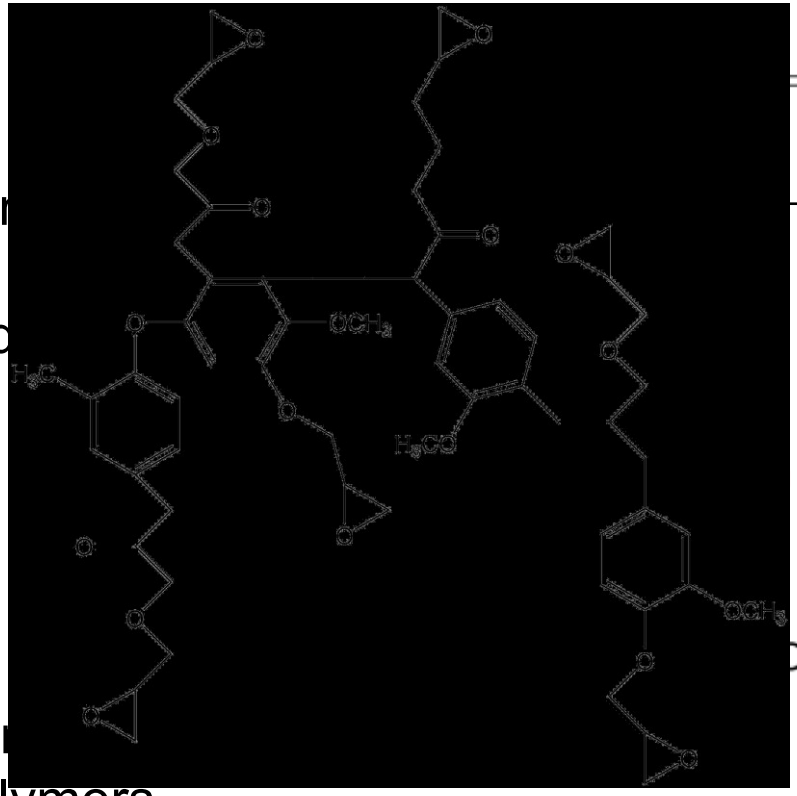
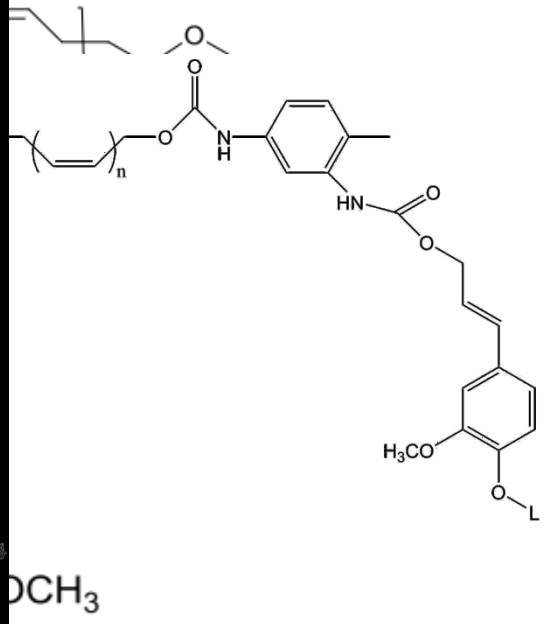
Belgrade online training school '*Modified Lignin Materials for Reactive Polymer Composites: Processing and Characterization*'

# Novel lignin based materials

Thermosets

- Polyester Resi
- Epoxy Resins
- Phenol-formalc
- Polyurethanes

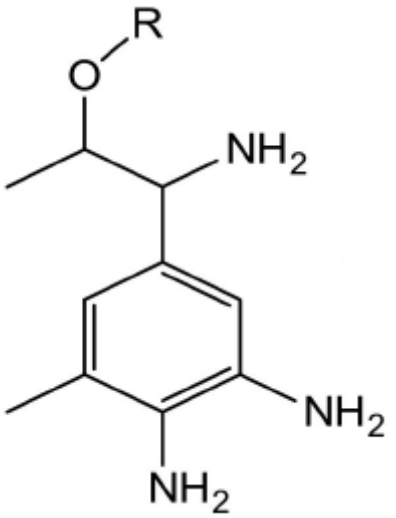




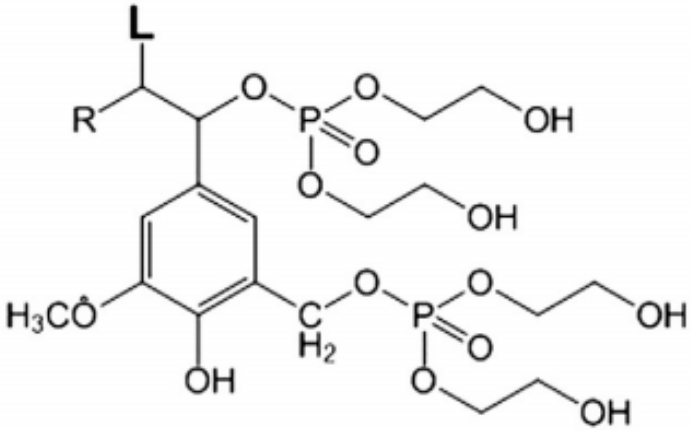
Thermoplastics

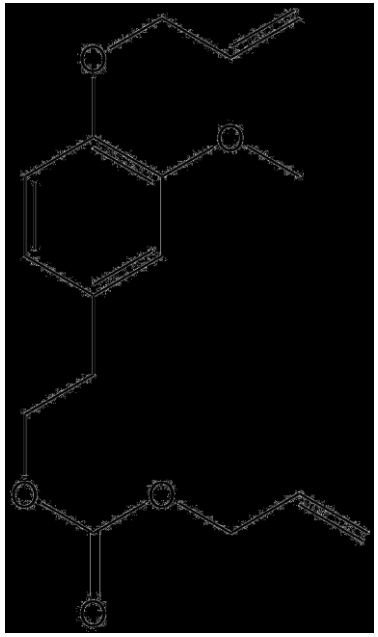
- Polymer ble
- Block co-polymers

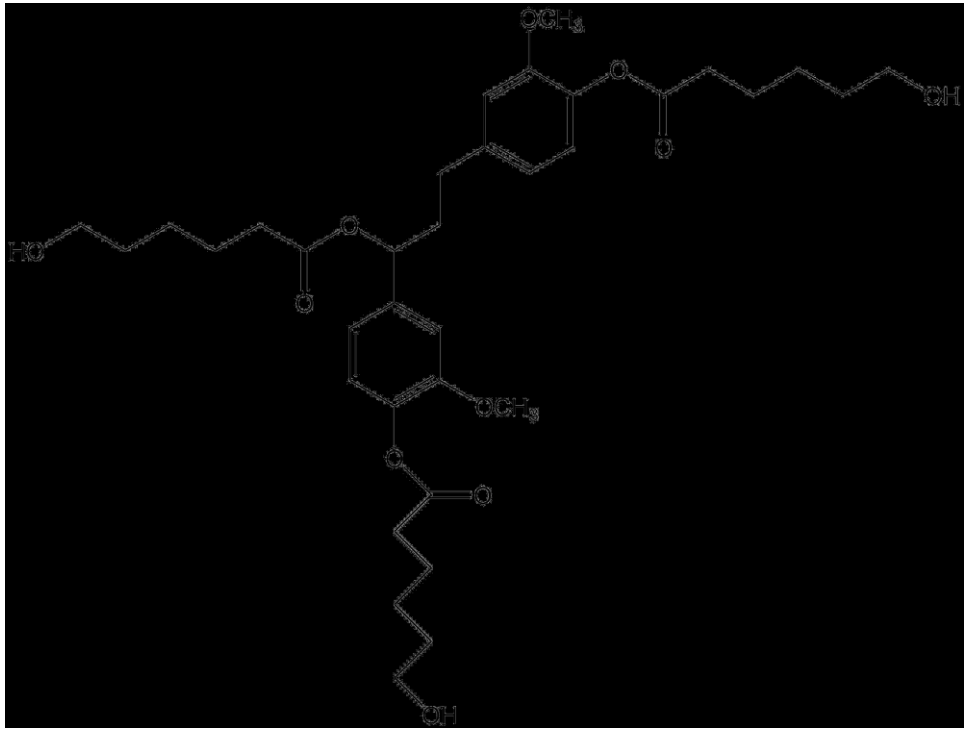
# Novel lignin based materials



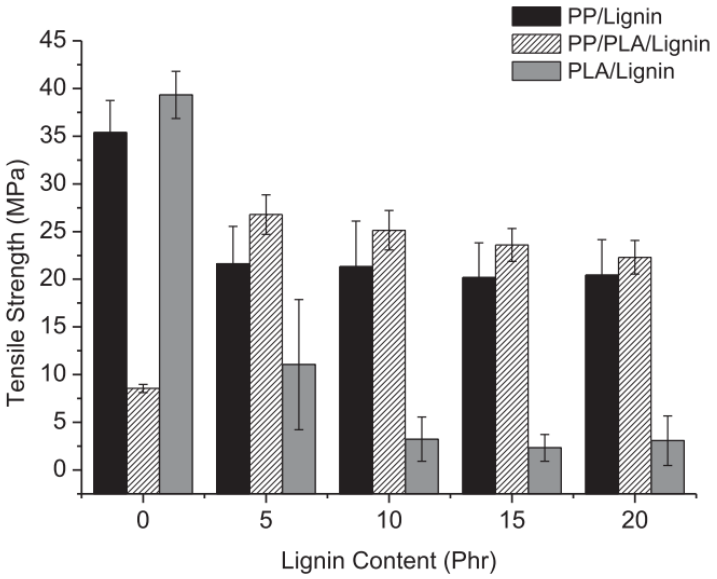

- Lignin as reinforcement in thermosets and thermoplastics

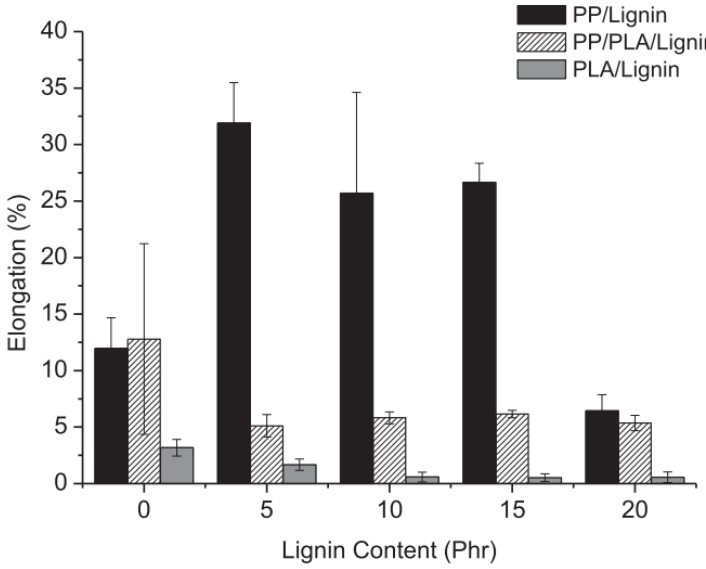




# Mechanical properties of lignin-based materials



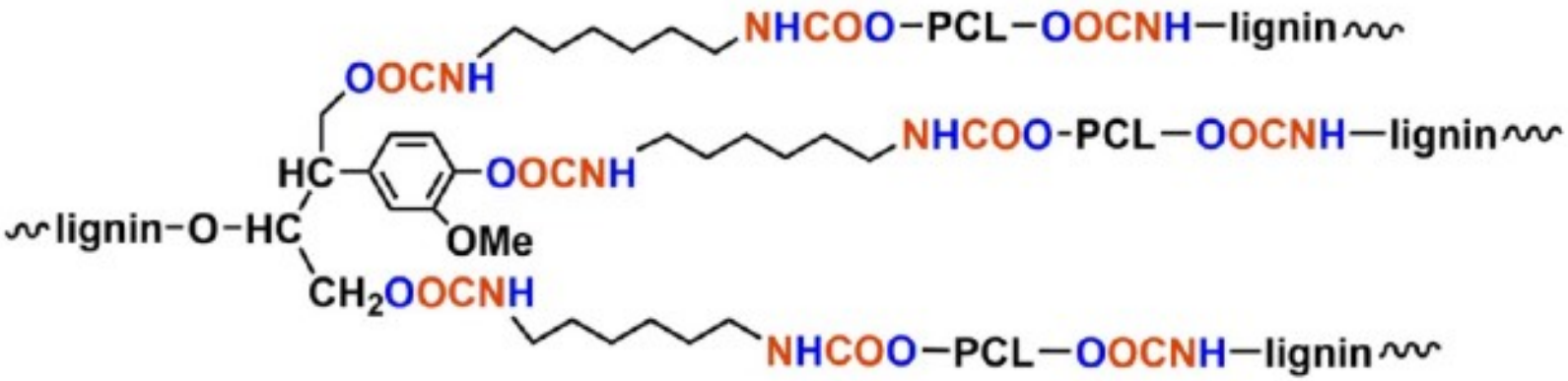




| Sample | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|
| PP | 35.4 ± 3.4 | 11.9 ± 2.7 |
| PP/lignin 5 | 21.7 ± 3.9 | 31.9 ± 3.6 |
| PP/lignin10 | 21.3 ± 4.8 | 25.7 ± 8.9 |
| PP/lignin 15 | 20.2 ± 3.6 | 26.6 ± 1.7 |
| PP/lignin 20 | 20.4 ± 3.7 | 6.4 ± 1.4 |
| PLA | 39.3 ± 3.5 | 3.2 ± 0.7 |
| PLA/lignin 5 | 11.05 ± 6.8 | 1.7 ± 0.5 |
| PLA/lignin 10 | 3.2 ± 2.3 | 0.6 ± 0.4 |
| PLA/lignin 15 | 2.3 ± 1.4 | 0.5 ± 0.3 |
| PLA/lignin 20 | 3.1 ± 2.6 | 0.6 ± 0.5 |
| PP/PLA | 8.6 ± 0.4 | 12.8 ± 8.4 |
| PP/PLA/lignin 5 | 26.8 ± 2.1 | 5.1 ± 0.9 |
| PP/PLA/lignin 10 | 25.1 ± 2.1 | 5.8 ± 0.5 |
| PP/PLA/lignin 15 | 23.6 ± 1.7 | 6.2 ± 0.3 |
| PP/PLA/lignin 20 | 22.3 ± 1.8 | 5.4 ± 0.7 |

- Incompatibility of hydrophobic PP with the polarity of PLA and lignin - lower tensile strength and higher elasticity (PP/lignin)
- Higher tensile strength of PP/PLA/lignin biocomposite – lignin acts as a compatibilizer between PP and PLA
- Decreasing of elongation at break of PP/PLA/lignin - good interfacial adhesion
- PLA is very brittle material - elongation at break less than 10%

E. Triwulandari, M. Ghozali, D. Sondari, M. Septiyanti, Y. Sampora, Y. Meliana, S. Fahmiati, W. Kartika Restu & A. Haryono, Effect of lignin on mechanical, biodegradability, morphology, and thermal properties of polypropylene/polylactic acid/lignin biocomposite, Plastic, Rubber and Composites, 48:2, 2019, 82-92

# Mechanical properties of lignin-based materials

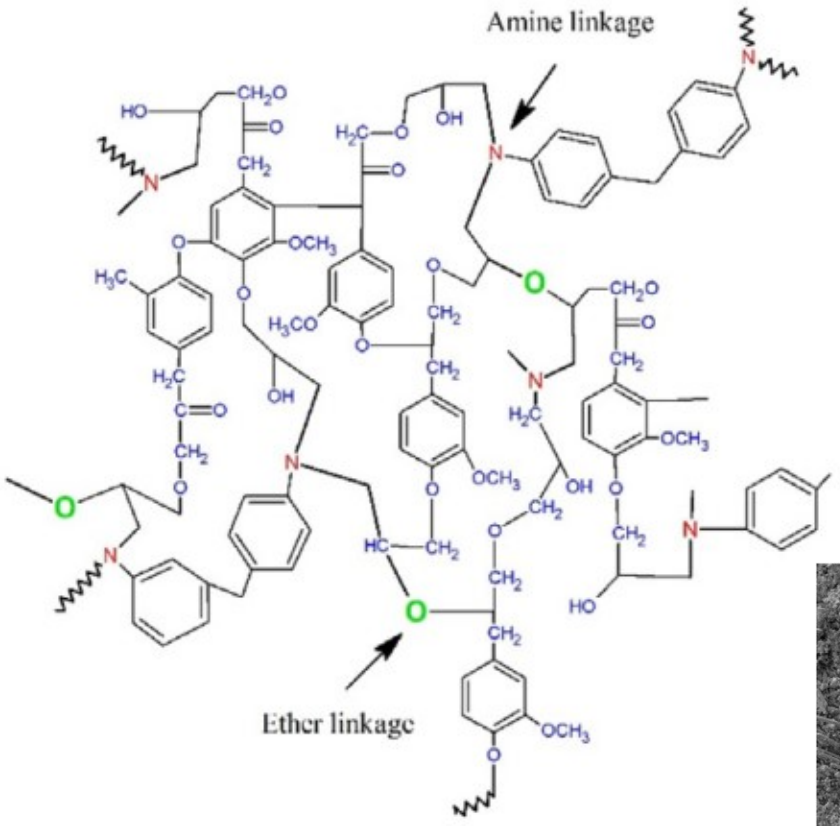



| Sample | $C_{lignin}$(%) | σ (MPa) Tensile strength | δ (%) Elongation at break | Pb (kN/m) Right-angle tear strength |
|---|---|---|---|---|
| LPU-4 | 24.18 | 13.02 ± 0.41 | 296.95 ± 7.77 | 25.66 ± 0.64 |
| LPU-14 | 29.34 | 11.86 ± 0.15 | 259.86 ± 11.25 | 24.72 ± 0.75 |
| LPU-13 | 32.84 | 16.23 ± 0.79 | 233.05 ± 11.25 | 35.50 ± 3.03 |
| LPU-12 | 37.30 | 19.35 ± 0.96 | 188.36 ± 7.73 | 38.94 ± 1.17 |
| LPU-11 | 43.15 | 15.45 ± 1.23 | 29.15 ± 13.56 | 45.09 ± 2.99 |
| LPU-10 | 81.49 | [b] | | |

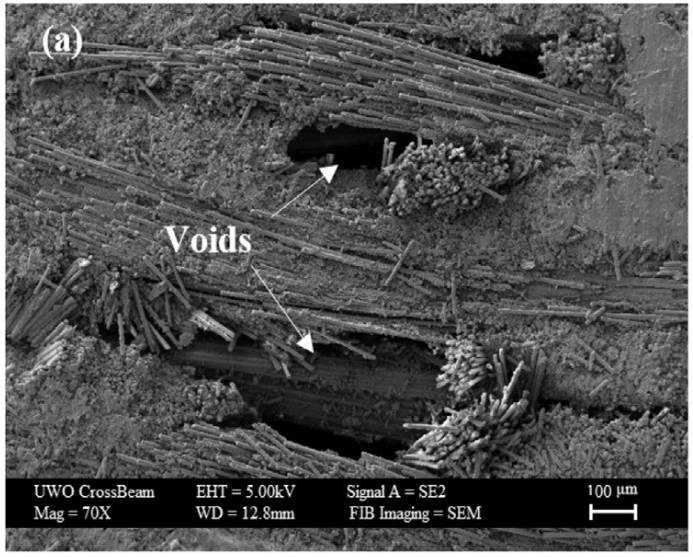
- Lignin rigidity increases tensile strength – up to 37.3% of lignin loading
- Higher lignin content - agglomeration which causes drop in tensile properties
- Higher lignin content , lower elongation at break – high cross-linking density and higher modulus

Y. Zhang, J. Liao, X. Fang, F. Bai, K. Qiao, L. Wang, Renewable High-Performance Polyurethane Bioplastics Derived from Lignin-Poly(ε-caprolactone) , ACS Sustainable Chemistry and Engineering, 2017, 5, 4276-4284

# Mechanical properties of lignin-based materials

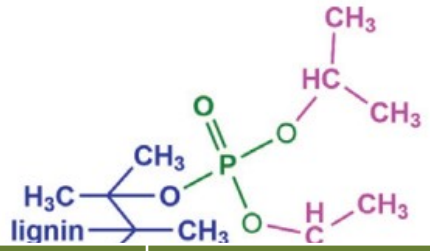


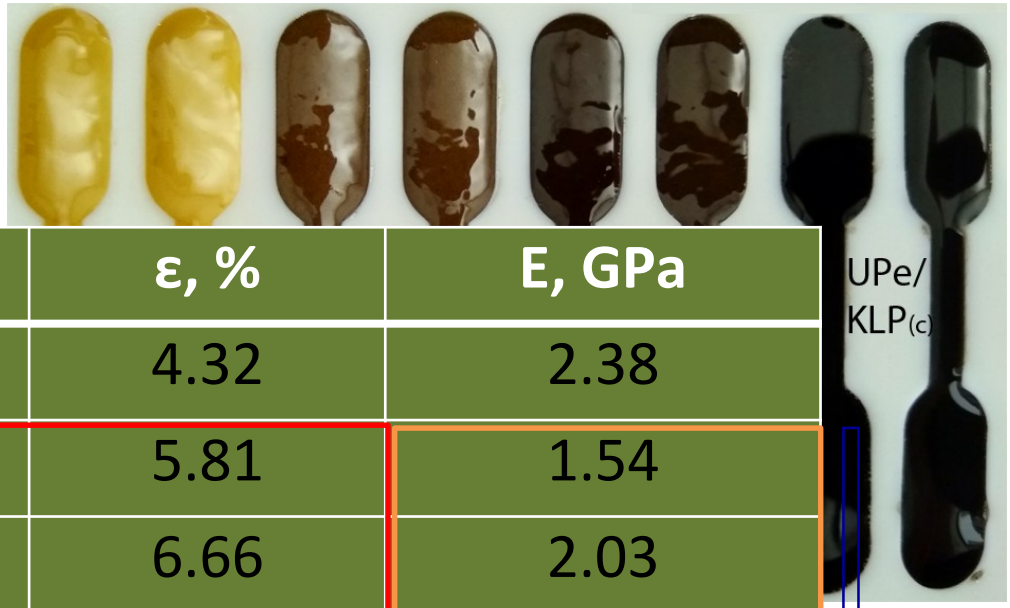

| Sample | Tensile strength (MPa) | Young's modulus (GPa) | Flexural strength (MPa) | Flexural modulus (GPa) |
|---|---|---|---|---|
| DGEBA-DDM | 214 ± 4 | 17.5 ± 0.4 | 266 ± 5 | 13 ± 0.3 |
| 25%DHL-Epoxy-DDMa | 187 ± 5 | 23.2 ± 0.7 | 258 ± 4 | 13.2 ± 0.2 |
| 50%DHL-Epoxy-DDM | 187 ± 6 | 18.5 ± 0.6 | 214 ± 4 | 13 ± 0.3 |
| 75%DHL-Epoxy-DDM | 182 ± 3 | 23.1 ± 0.4 | 149 ± 3 | 10.6 ± 0.2 |
| 100%DHL-Epoxy-DDM | 138 ± 4 | 12.3 ± 0.3 | 47 ± 2 | 5 ± 0.1 |



F. Ferdosian, Z. Yuan, M. Anderson, C. Xu, Synthesis and characterization of hydrolysis lignin-based epoxy resins , Industrial Crops and Products 91 (2016) 295–301

# Mechanical properties of lignin-based materials

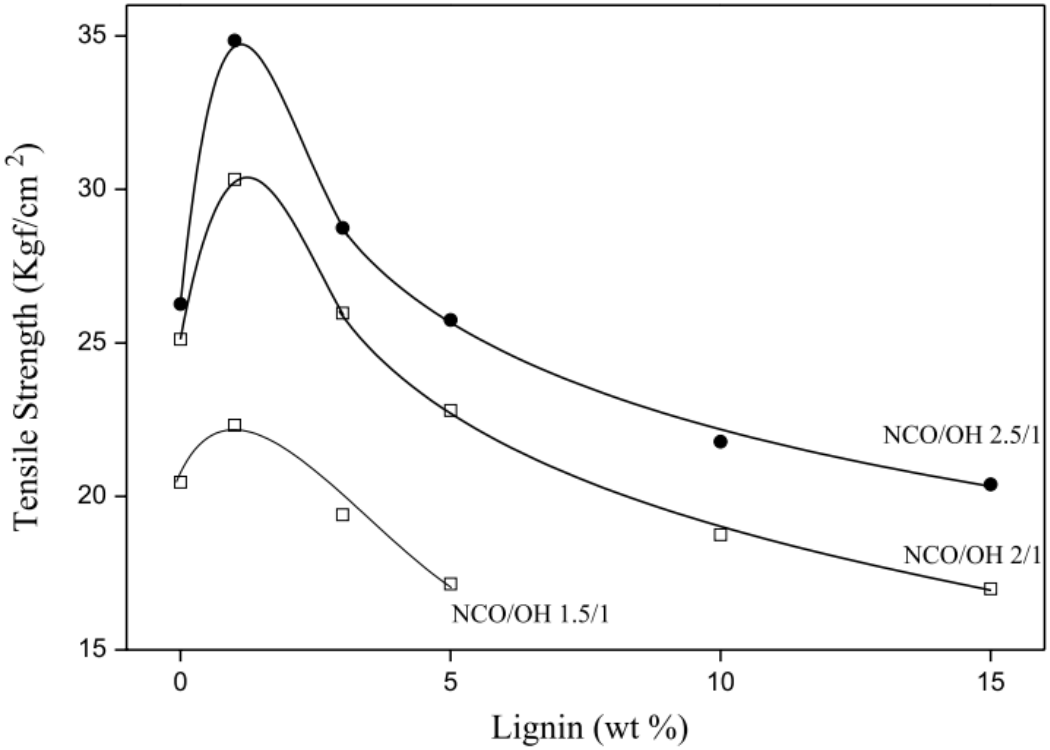


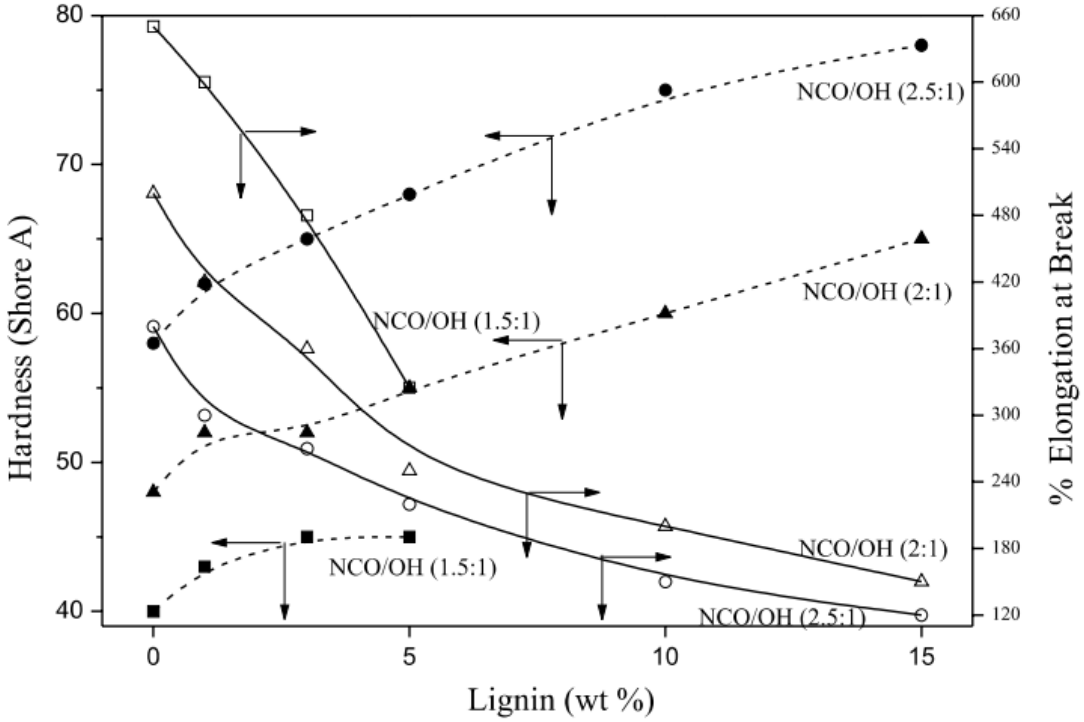




| Sample | σ, MPa | ε, % | E, GPa |
|---|---|---|---|
| UPe | 24.9 | 4.32 | 2.38 |
| UPe/KL$_{(a)}$ | 27.1 | 5.81 | 1.54 |
| UPe/KL$_{(b)}$ | 32.7 | 6.66 | 2.03 |
| UPe/KL$_{(c)}$ | 31.9 | 7.36 | 1.90 |
| UPe/KLP$_{(a)}$ | 27.3 | 3.9 | 5.55 |
| UPe/KLP$_{(b)}$ | 19.3 | 4.29 | 5.99 |
| UPe/KLP$_{(c)}$ | 17.4 | 2.47 | 6.15 |

J. Rusmirović, D. Daničić, T. Kovačević, M. Bogosavljević, S. Brzić, A. Marinković, Phosphorzlated Kraft lignin based flame retardant: Efficient method for improvement of lignin flame retardancy and nechanical action in polyester, 8th OTEH, Belgrade, Serbia, 11-12 October 2018, 538-543

# Mechanical properties of lignin-based materials



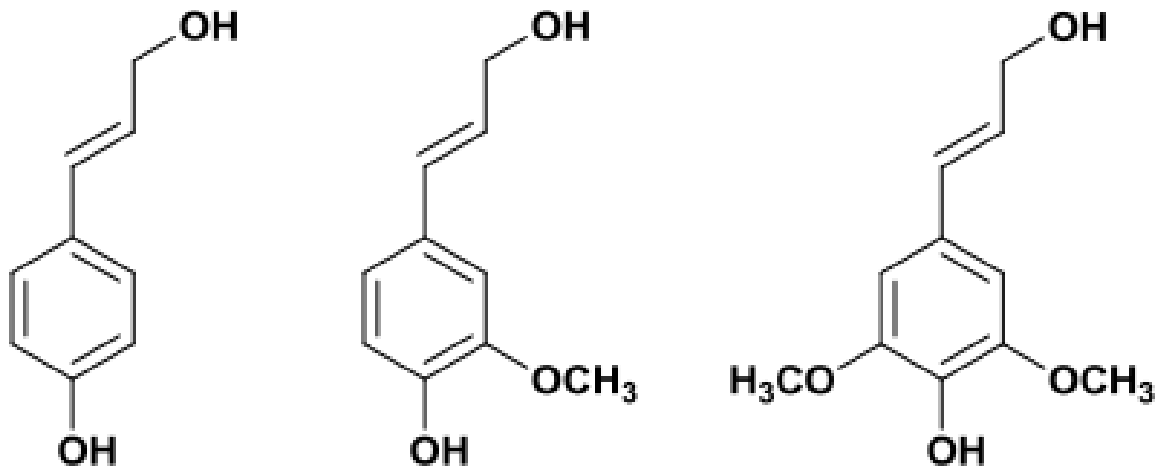




- Lower tensile strength – lack of rigidity in the soft backbone chain in HTPB
- Higher NCO/OH ratio – higher tensile strength due to higher cross-link density
- Higher hardness and lower elasticity

- Lignin amount greater than 1wt% - lower tensile strength (a lot of unreacted lignin – irregularity in the three-dimensional network structure

S. Sarkar, B. Adhikari, Synthesis and characterization of lignin – HTPB copolyurethanes, European Polymer Journal, 37 (2001), 1391-1401

# Rheological properties of lignin-based materials



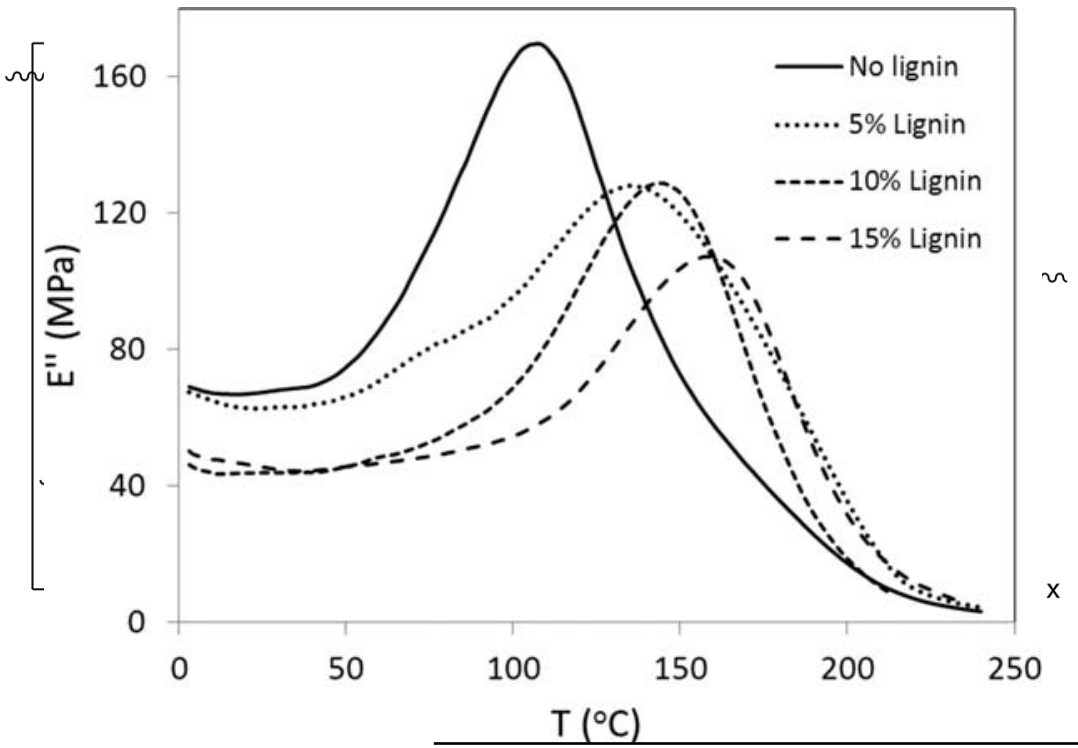

**H** H – p-hydroxyphenyl

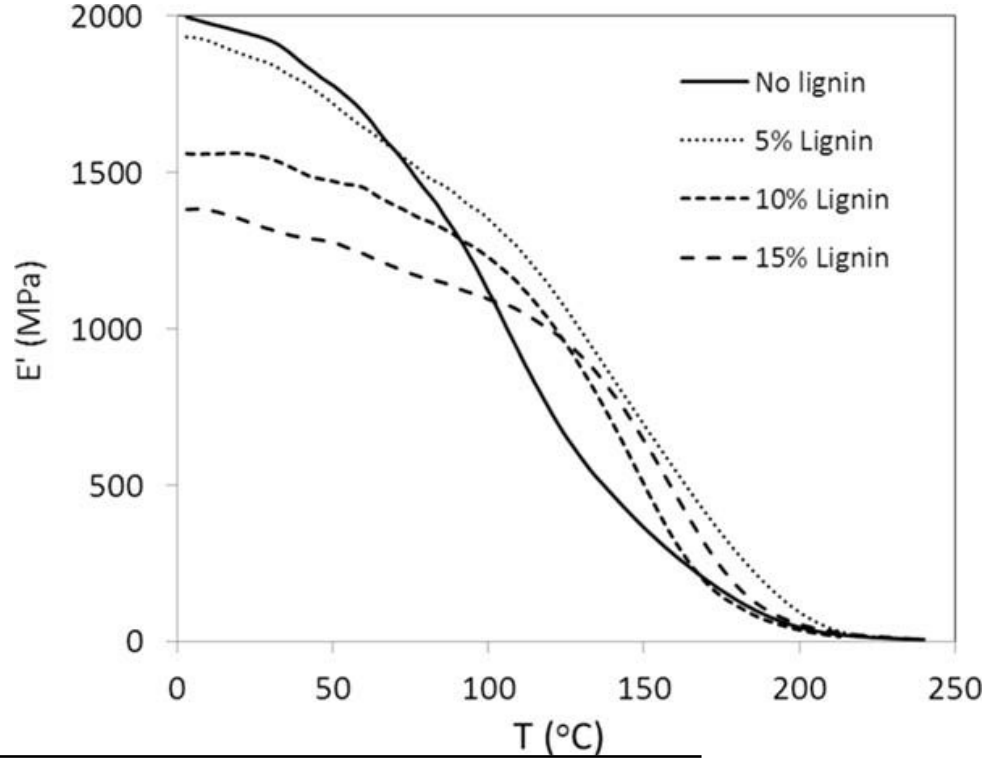
**G** G - guaiacyl

**S** S - syryngyl

- Softwood lignin – high glass transition temperature ($T_g$ between 138 – 160 °C)
- Hardwood lignin – lower glass transition temperature ($T_g$ between 110 – 130 °C)
- Kraft lignin - poly-dispersed, branched, phenol rich polymeric material obtained from the native lignin by the kraft (sulphate) pulping process – $T_g$ between 124 and 174˚C
- Organosolv lignin - obtained by pulping processes that use organic solvents (ethanol, acetic acid, formic acid) and water – $T_g$ between 91 and 97˚C

# Rheological properties of lignin-based materials

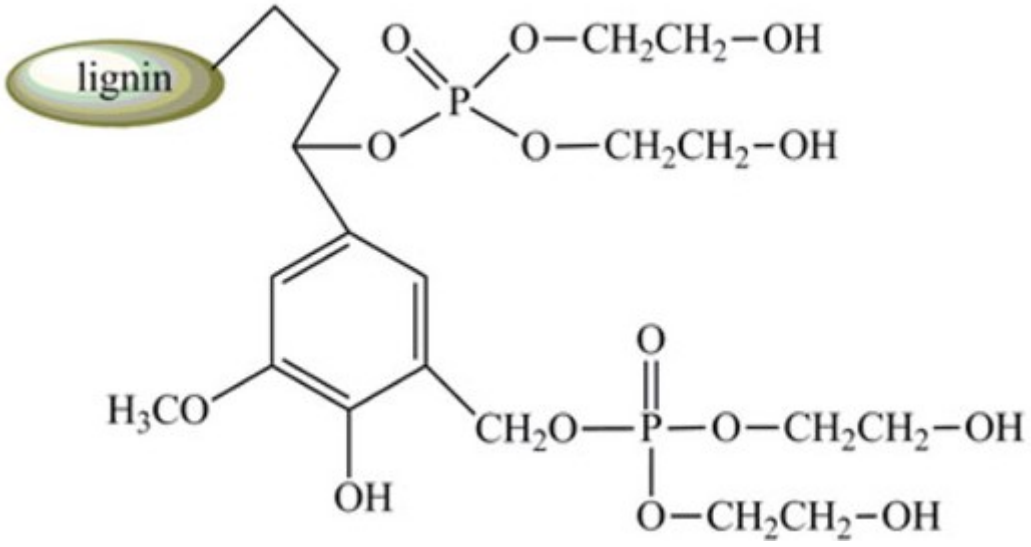


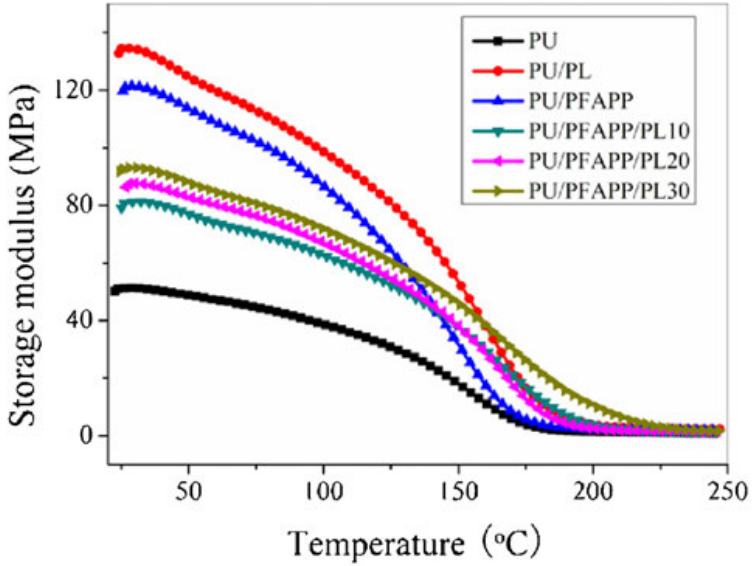



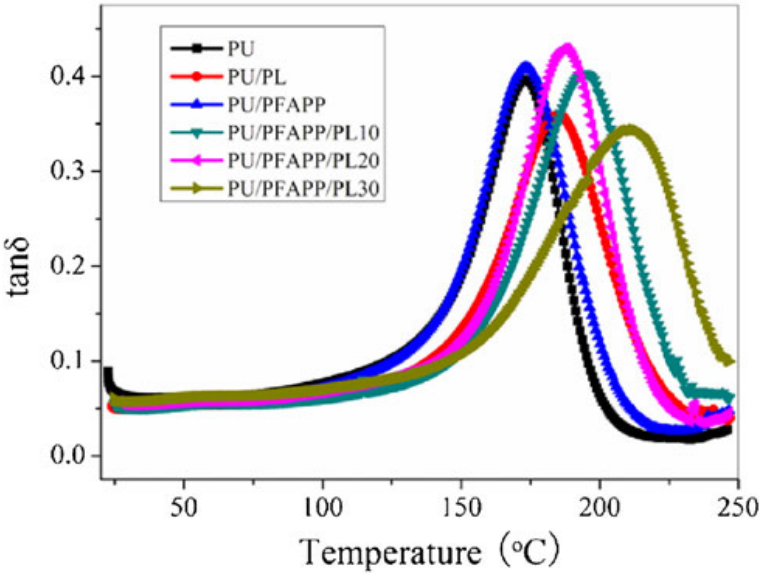

| Sample | Lignin (%) | $T_{g1}$,°C (DSC) | $T_{g2}$,°C (DSC) | $T_g$,°C (DMA) | E' (MPa) at 20°C |
|---|---|---|---|---|---|
| L0 | 0 | -21.9 | 94.8 | 80 | 2000 |
| L5 | 5 | -20.9 | 112.4 | 95 | 1930 |
| L10 | 10 | -22.6 | 127.5 | 98 | 1560 |
| L15 | 15 | -23.1 | 132.4 | 106 | 1380 |

H. Pohjanlehto, H. M. Setala, D. E. Kiely, A. G. McDonald, Lignin-Xylaric Acid-Polyurethane-Based Polymer Network Systems: Preparation and Characterization, Journal of Applied Polymer Science, 131:1, 2014, 39714

# Rheological properties of lignin-based materials



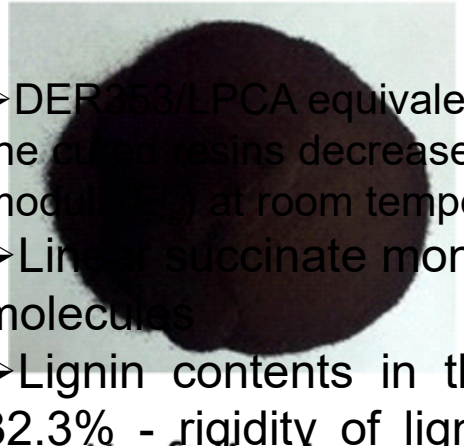



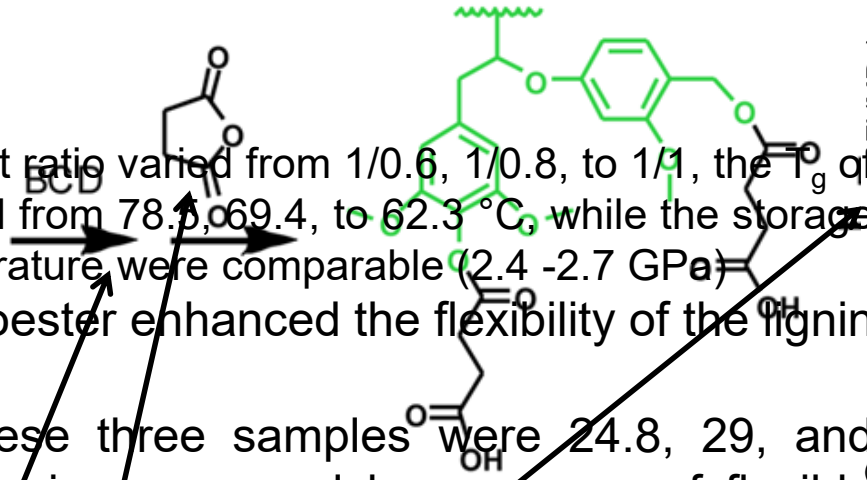

- Microencapsulated APP with phenolic shell (PFAPP), functionalized lignin and MDI – rigid polyurethane foam

- E' values of PU/PL and PU/PFAPP are significantly higher than that of pure RPUF - hydroxyl groups of PL and PFAPP participate in cross-linking with isocyanate
- Tg of composite foams are increased compared with that of pure RPUF except PU/PFAPP - reinforced rigid filler system limits the mobility of the polymer chains and PFAPP exhibit more elastic than viscous nature

W. Xing, H. Yuan, P. Zhang, H. Yang, L. Song, Y. Hu, Functionalized lignin for halogen-free flame retardant rigid polyurethane foam: preparation, thermal stability, fire performance and mechanical properties, Journal of Polymer Research, (2013) 20:234

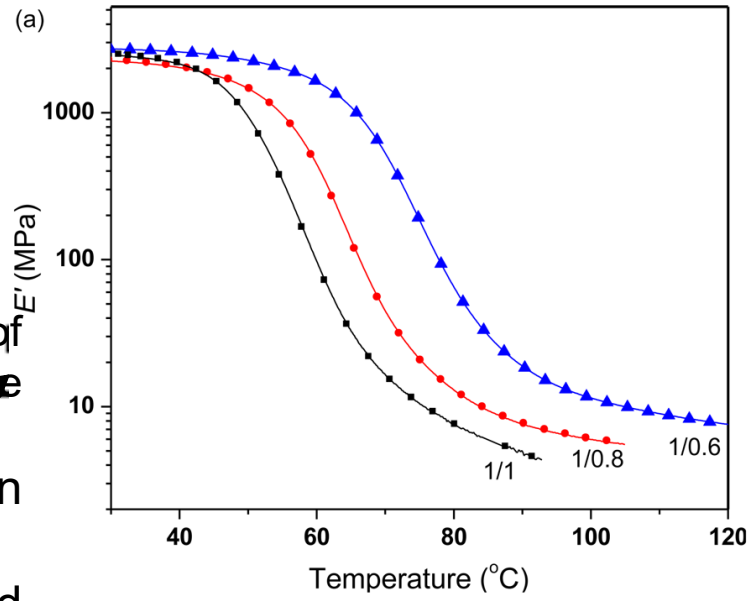
# Rheological properties of lignin-based materials

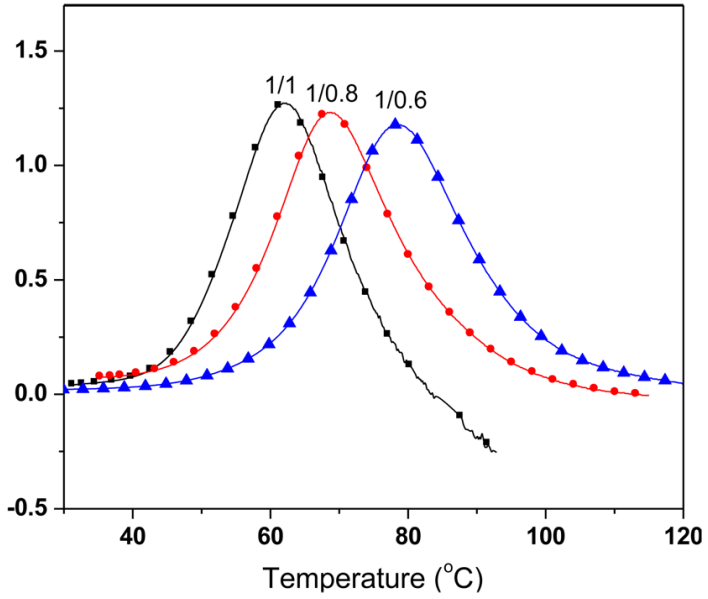



- DER353/LPCA equivalent ratio varied from 1/0.6, 1/0.8, to 1/1, the $T_g$ of the cured resins decreased from 78.5, 69.4, to 62.3 °C, while the storage modulus (E') at room temperature were comparable (2.4 -2.7 GPa)
- Linear succinate monoester enhanced the flexibility of the lignin molecules
- Lignin contents in these three samples were 24.8, 29, and 32.3% - rigidity of lignin is overcomed by presence of flexible domains from succinate monoester

- Partially base catalyzed depolymerization of Kraft lignin in supe
- Conversion of BCD to lignin-based polycarboxylic acid (LPCA)
- LPCA is soft solid - glycerol tris(succinate monoester) (GTA) is and a diluent for LPCA
- DER 353 – curing agent

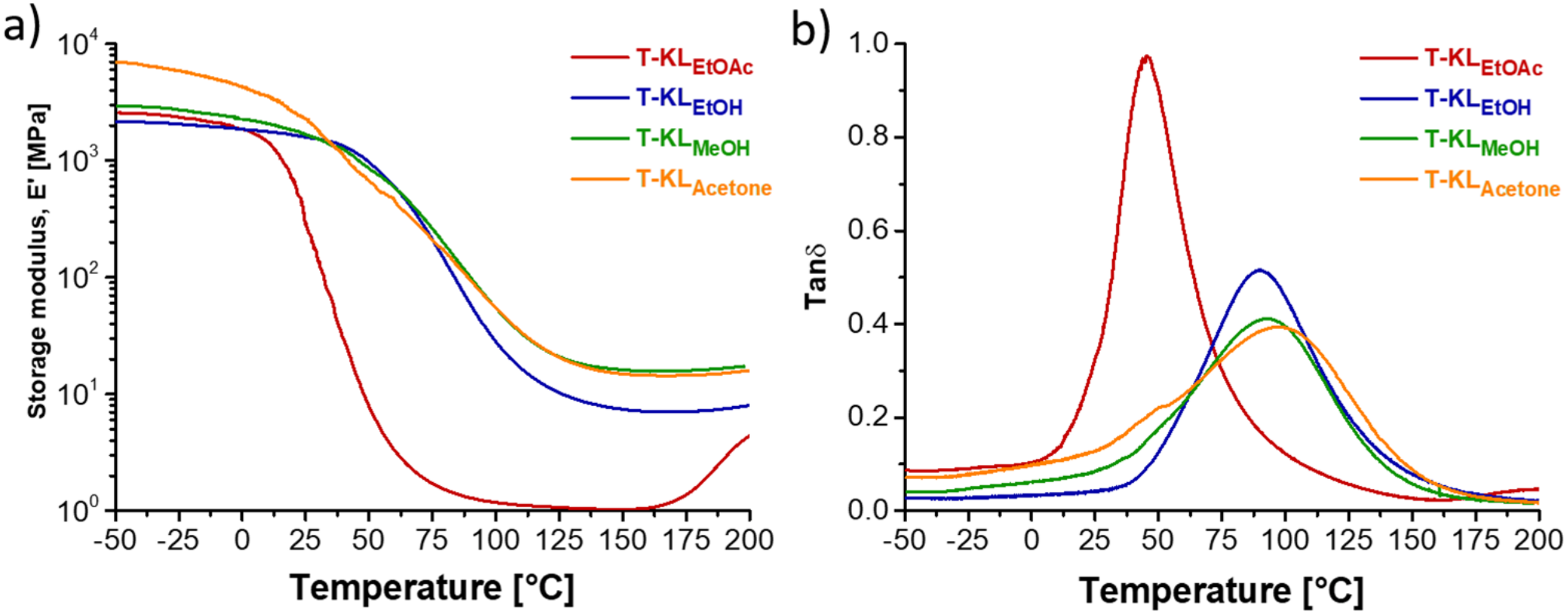



J. Qin, M. Wolocct, J. Zhang, Use of Polycarboxylic Acid Derived from Partially Depolymerized Lignin As a Curing Agent for Epoxy Application, ASC Sustainable Chemistry and Engineering, 2014, 2, 188-193

# Rheological properties of lignin-based materials

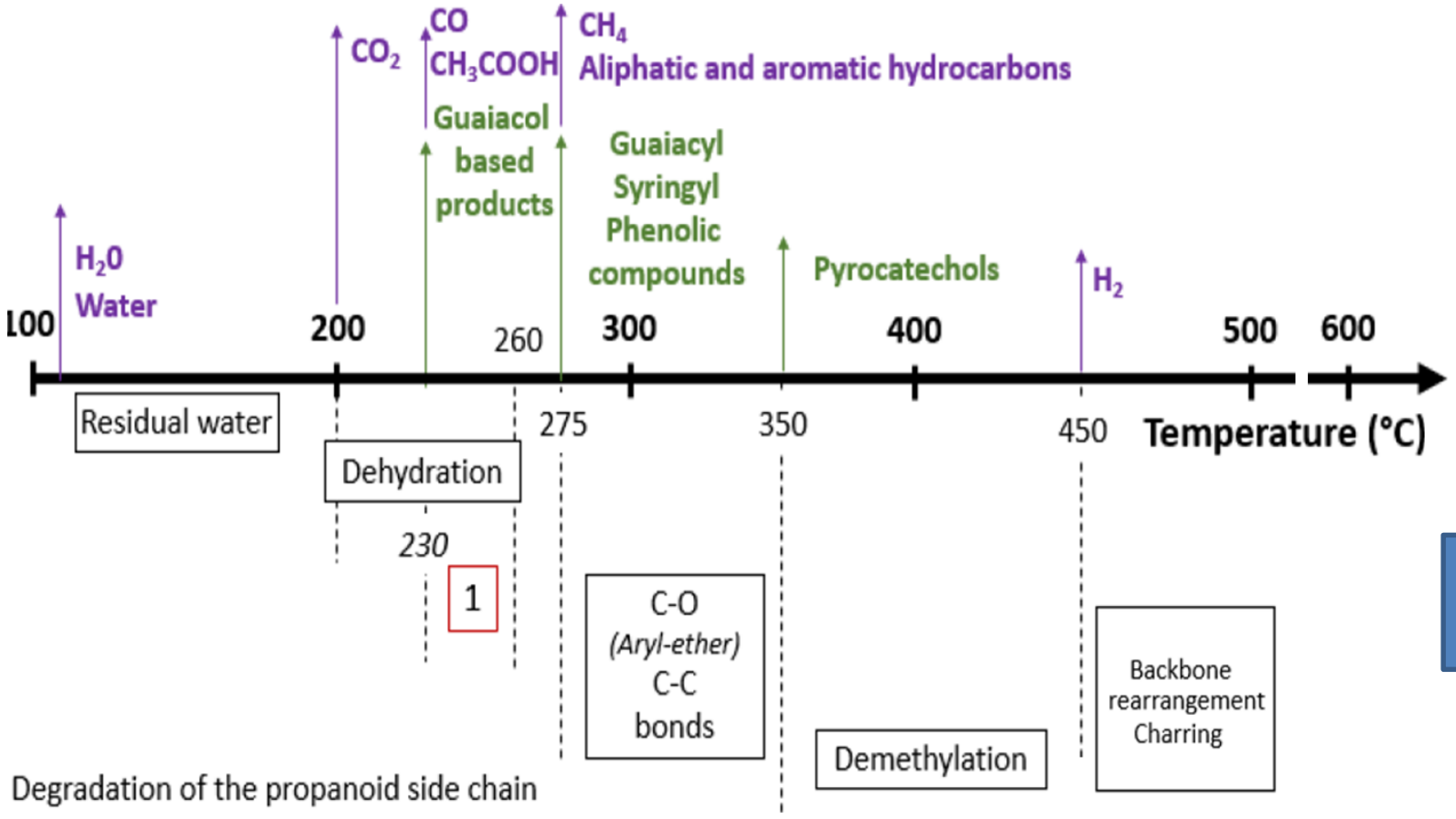
- Four types of LignoBoost Kraft lignin is obtained - $KL_{MeOH}$ , $KL_{EtOAc}$, $KL_{EtOH}$ and $KL_{Acetone}$
- A-$KL_{Fraction}$ – used for production of Thiol-Ene Resin (TMP is used as a curing agent, EtOAc as cosolvent

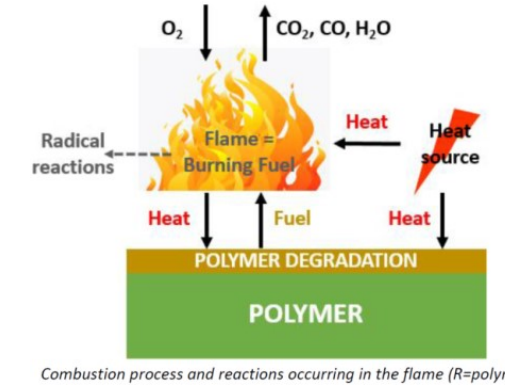



M. E. Jawerth, C. J. Brett, P. T. Larsson, M. Lawoko, S. V. Roth, S. Lundmark, M. Johansson , Mechanical and Morphological Properties of Lignin-Based Thermosets , ASC Applied Polymer Materials, 2020, 2, 668-676

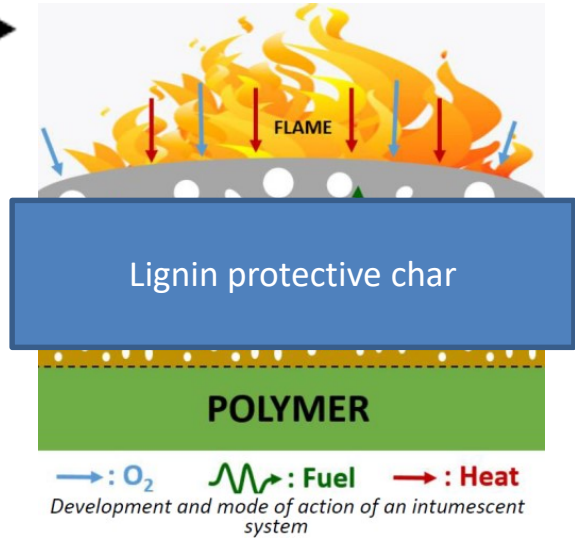
# Thermal properties of lignin-based materials

- Reduce heat release rate for polymer combustion
- Rearrangement of backbone producing aromatic structure like char



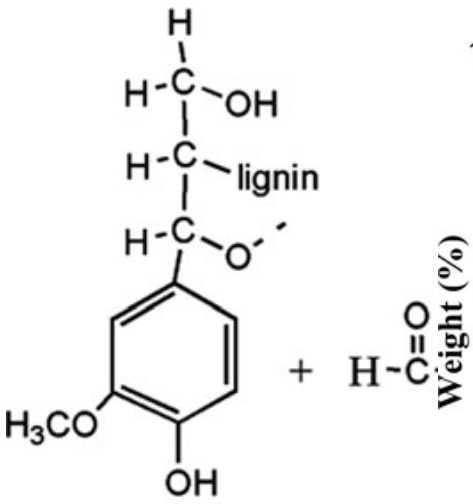




*Combustion process and reactions occurring in the flame (R=polymer)*

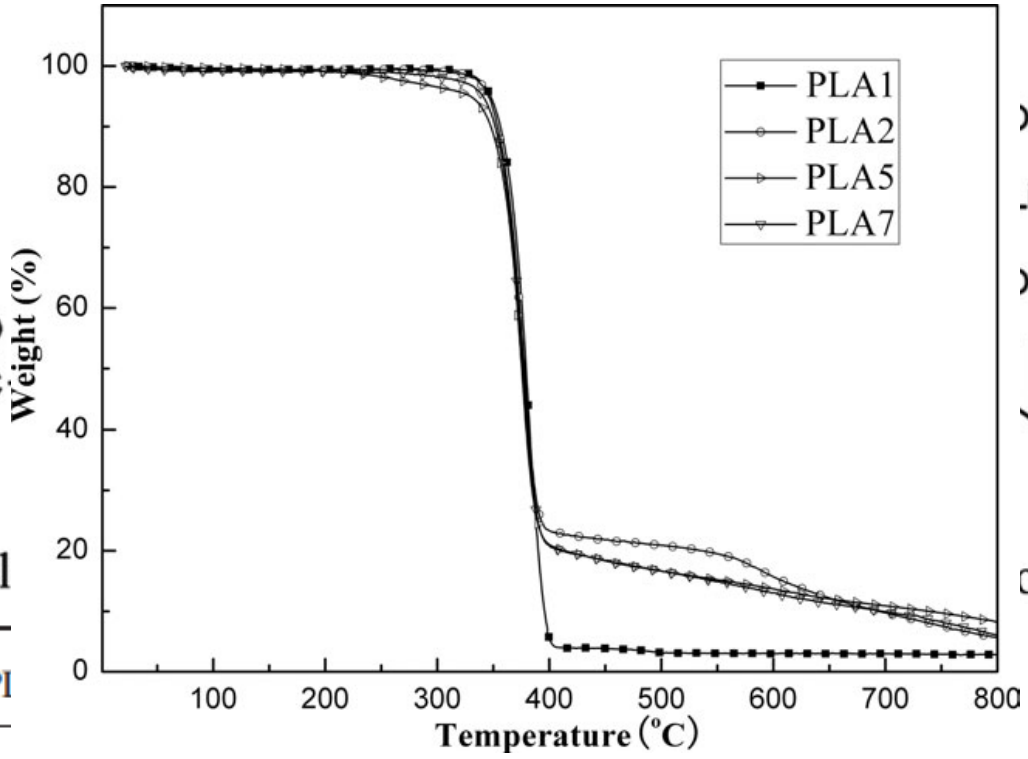



*Development and mode of action of an intumescent system*

# Thermal properties of lignin-based materials




+ H-C(=O)




OH
ignin
C-NH-C-NH
H2
odefied Lignin

Lignin Formal

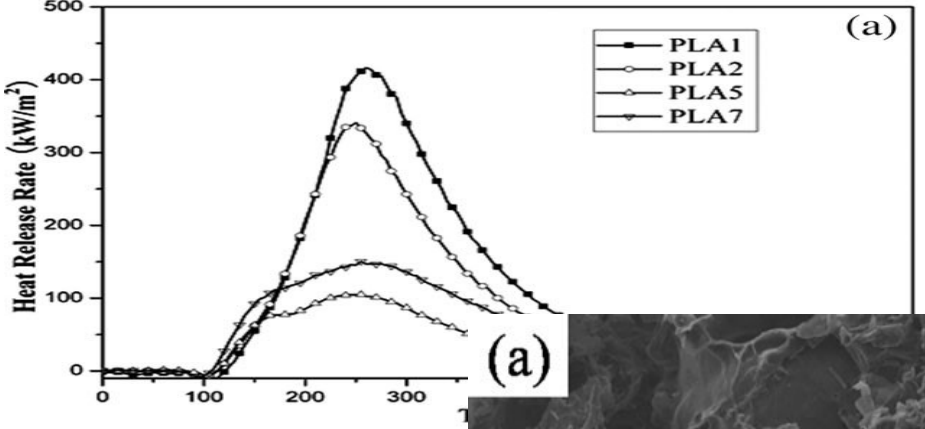
| Sample code | Pl |
|---|---|
| PLA1 | |
| PLA2 | |
| PLA3 | |
| PLA4 | |
| PLA5 | |
| PLA6 | |
| PLA7 | |

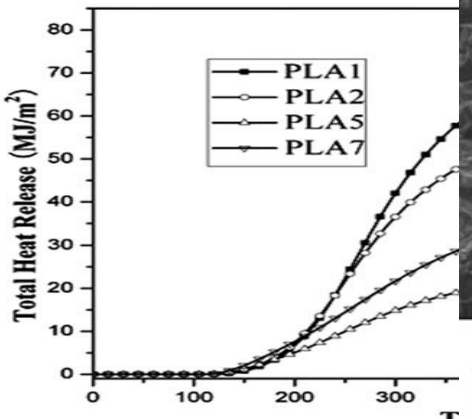
V-0

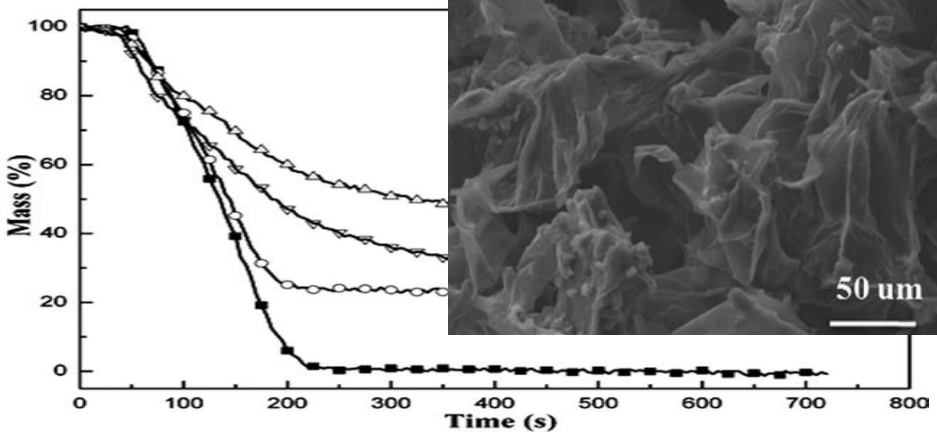
| Sample | $T_5$ (°C) | $T_{50}$ (°C) | $T_{max}$ (°C) | Residue at 800°C (wt%) |
|---|---|---|---|---|
| PLA1 | 348 | 379 | 380 | 2 |
| PLA2 | 345 | 376 | 375 | 5 |
| PLA5 | 329 | 373 | 373 | 9 |
| PLA7 | 340 | 376 | 376 | 6 |

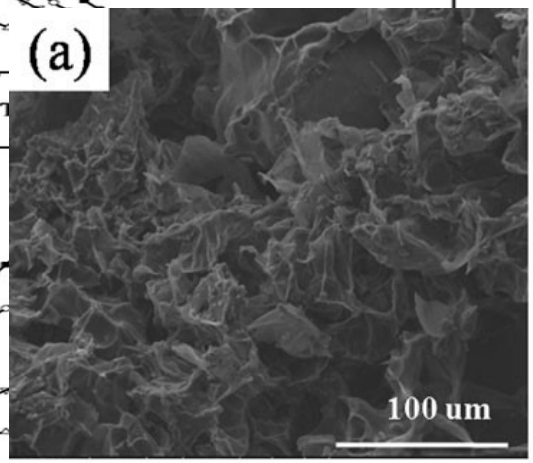
R. Zhang, X. Xiao, Q. Tai, H. Huang, Y. Hu, Modification of Lignin and Its Application as Char Agent in Intumescent Flame-Retardant Poly(lactic acid), Polymer Engineering and Science, 52(12), 2012, 2620-2626

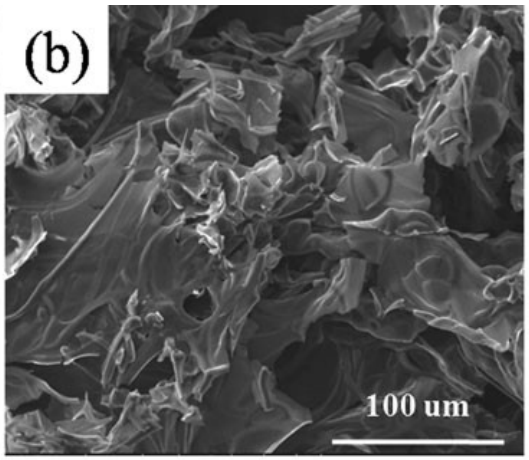
# 'mal properties of lignin-based materials

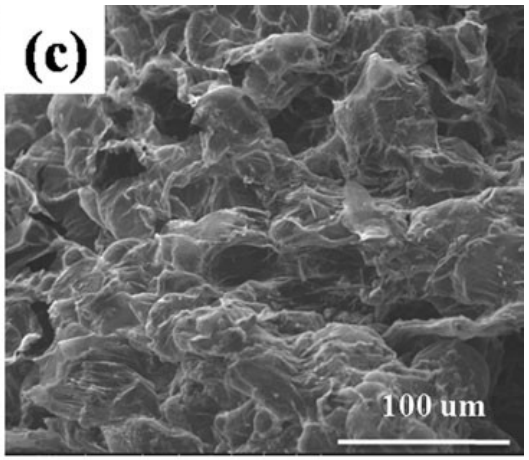


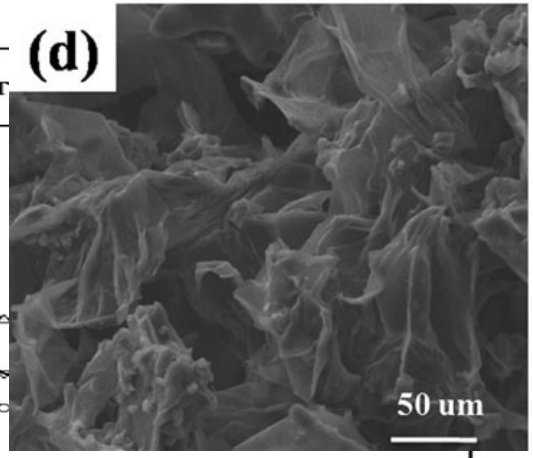



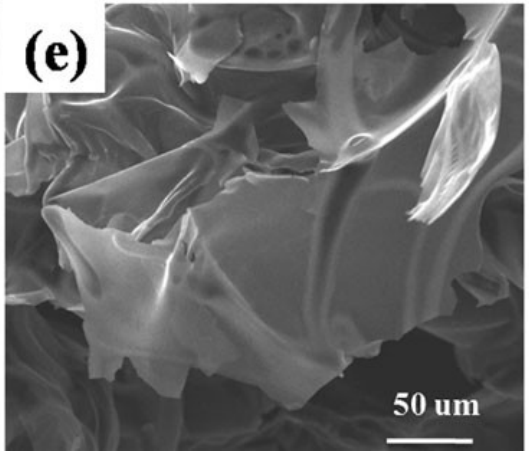



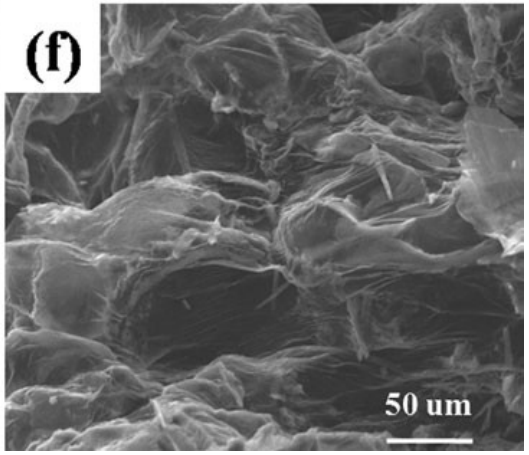



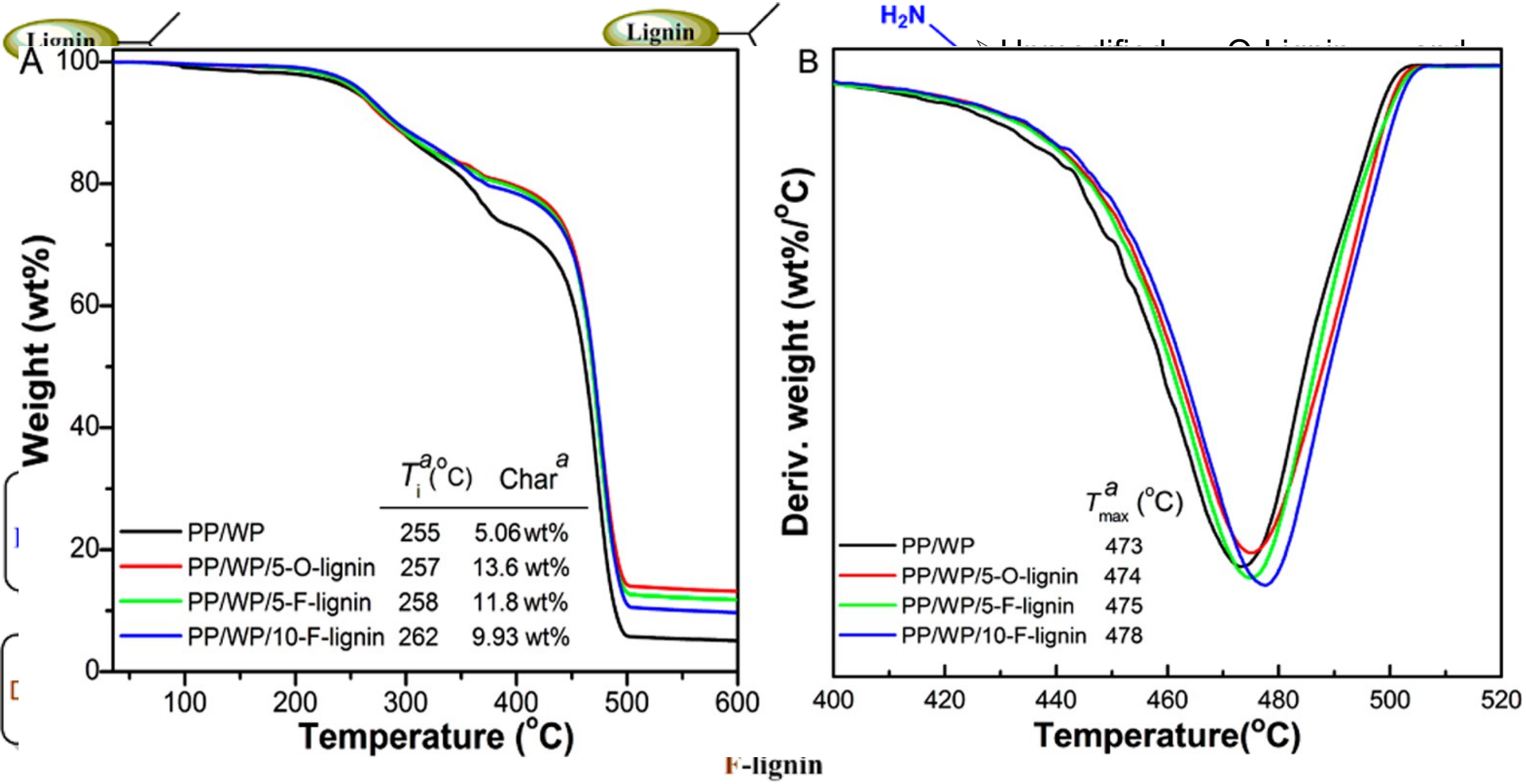




R. Zhang, X. Xiao, Q. Tai, H. Huang, Y. Hu, Modification of Lignin and Its Application as Char Agent in Intumescent Flame-Retardant Poly(lactic acid), Polymer Engineering and Science, 52(12), 2012, 2620-2626

# Thermal properties of lignin-based materials




P. Song, Y. Yu, S. Fu, Fabrication of Green Lignin-based Flame Retardants for Enhancing the Thermal and Fire Retardancy Properties of Polypropylene/Wood Composites, ASC Sustainable Chemistry and Engineering, 2016, 4, 2422-2431

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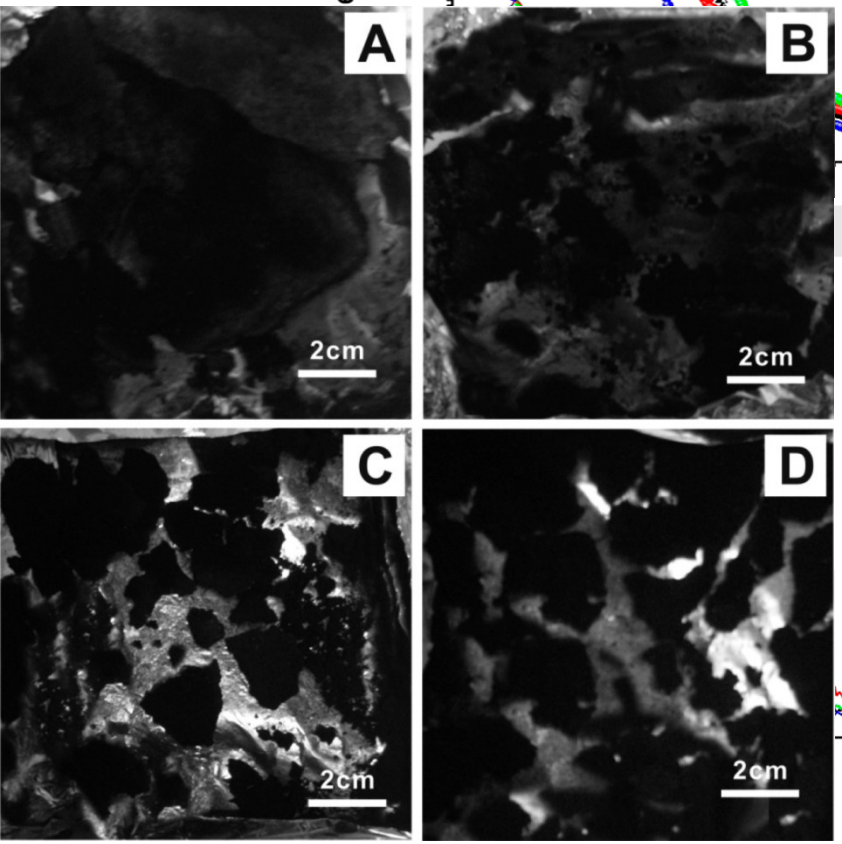
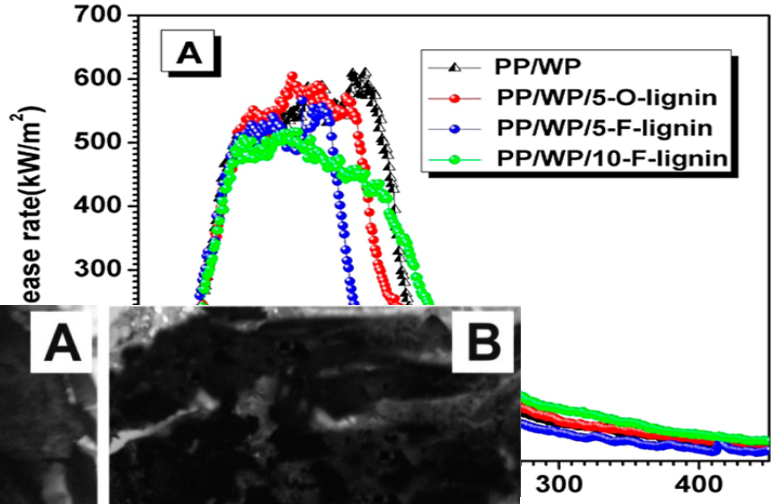
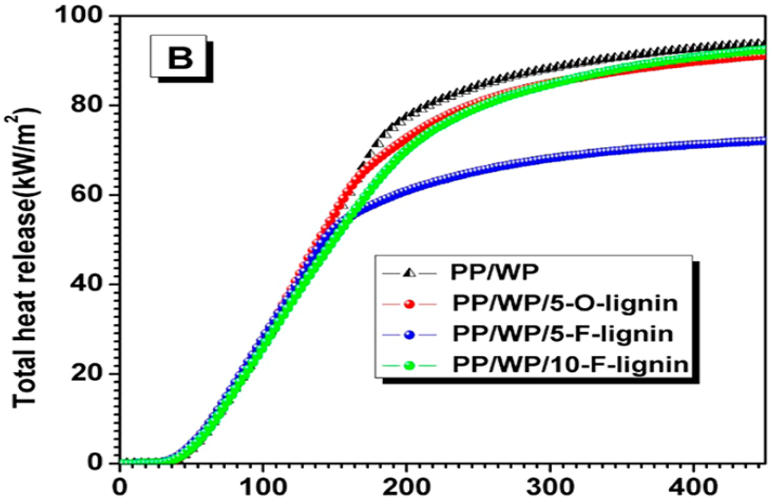
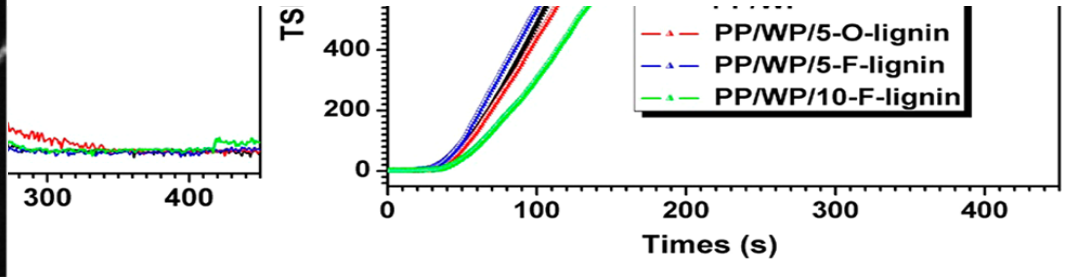



| no. | $t_{ign}$[a] (°C) | PHRR[a] (kW/m²) | THR[a] (MJ/m²) | residue[a] (wt %) |
|---|---|---|---|---|
| PP/WP | 18 ± 1 | 595 ± 15 | 93.9 ± 2.2 | 8.40 ± 0.3 |
| PP/WP/5-O-lignin | 20 ± 1 | 611 ± 18 | 91.5 ± 1.9 | 9.61 ± 0.4 |
| PP/WP/15-O-lignin | 22 ± 1 | 580 ± 20 | 85.3 ± 1.7 | 9.72 ± 0.5 |
| PP/WP/2.5-F-lignin | 19 ± 1 | 602 ± 16 | 90.2 ± 1.5 | 9.49 ± 0.3 |
| PP/WP/5-F-lignin | 22 ± 1 | 542 ± 10 | 60.5 ± 1.8 | 10.9 ± 0.2 |
| PP/WP/10-F-lignin | 23 ± 1 | 575 ± 12 | 72.3 ± 1.4 | 10.3 ± 0.2 |
| PP/WP/15-F-lignin | 24 ± 1 | 470 ± 15 | 70.2 ± 1.7 | 10.4 ± 0.3 |

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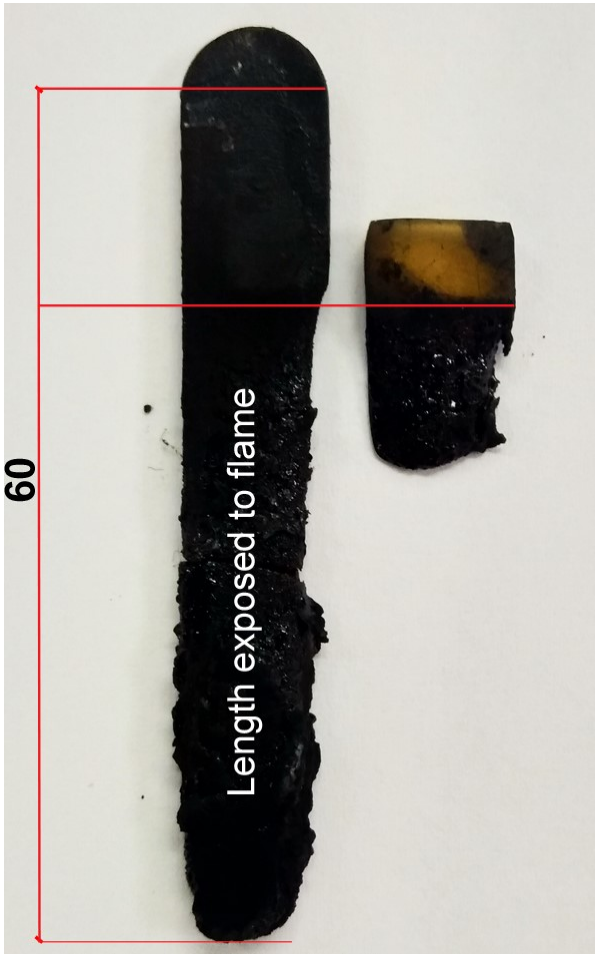


- UPe specimens exhibit bad fire properties, and dropping occurs instantaneously, with the inflamed drops burning the cotton
- The introduction of 5.0% of phosphorylated KL allows an improvement in the fire reaction of UPe blends
- UPe/KLP(c) sample can be classified in V-1 category

J. Rusmirović, D. Daničić, T. Kovačević, M. Bogosavljević, S. Brzić, A. Marinković, Phosphorzlated Kraft lignin based flame retardant: Efficient method for improvement of lignin flame retardancy and nechanical action in polyester, 8th OTEH, Belgrade, Serbia, 11-12 October 2018, 538-543

**THANK YOU FOR YOUR ATTENTION!!!**