# Green Epoxy Resin System Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt

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# Outlines

- ❖ Background
- ❖ Partially depolymerization of lignin
- ❖ Preparation and characterization of lignin based epoxy monomer
- ❖ Preparation and characterization of epoxy asphalt
- ❖ Conclusions

# Background

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Rutting

Crack


Epoxy resin


Lignin

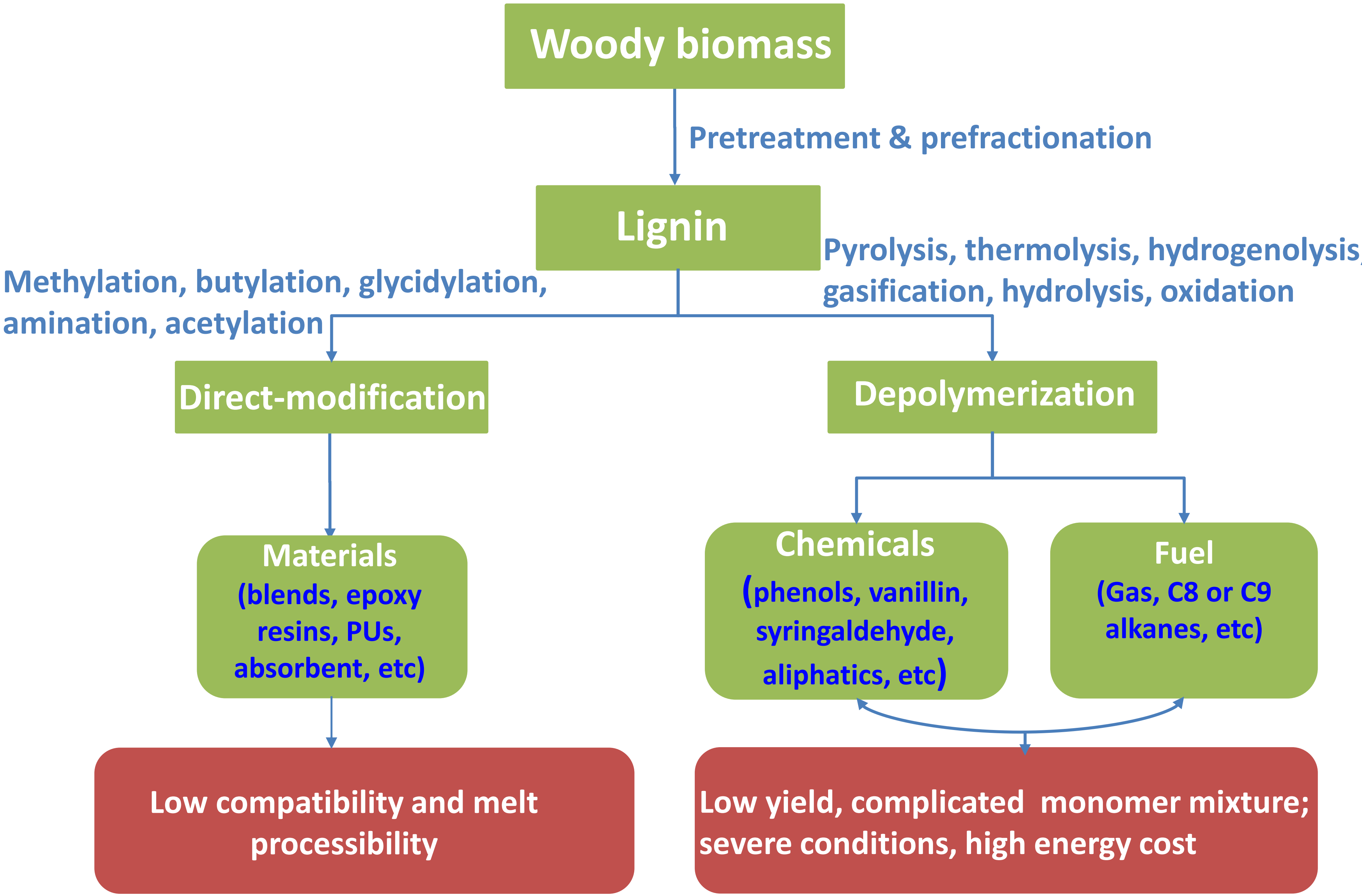
+

Vegetable oil

Bio-based epoxy resins

Epoxy asphalt

# Conversion of Lignin

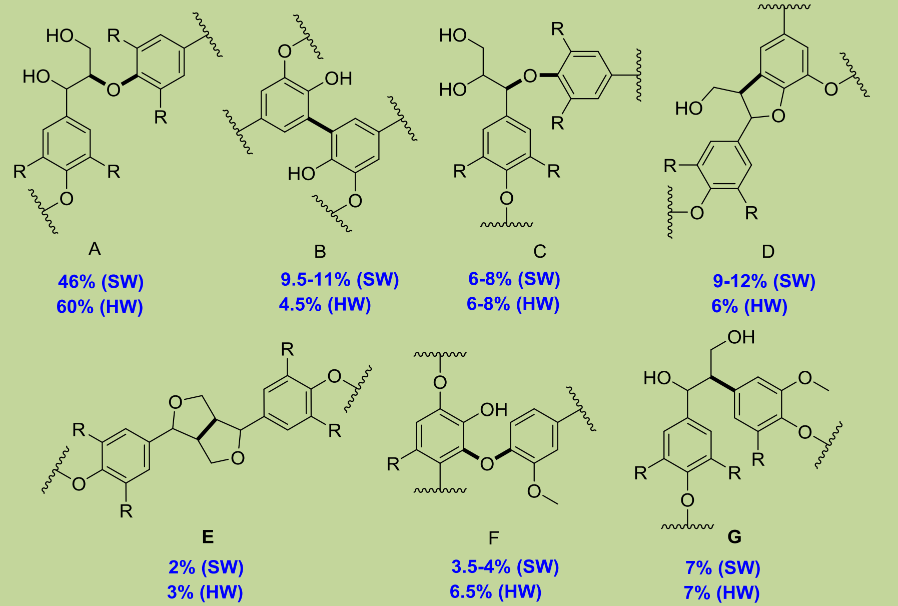


# Modification of lignin



Lignin

Major linkages




Major linkages found in lignin: (A) β-O-4, (B) 5-5, (C)α-O-4, (D)β-5, (E) β-β, (F)4-O-5, and (G) β-1

★ Mild depolymerization

Partial depolymerized lignin (PDL)

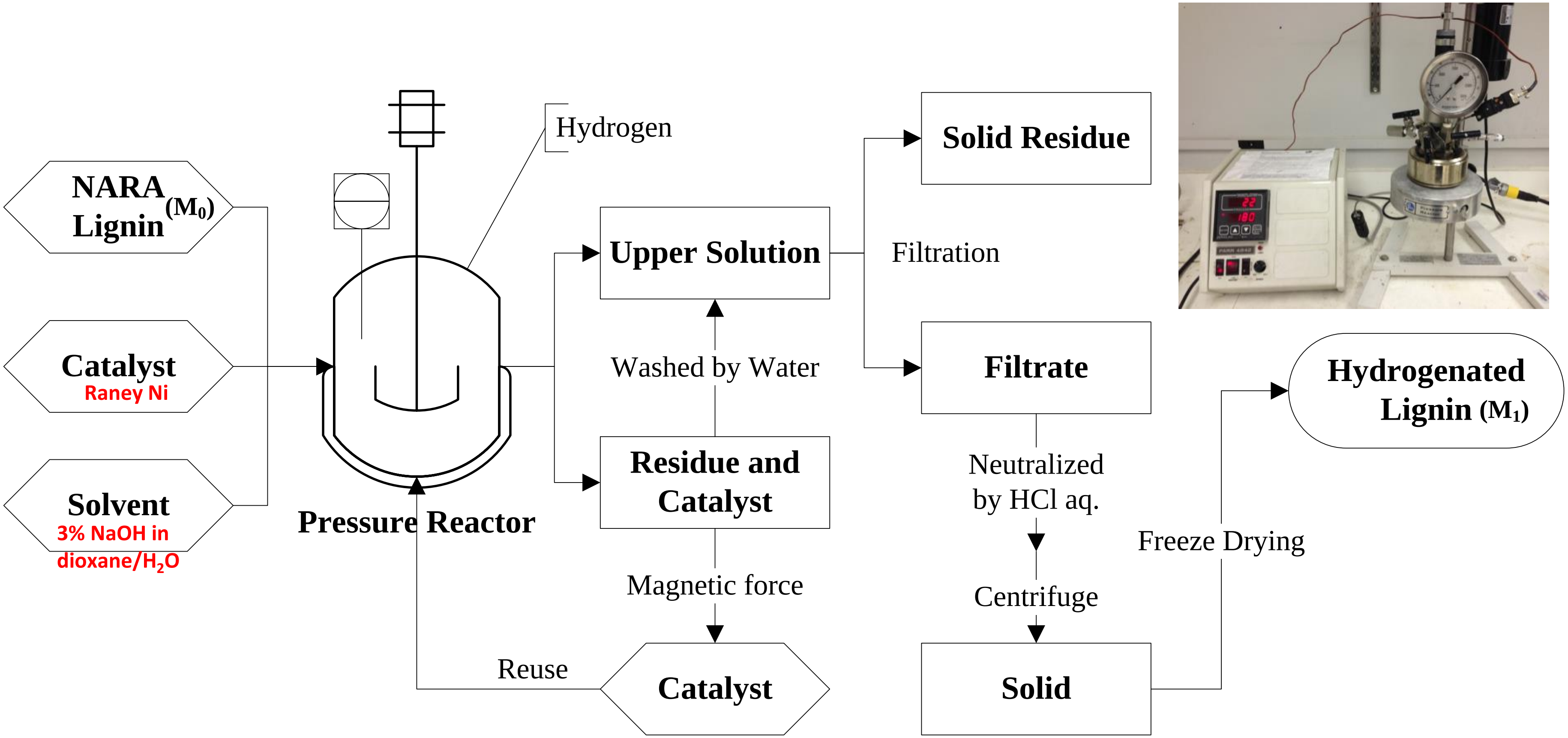
modification

Engineering polymer materials
(blends, epoxy resins, PUs)

Partially depolymerize C-O-C rather than C-C

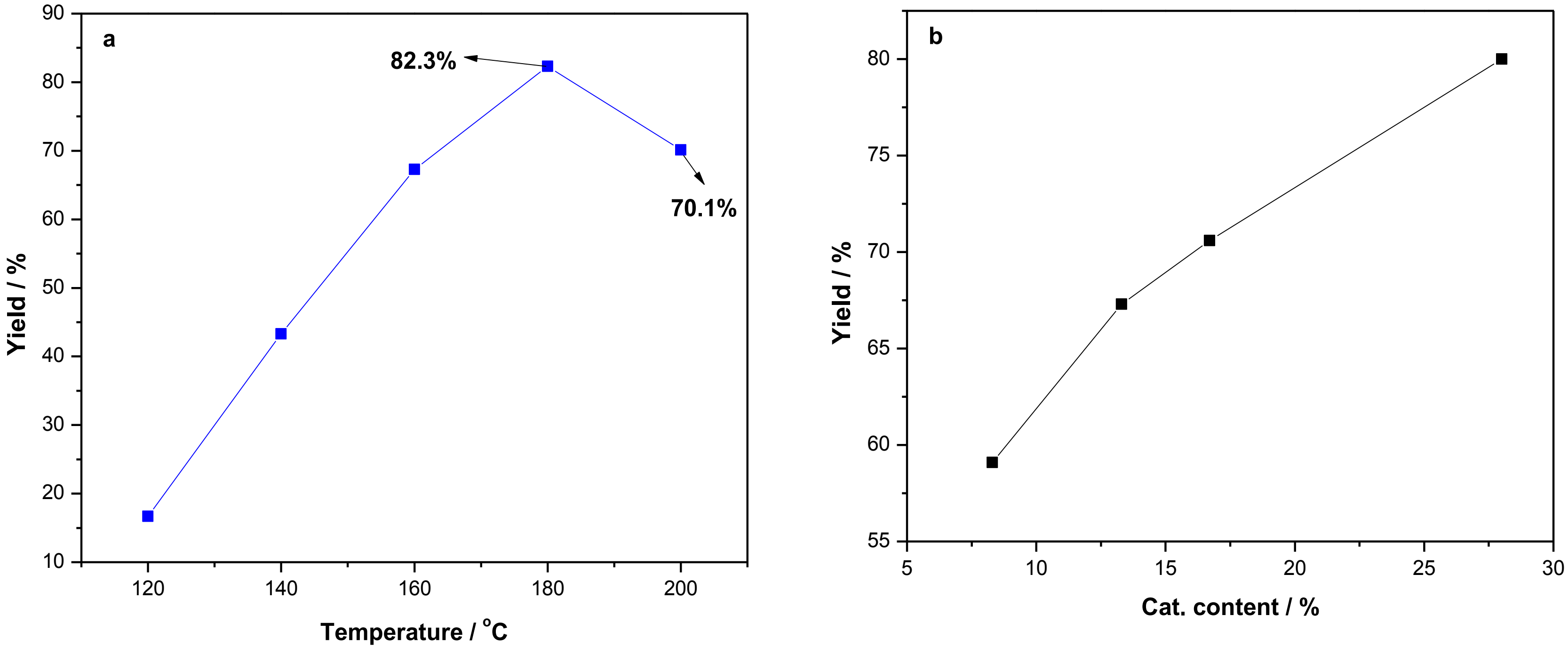
improved compatibility and melt processibility

# Partial depolymerization via mild hydrogenolysis




Xin J, Zhang P, Wolcott M P, et al. Partial depolymerization of enzymolysis lignin via mild hydrogenolysis over Raney Nickel[J]. Bioresource technology, 2014, 155: 422-426.

# Effect of reaction parameters on yield




Effects of temperature (a) and catalyst content (b) on yield of hydrogenation of enzymolysis lignin. Reaction conditions: lignin/solvent = 15 mg/mL, $H_2$ pressure = 2.0 MPa, t = 3.5 h, Raney Ni Conc. = 13.3% (a), T = 160 ºC (b).

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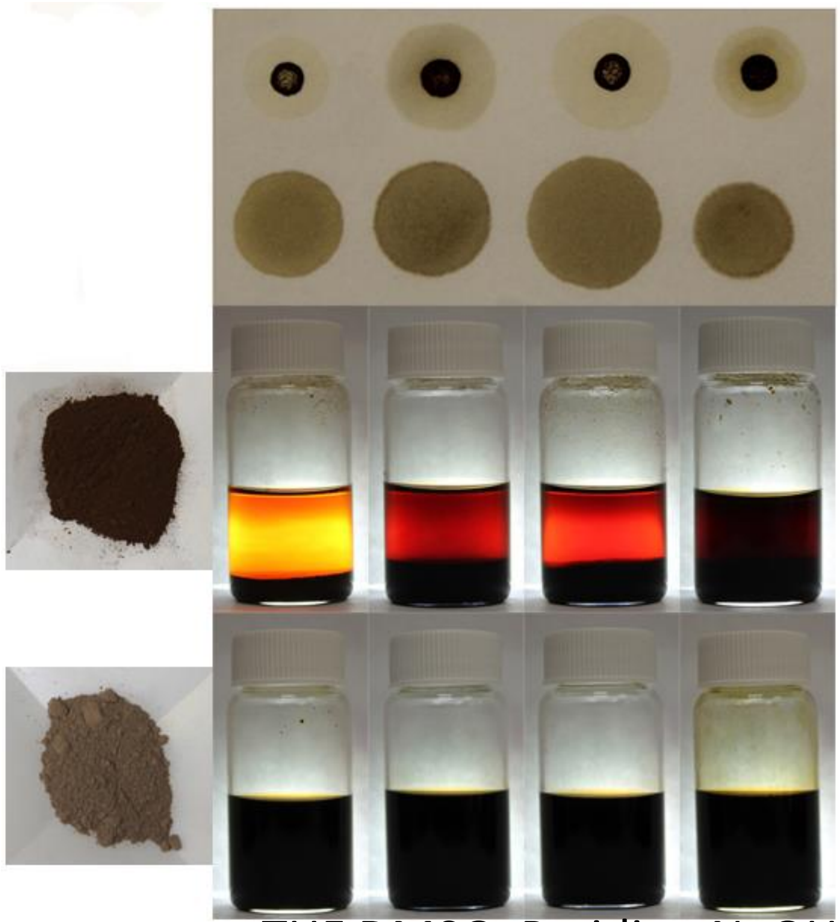
# Solubility of lignin before and after hydrogenolysis



Lignin

Depolymerized lignin

Lignin

Depolymerized lignin

THF DMSO  Pyridine NaOH sol

Concentration: 300mg/10mL

NaOH Sol. = NaOH 3% in dioxane/water (1/1, v/v)

# $^{31}P$ NMR characterization

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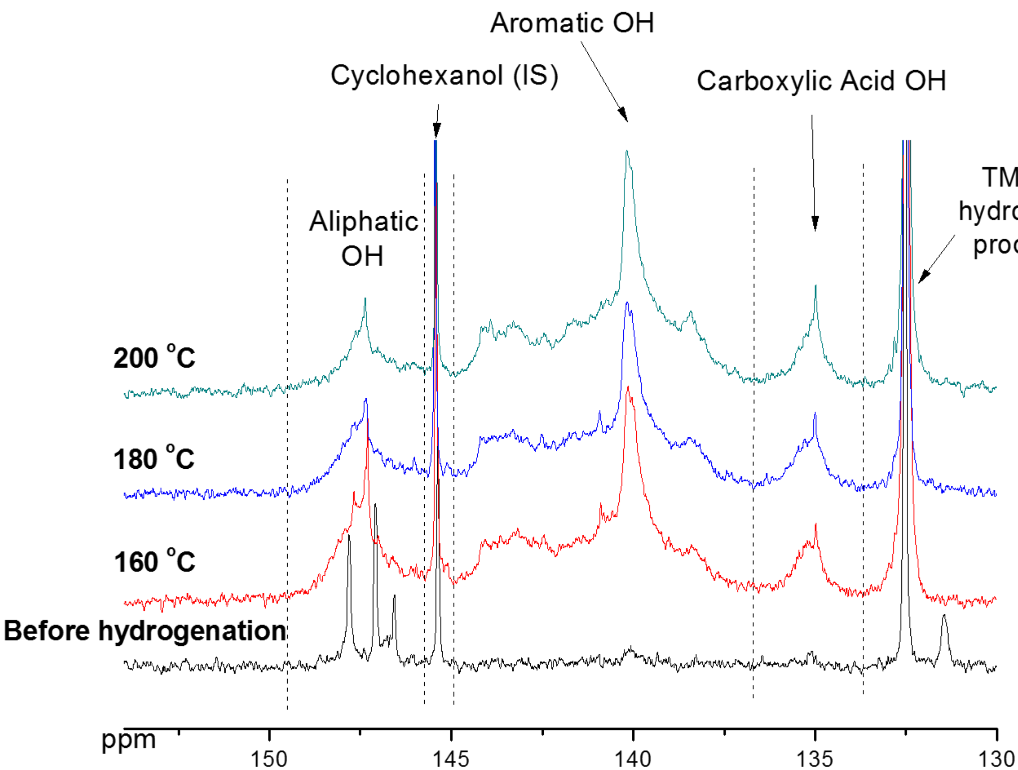
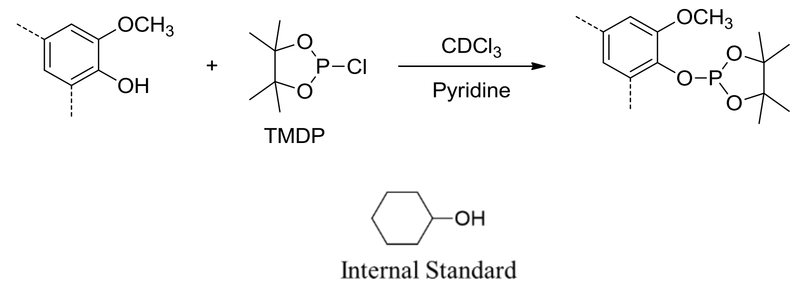
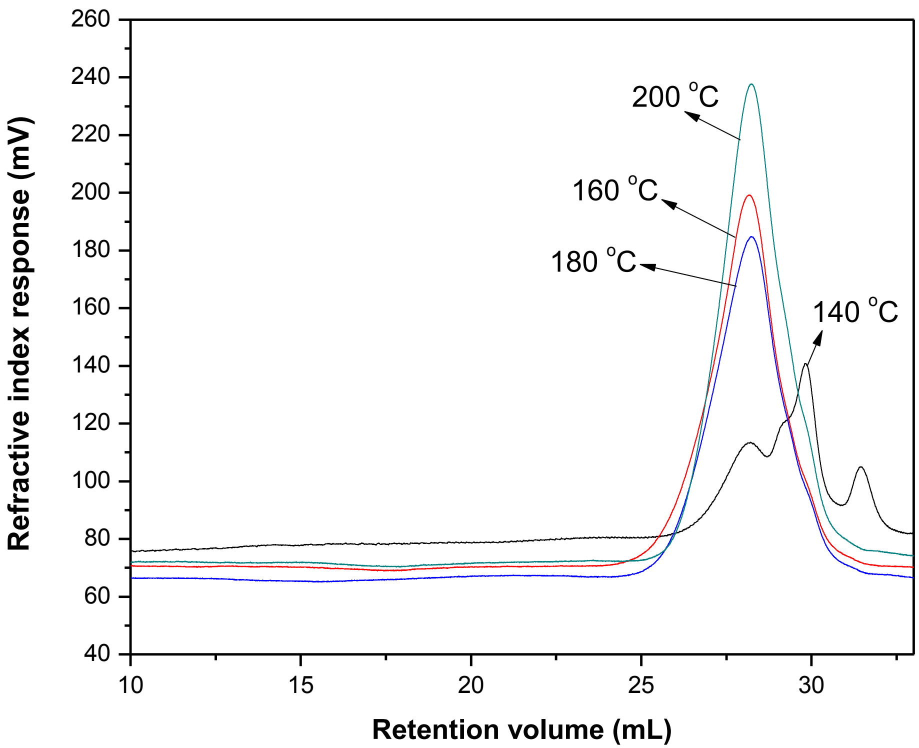



| Structure | $^{31}$P NMR (ppm) | Hydroxyl value (mmol/g) | | |
|---|---|---|---|---|
| | | 160 ℃ | 180 ℃ | 200 ℃ |
| Aliphatic | 145.5-150.0 | 0.81 | 0.71 | 0.66 |
| Aromatic | 136.6-144.7 | 2.40 | 2.68 | 3.22 |
| Carboxylic | 133.6-136.6 | 0.37 | 0.44 | 0.50 |
| Total | | 3.58 | 3.83 | 4.38 |

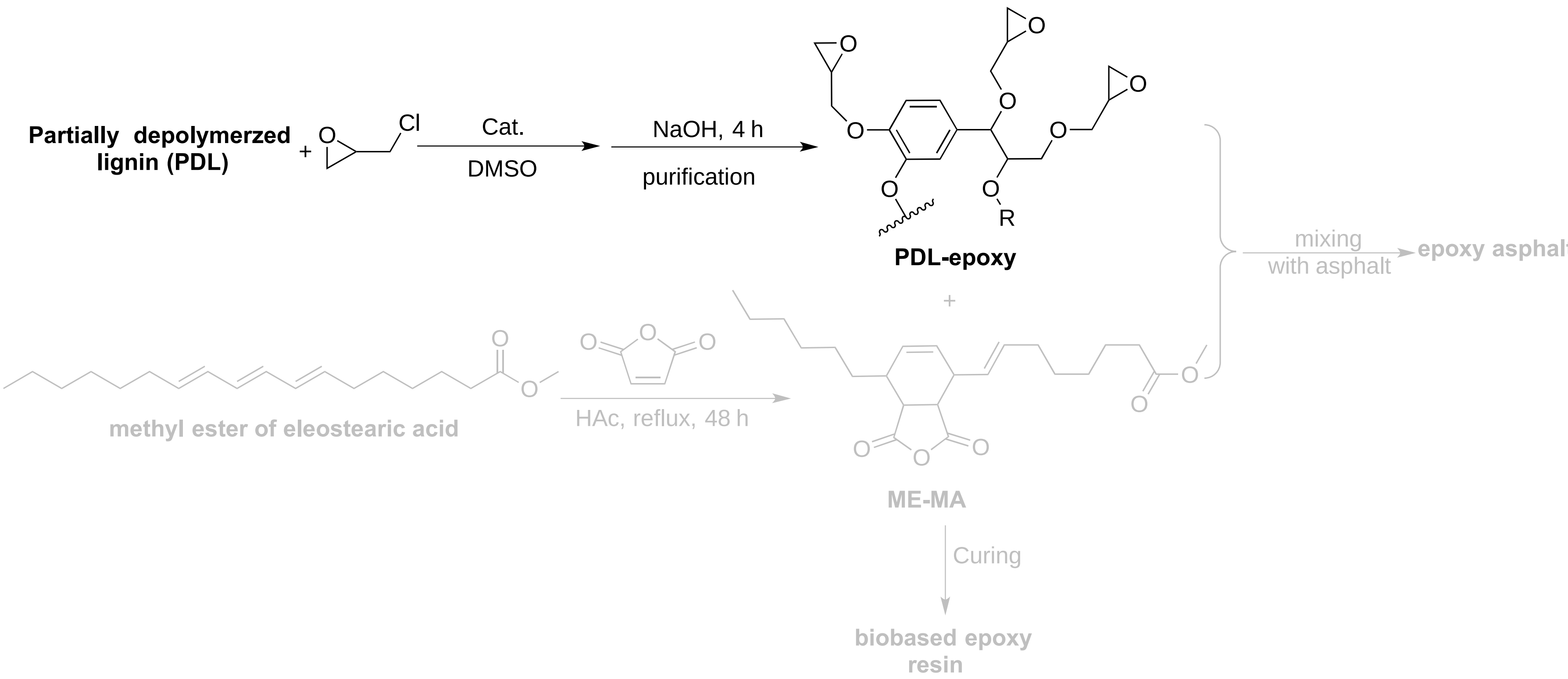
# Molecular weight of PDL






| Hydrogenolysis Temp. | Mw (g/mol) | Mn (g/mol) | Mw/Mn |
|---|---|---|---|
| **140 ℃** | 991 | 714 | 1.39 |
| **160 ℃** | 1359 | 804 | 1.69 |
| **180 ℃** | 1147 | 764 | 1.50 |
| **200 ℃** | 959 | 719 | 1.33 |

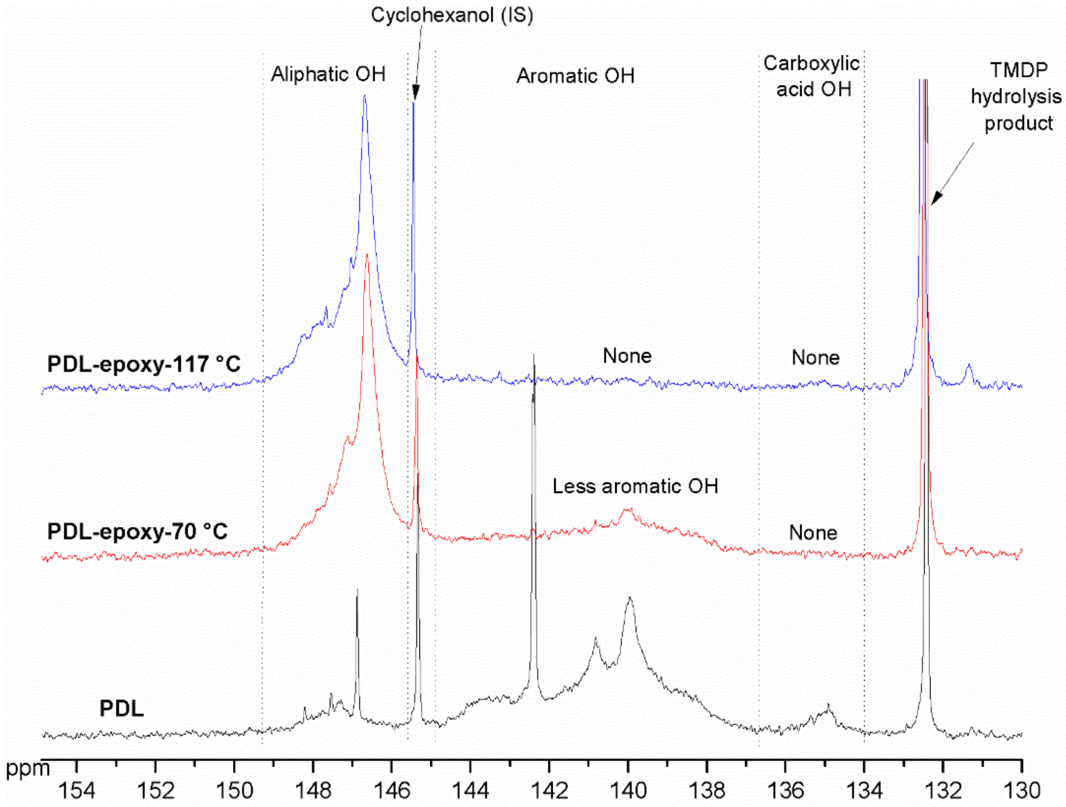
# Preparation of Lignin (PDL)-derived epoxy monomer




Xin J, Li M, Li R, et al. Green epoxy resin system based on lignin and tung oil and its application in epoxy asphalt[J]. ACS Sustainable Chemistry & Engineering, 2016, 4(5): 2754-2761.

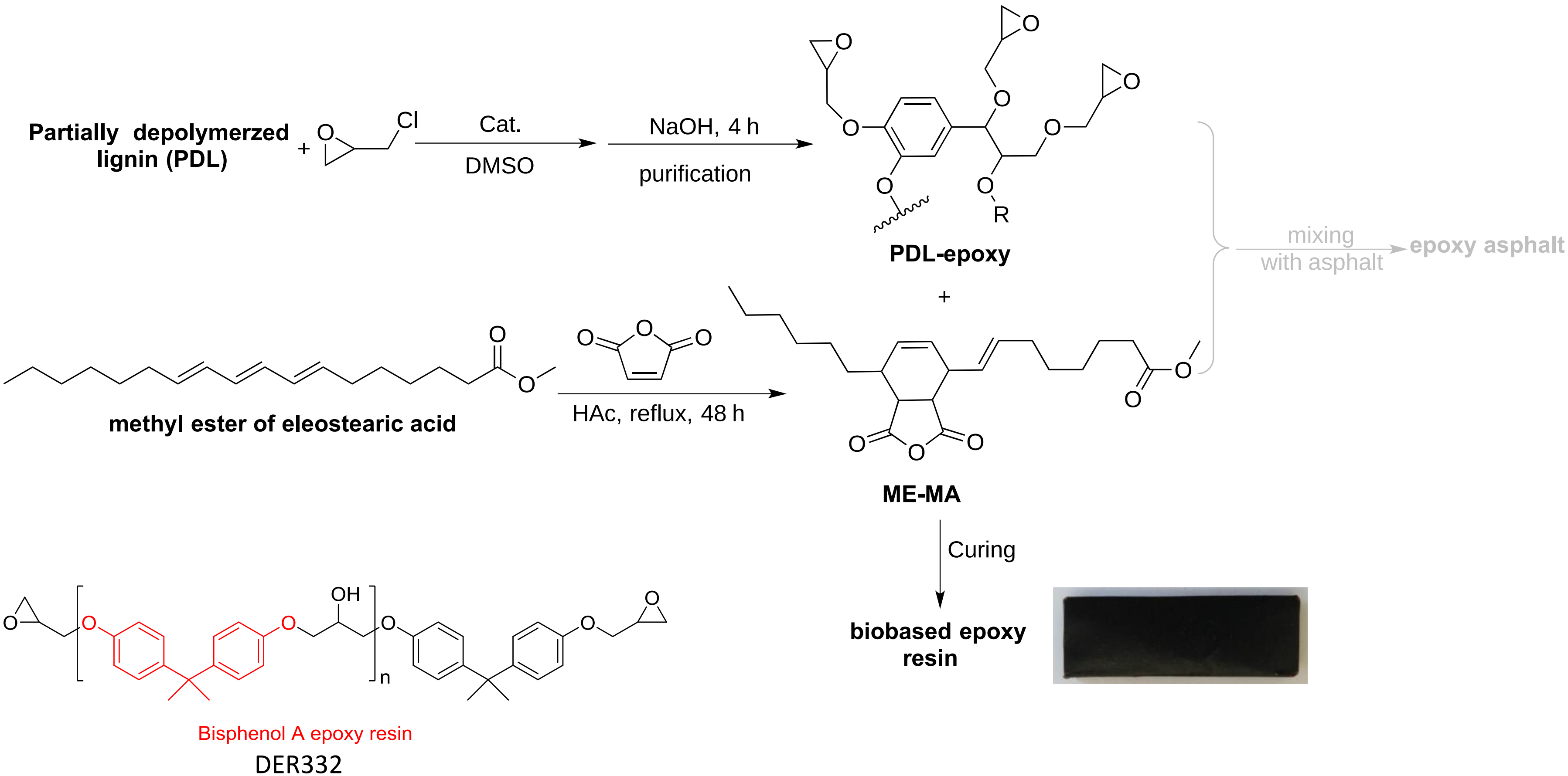
# $^{31}$P NMR characterization of PDL-epoxy monomers






| | Hydroxyl value (mmol/g) | | | Total |
|---|---|---|---|---|
| | Aliphatic | Aromatic | Carboxylic | |
| **PDL-epoxy-117 °C** | 2.7 | 0 | 0 | 2.7 |
| **PDL-epoxy-70 °C** | 2.4 | 1.7 | 0 | 4.1 |
| **PDL** | 0.7 | 3.7 | 0.3 | 4.7 |

# Preparation of Lignin (PDL)-derived epoxy based epoxy resin

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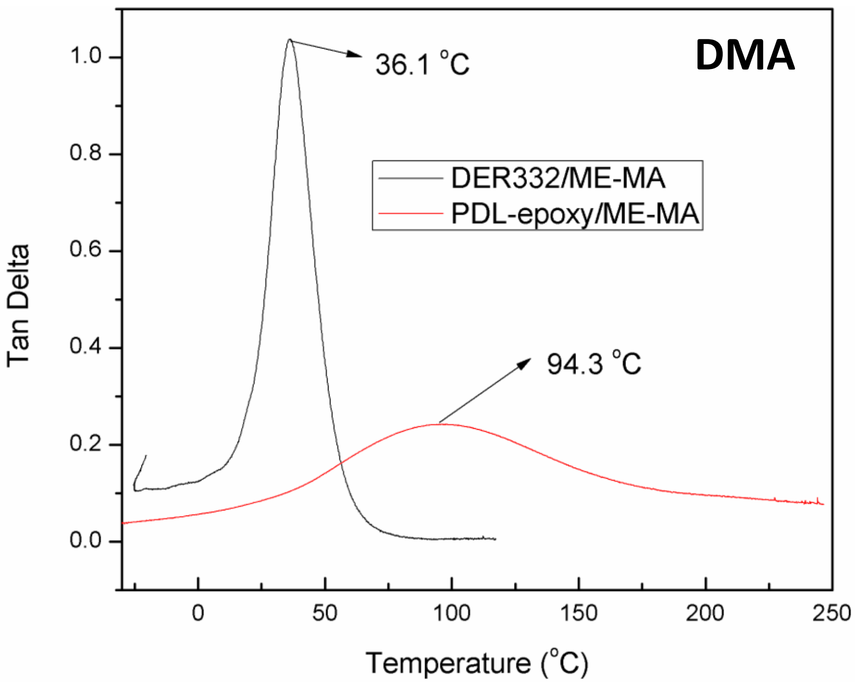
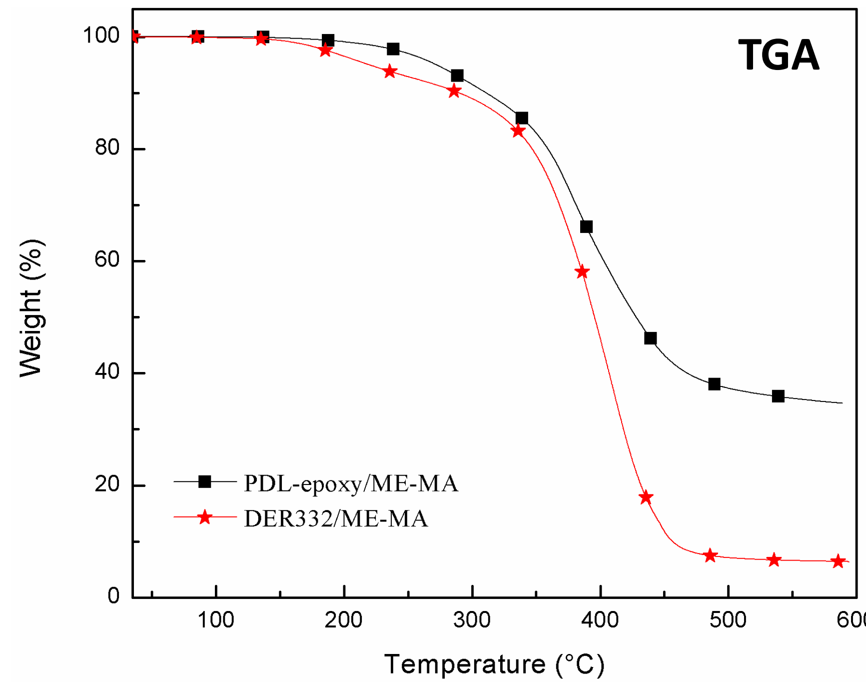
# Thermal mechanical properties and thermal stability

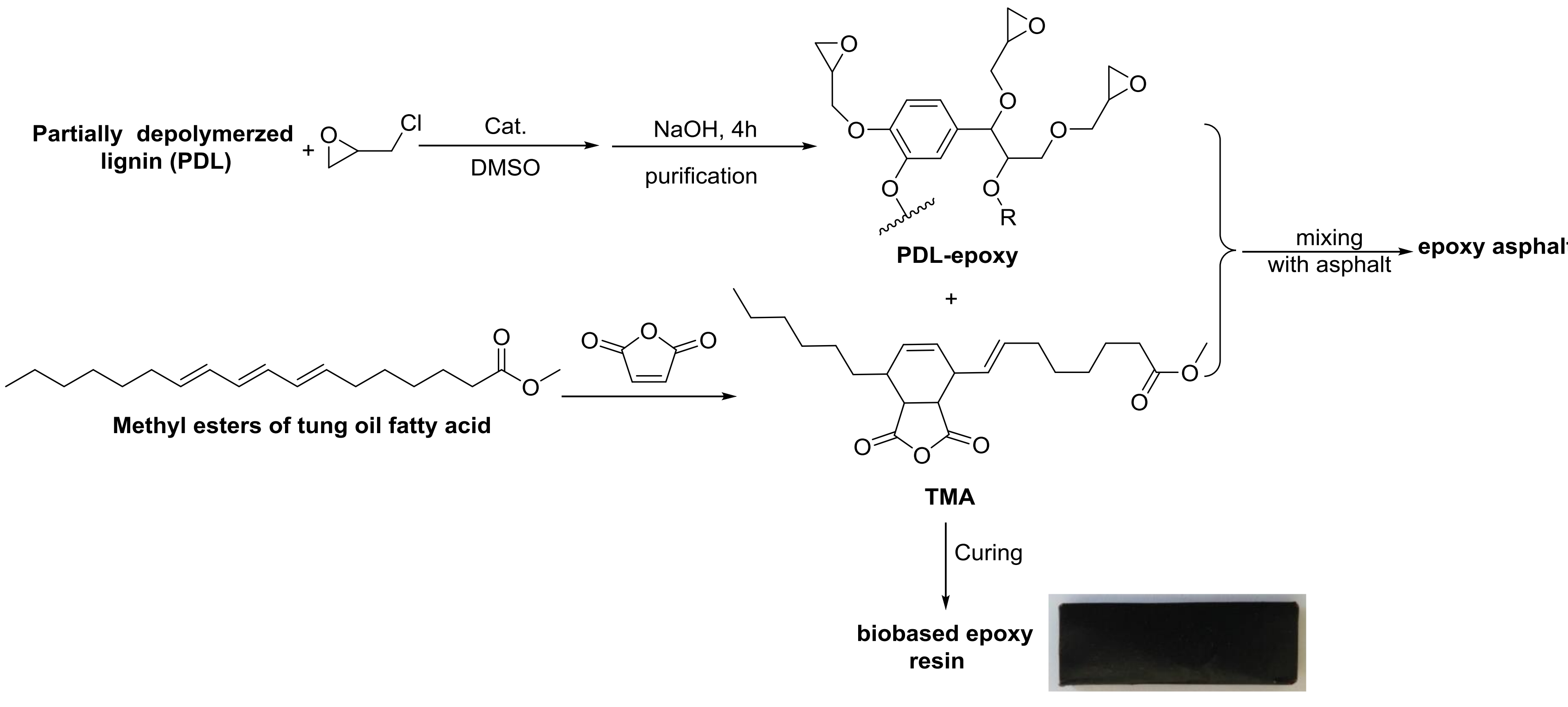



| Epoxy | $T_g$ (°C) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | Char yield at 585 °C |
|---|---|---|---|---|
| **PDL-epoxy/ME-MA** | 94.3 | 272.3 | 311.1 | 34.7 % |
| **DER332/ME-MA** | 36.1 | 219.8 | 289.9 | 6.43 % |

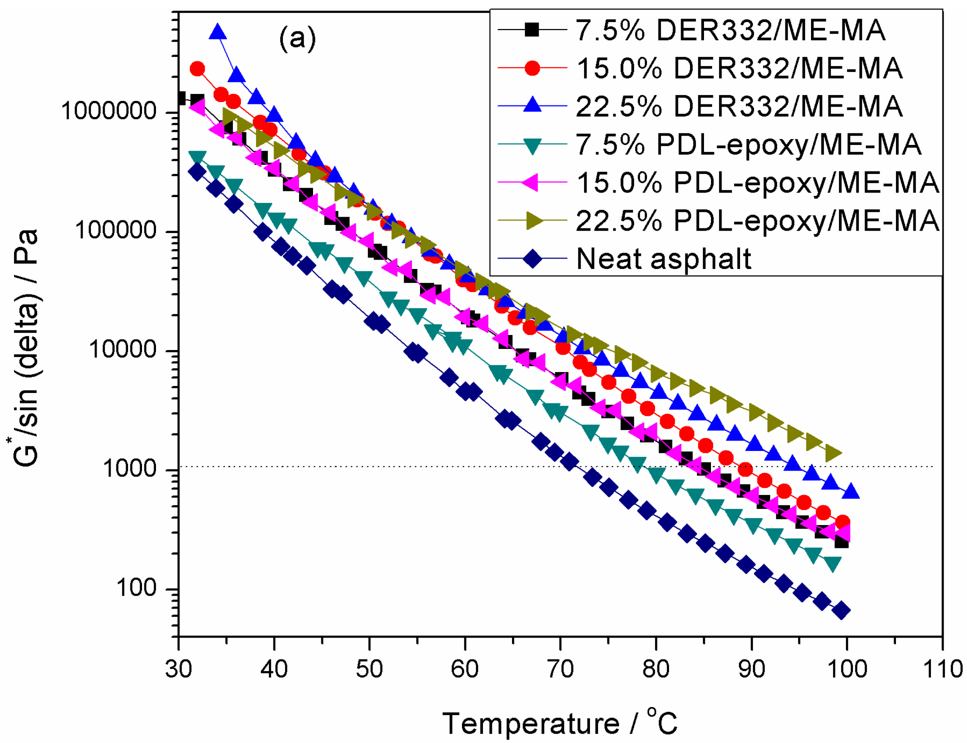
$T_{5\%}$ and $T_{10\%}$ - temperature of 5% degradation and 10% degradation.

# Application of Lignin (PDL)-derived epoxy for epoxy asphalt




Xin J, Li M, Li R, et al. Green epoxy resin system based on lignin and tung oil and its application in epoxy asphalt[J]. ACS Sustainable Chemistry & Engineering, 2016, 4(5): 2754-2761.

# Effects of epoxy resin contents on the rheological properties of modified asphalt blends by PDL-epoxy and DER332.




| Sample | *High-performance grade (PG, ℃) | | |
|---|---|---|---|
| | 7.5 % | 15 % | 22.5 % |
| DER332/ME-MA | 84 | 89 | 94 |
| PDL-epoxy/ME-MA | 78 | 84 | ＞100 |

*The temperature at which G*/sin δ is equal to 1 kPa
(Strategic Highway Research Program (SHRP) tests

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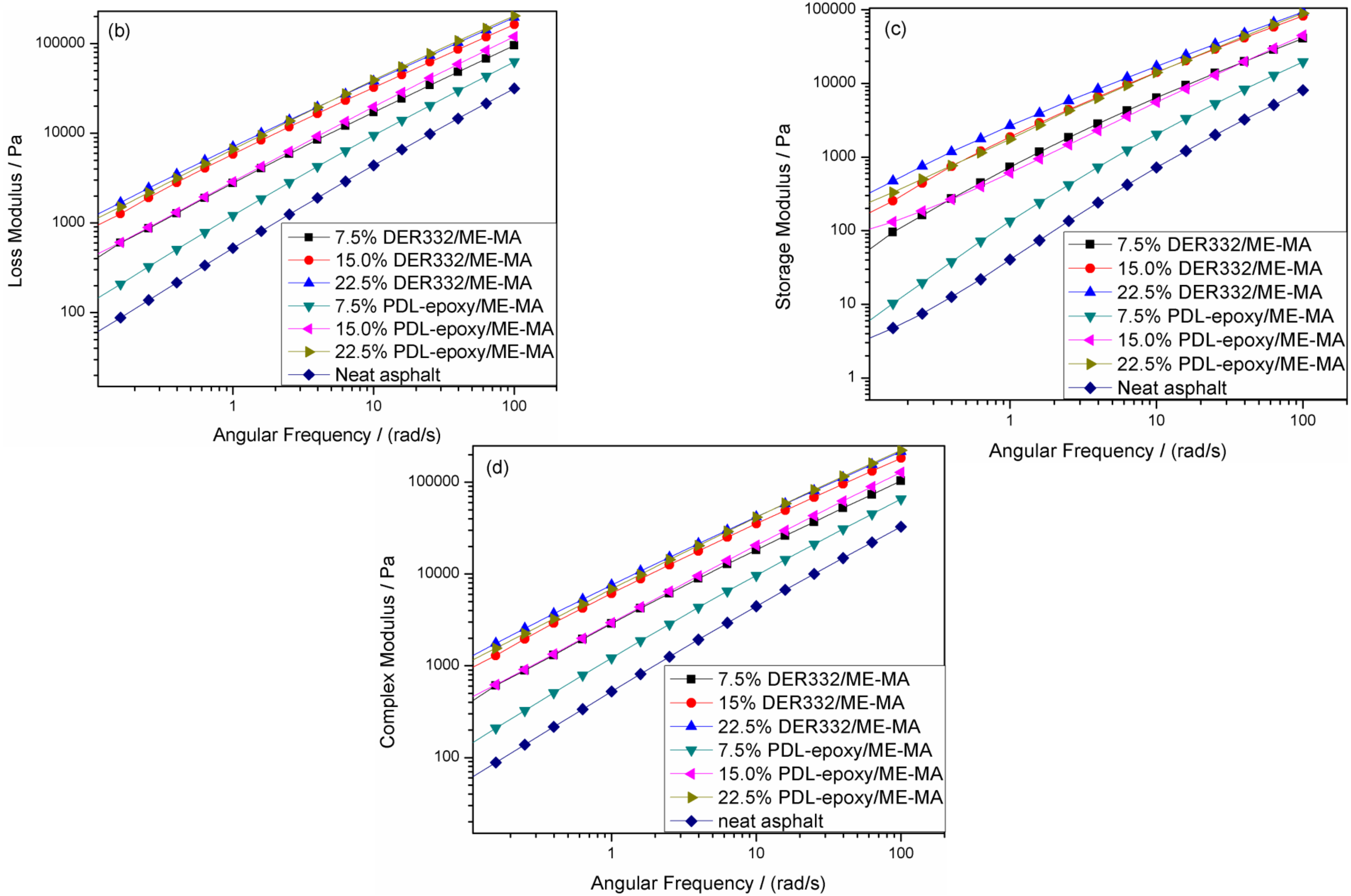

# Conclusions

- Lignin can be partially depolymerized to yield low MW oligomers by hydrogenolysis under the catalysis of Raney Ni in alkaline solution of mixed dioxane/$H_2O$ solvent or base catalyzed depolymerization in methanol under moderate temperature and pressure.

- The resulting PDL can be effectively turned into epoxy monomer by reacting with epicholorhydrin.

- Addition of epoxy resin has improved the high temperature performance and viscoelasticity of the asphalt binder .

- The properties of epoxy asphalt increased with the increasing of the epoxy resin contents.

- By varying the epoxy resin content, rheological properties of the modified asphalt can be greatly regulated.

# Acknowledgements

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## Contributors

- Junna Xin
- Mei Li
- Pei Zhang
- Jinwen Zhang

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# Thank You!