IOWA STATE UNIVERSITY
Mechanical Engineering Department

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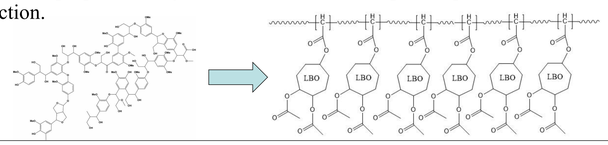
Yixin Luo, Wangda Qu, Eric Cochran, Xianglan Bai

Enabling property tunable high Tg thermoplastic polymers and high-quality carbon fiber from pyrolytic oil of lignin

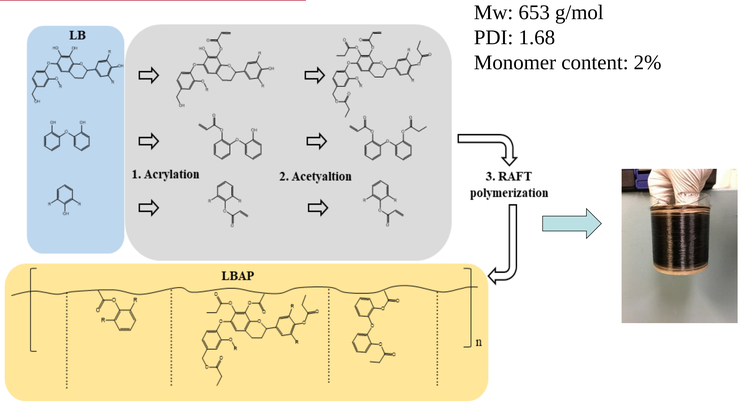
Introduction

- Carbon fiber is light weight material with exceptional mechanical properties and chemical resistance, widely used in automobiles, aerospace, wind turbine and others.
- Commercial carbon fiber produced using polyacrylonitrile (PAN), a petroleum-based polymer, is costly due to the high costs of PAN.
- Although lignin can be a low-cost alternative precursor of PAN, the mechanical properties of lignin-based carbon fibers are much inferior to commercial grade carbon fibers.
- The intrinsically lignin structure without molecular orientation is mainly responsible for the poor quality of carbon fibers.
- In this work, a novel "Lignin Deconstruction followed by Controlled Reconstruction" approach is proposed to synthesize a linear thermoplastic precursor for carbon fiber production.



Materials and Methods

- Lignin Bio-oil (LBO):
Mw: 653 g/mol
PDI: 1.68
Monomer content: 2%



Polymer precursor synthesis:

- Lignin bio-oil (LBO) is converted to arylated polymers via a two-step synthesis method.
- In step 1, LBO is first functionalized to arylate monomers using hybrid functionalization method that combines acrylation and acetylation to control the abundancy of vinyl groups.
- In step 2, the acrylate monomers are polymerized into a linear polymer using Reversible addition-fragmentation chain transfer (RAFT) technique to control the degree of crosslinking.

Carbon fiber production:

- The lignin-derived acrylate polymer is melt spun at 130°C followed by stabilization to 280°C under air environment and carbonization at 1000°C.

Results and Discussion

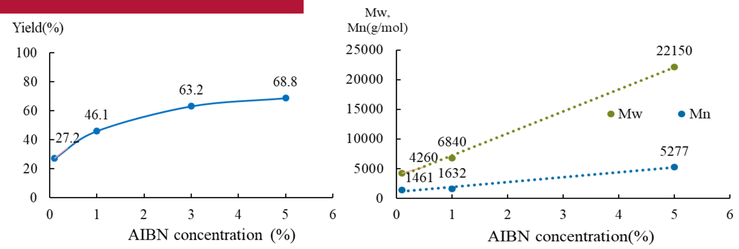


Figure 1.The effect of AIBN concentration on polymer yields and molecule weight distribution

- The increased concentration of AIBN increases the yields of 1.5Acry polymers gradually from 27.2% to 68.8%.
- The Mw of the polymers increases from 4260 g/mol to 22150 g/mol.
- AIBN concentration higher than 5% did not further increase yield and Mw .

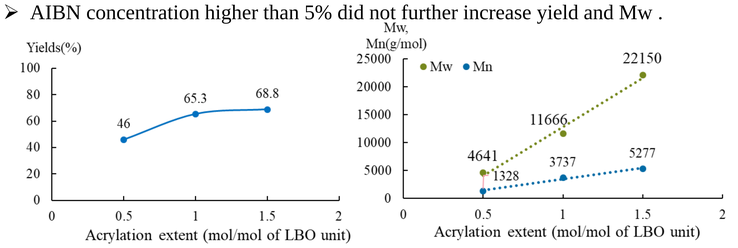


Figure 2.The effect of acrylation extent on polymer yields and molecule weight distribution

- The increased acrylation extent increases the yields of polymers with 5% AIBN from 46% to 68.8%.
- Increasing acrylation extent leads to the increase the Mw of the polymers with similar trend. Further acrylation extent will lead to the gelation of polymers according to the previous study.

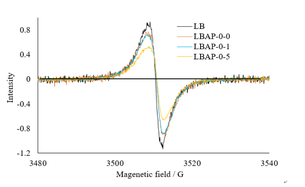


Figure 3. EPR spectra of (a) LB; (b) LBAP-0-0; (c) LBAP-0-1; (d) LBAP-0-5.

- LBO itself contains large amount of stable free radicals.
- The content of the intrinsic free radicals was reduced in the presence of AIBN.
- The free radicals consumed AIBN, which might be the reason why we need excess AIBN to obtain large polymers.

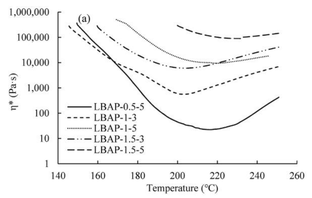
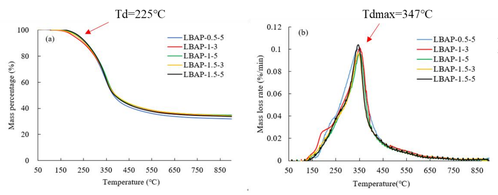


Figure 4. Complex viscosity (η*) changes of LBAPs

- Complex viscosity decreased with increasing temperature, less AIBN and less extent of acrylation.
- LBAP-1-3 was chosen eventually as the precursor for carbon fiber production.



- All polymers have close thermal stabilities with decomposition temperature of 225℃ and high fixed carbon content at about 36%.

Figure 5. TGA/DTG graphs of thermoplastic polymers

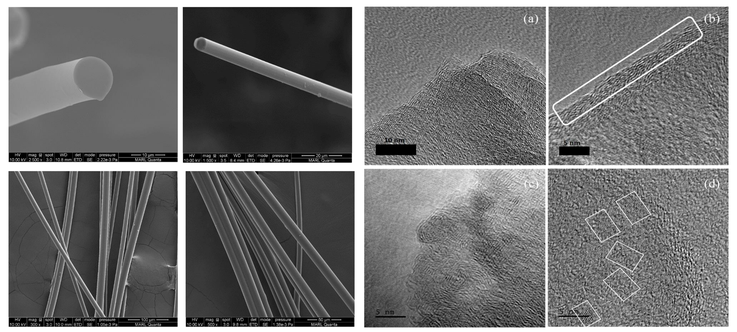


Figure 6. SEM and TEM graphs of carbon fiber

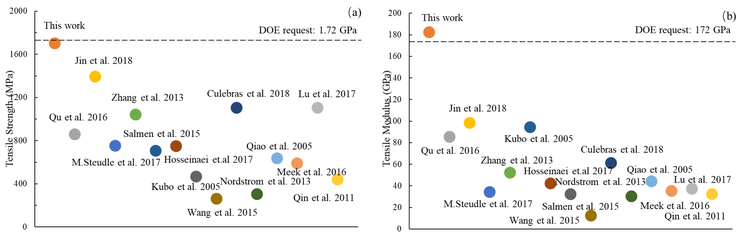


Figure 7. Tensile property of resulting LBAP-1-3 carbon fiber and the compare with other's work

- The resulting linear polymer based carbon fiber achieved record-high tensile strength and tensile modulus of 1.70GPa and 182GPa.

Conclusions

- Lignin-based acrylate polymers were produced using a two-step functionalization of the LBO followed by controlled radical polymerization.
- The resulting polymers' rheological properties can be adjusted by changing different levels of acrylation and different concentrations of AIBN.
- The carbon fiber fabricated in this study achieved an average tensile strength of 1.70 GPa and a tensile modulus of 182 Gpa.

➢ This work has been published in Journal of Cleaner Production

Luo Y, Qu W, Cochran E, et al. Enabling high-quality carbon fiber through transforming lignin into an orientable and melt-spinnable polymer[J]. Journal of Cleaner Production, 2021, 307: 127252.