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Internships - Biocomposites		

### Problem/assignment

Due to the environmental issues caused by excessive CO<sub>2</sub> emissions, there is an urgent need to incorporate raw materials from renewable sources into production chains. This shift aims to partially or entirely replace the use of fossil-based sources. Lignocellulosic biomass, one of the most abundantly produced natural resources globally, generates approximately 200 billion tons annually. This biomass primarily consists of cellulose, lignin, and hemicellulose, derived from both wood and non-wood sources.

Cellulose, the most renewable and abundant biopolymer worldwide, is a homopolymer composed of cyclic glucose units. Recycled cellulose fibers are useful in producing polymeric composites due to their low cost, low density, good mechanical properties, recyclability, environmental friendliness, safety, and renewability. Lignin, the second most abundant biopolymer and the largest renewable source of aromatics, is a thermally stable material with characteristics such as UV absorbance and water impermeability. Currently, 98-99% of lignin is burned for steam and energy production, while the remaining 1-2% is processed into lignosulphonates through the sulfite process.

Aromatic rings contribute to increased rigidity, thermal stability, and glass transition temperature. Presently, the raw materials used for producing thermosets are derived from non-renewable sources. As the world moves towards a circular economy, research is focused on developing more sustainable methods for producing thermosets. Consequently, the objective of this work was to cross-link lignin with itself, complementing the development of a biocomposite based on recycled cellulose, lignin, and biobased resin.

### Used methods/project phases

The project was divided into two parts, one for the cross-linking of lignin with itself and the other was the development of the biocomposite with recycled cellulose and lignin. But before starting these two parts, one-step fractionation of the lignin was carried out using acetone as a solvent, as, after this process, it is possible to obtain a purer material, with lower molecular weights and a less complex structure.

First part: Cross-linking of lignin with itself From the Luo et al. (2018)'s article, named: "Cross-linking of technical lignin via esterification and thermally initiated free radical reaction", it was used the same procedure to make the cross-linking of the lignin with itself.

Second part: Thermoset with lignin and recycled cellulose Some thermosets were made using different concentrations of lignin and cellulose, from the purification of cellulose, followed by the melting process following the article by Wang et al. (2021). Then, a hot-pressing process was carried out.

After carrying out the above procedures, tests were carried out, which are:

- In lignin: Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FT-IR)

### Used methods/project phases

- Lignin cross-linking: the test was only carried out with common solvents to check whether the cross-linking worked.
- Lignin and cellulose thermosets: Thermogravimetry (TGA) and Microscopy were performed.

### Results

- The fractionation yielded 68% of mass solubilized by acetone.
- FT-IR analysis showed improvements in the lignin after the fractionation process, with better detection of the functional groups. Furthermore, this instrument was used to confirm the insertion of the ester group into the chemical structure of lignin after the esterification process.
- Regarding DSC, the lignins exhibited different Tg's after fractionation and esterification, with the acetone-insoluble lignin showing the highest glass transition point, followed by the initial lignin, acetone-soluble lignins, and the esterified ones. The first three have higher Tg's due to their complex structure and amount of OH groups. After fractionation, the fractionated lignin presents less complexity, which reduces its Tg. For esterified lignins, it was observed that after the replacement of OH groups by ester groups, the hydrogen bonds decreased, giving the molecules greater mobility, thus lowering their Tg's compared to their precursors.
- Cross-linking was successful, as the esterified lignins, after mixing with DCP and hot pressing, were no longer soluble in common solvents like acetone and chloroform. The formation of new bonds created a complex, three-dimensional structure that prevented this solubility. However, the formation of the thermoset for further testing was not possible, as the material spread within the pressing mold.
- The TGA results showed varying outcomes, with the thermosets having the following proportions of lignin and cellulose showing the best results: 15% FGL + 85% cellulose; 15% GL + 85% cellulose; 20% IGL + 80% cellulose; 20% GL + 80% cellulose; and 30% IGL + 70% cellulose. It was noted that the addition of cellulose to lignin aids in the thermal stability of the material as a whole. Different results can still be found, as for each amount of cellulose, there is an optimal amount of lignin, as observed by Wang et al. (2021), that excess lignin can hinder interactions between the two materials.
- Microscopy revealed that the melting and pressing process formed a well-compacted thermoset, with no porosity. Additionally, the material showed a homogeneous appearance, indicating that the mixing and dispersion process was well-executed, as it is possible to distinguish lignin and cellulose separately.
- DMA testing on the lignin-cellulose thermosets showed that the material became quite brittle. It is likely that during the melting process, various bonds were already being formed, making the material a thermoset, meaning it could no longer be remolded. Since another process involving hot pressing was applied, it is possible that the formed bonds were broken during this step, causing brittleness. Therefore, it is now necessary to find a way to perform the melting and pressing process in a single step and check whether there is an improvement in the material's physicochemical properties.

### Extra info/advice/link to final document and presentation

