

# Revitalizing lignin

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# Summary

Among multiple biobased platform molecules, lignin plays a special role as one of the most abundant feedstocks available, while at the same time being the most abundant renewable source of aromatic compounds. Despite that, only less than 5% of lignin is used in value-added applications that do not include the energy sector. Commercially available technical lignins often have low quality: they are condensed, have high molecular weight and dispersity, lack in functionality, contain sulphur, and have various impurities, which decrease their solubility in organic solvents and overall limit their application pool, especially in polymeric materials. While incorporation of lignin in polymeric materials by blending or replacement of structural units, can bring added properties to the final materials, such as UV-blocking and antioxidant properties, the mechanical properties typically deteriorate upon incorporating high quantities of lignin in polymeric materials.

A possible solution to that issue is using fractionated or depolymerized lignin fractions, which show advantageous properties in terms of molecular weight, functionality, and purity compared with technical lignins. In this thesis, lignin fractions originating from different biomass feedstocks, obtained via various processing methods such as state-of-the-art isolation of technical lignins, solvolysis of technical lignin, 'lignin-first' process, and separation of lignin fractions were evaluated. Above-mentioned lignins were incorporated in various polymeric materials using novel synthetic approaches. Those materials are suitable for applications such as adhesives, coatings, additives, and adsorbents, and their performance was benchmarked against state-of-the-art equivalent products. The structure-property relationships between the performance and structural features of lignin fractions were also determined.

The focus of chapter 2 was the development of lignin-based resins suitable for wood adhesion applications. This study involved thermal cross-linking of a lignin-based resin via thiol-yne "click" chemistry and investigated a post-curing strategy via Claisen rearrangement. Two lignin fractions were evaluated as a starting material: commercial Protobind 1000 lignin and methanol soluble Protobind 1000 lignin fraction after mild solvolysis. Although these two lignin fractions varied in characteristics such as molecular weight and functionality, the difference in their performance was rather small. It may be connected with the fact, that Protobind 1000 lignin is one of the purest and lowest molecular weight and technical lignins available on the market. It was shown that the properties of the networks (such as  $T_g$ , thermal stability, and insoluble fraction) could be tuned by selection of the curing scenario and the composition of the formulation (amount of reactive diluent, P-4MS). Resins

prepared in this chapter were tested as a wood adhesive and possessed a desirable performance, comparable to state-of-the-art phenol-formaldehyde resins. The main benefits over the phenol-formaldehyde approach are that higher lignin loadings are possible to achieve (usually less than 50% of phenol can be replaced by lignin in lignin-phenol-formaldehyde resins, vs 75-100% lignin shown here, in both cases the cross-linker is excluded from the calculations) and no volatiles are emitted during the resins processing and use.

The synthesis and characterization of lignin-based protective coatings with anticorrosive properties was explored in chapter 3. Thermosetting coatings with high amounts of lignin-based components were prepared by means of a tandem UV-initiated thiol-yne “click” synthesis and Claisen rearrangement strategy. Lignin fractions investigated in this study were obtained from the ‘lignin-first’ process using Ni/SiO<sub>2</sub> as a catalyst. Three fractions were benchmarked, namely the mixture of lignin oligomers and monomers after ‘lignin-first’ process without fractionation, or fractionated samples via extraction and membrane separation processes. The above-mentioned lignin fractions differed in the monomer content and composition. Membrane separation turned out to be more effective than extraction in order to reduce the monomer content in the ‘lignin-first’ mixture of monomers and oligomers after depolymerization. The obtained protective coatings exhibited remarkable adhesion to steel surfaces and excellent solvent resistance, even after exposure to corrosive environment. Moreover, the coatings showed excellent barrier and corrosion protection even after 21 days of exposure. This chapter revealed that the separation of the ‘lignin-first’ mixture did not improve the performance of the polymeric coating, compared with the unseparated sample, which is an advantage in terms of process sustainability and techno-economics. The take home message of this chapter is that more efforts should be made in order to utilize mixtures of lignin monomers and oligomers as such in other kinds of resins, especially that separation may not bring improved performance.

While the two previous chapters explored the use of lignin in polymeric resins, chapter 4 concentrated on the application of lignin as antioxidant additive. A potential application of such antioxidant additive was selected in the field of biolubricants. Currently used petroleum-based lubricants are in general toxic and nonbiodegradable. As an alternative, biolubricants such as vegetable oils could be used instead. However, the biggest drawback of using vegetable oils in lubricant applications is their lack of thermo-oxidative stability, which as shown in chapter 4, could be improved by adding lignin-based antioxidant additives. In order to ensure good dispersibility of the additive in a vegetable oil matrix, lignin fractions were partially esterified to increase their lipophilicity. Four lignin-based fractions, namely commercial Protobind P1000 soda lignin, solvolytically fractionated Protobind P1000

lignin and two lignin fractions from the 'lignin-first' process, were studied in biolubricant formulations after esterification. The evaluated lignin fractions exhibited excellent performance compared to butylated hydroxytoluene, a state-of-the-art antioxidant. One of the 'lignin-first' fractions, palmitoylated Pd/C hexane residue, showed significant improvement of thermo-oxidative stability in a vegetable oil matrix, while other lignin-based additives showed similar performance with BHT. From rheological and tribological perspective, the majority of the biolubricant formulations exhibited lubricating properties comparable with vegetable oil. This study demonstrated the successful incorporation of lignin-based antioxidants in biolubricant formulations, tackling the major disadvantage of vegetable oils as environment-friendly lubricants. Moreover, the relationship between antioxidant properties and structural characteristics was established. The molecular weight of lignin-based fractions and S+G hydroxyl content were the most important characteristics influencing the antioxidant activity.

The last application investigated in chapter 6 is the use of lignin as precursor in the synthesis of carbonous materials suitable for adsorption of contaminations in water. In this chapter, a series of lignin-based mesoporous carbons was successfully prepared using a Claisen rearrangement route via the soft-template methodology. Depending on carbonization conditions and the used template, the properties of the mesoporous carbons such as surface area, elemental composition, pore size, and pore volume could be tuned. Lignin-based mesoporous carbons were evaluated as humic acid adsorbent, and showed excellent performance in water purification, compared with the commercial activated carbon and other carbonous adsorbents reported in the literature. This synthetic route yielding lignin-based mesoporous carbons was demonstrated to be suitable for the preparation of adsorbents, but it is expected that it is possible to use these kind of materials for other applications including supercapacitors and energy storage materials.

Overall, this thesis showcased different possible uses of lignin in polymeric materials and additives. As shown in Chapters 2, 4, and 6, the proof-of-concept products in which technical or fractionated lignin have been incorporated showed comparable or improved performance compared to their state-of-art references. However, upscaling activities and further evaluation of their performance and should be performed to fully evaluate usability of lignin in these applications.

Evaluated lignin fractions originated from novel lignin isolation and processing methods, such as 'lignin-first' processes and solvolysis. It is worth to highlight that lignin fractions used in this thesis had high amounts of functional groups and low molecular weight compared with most of available technical lignins. On the other hand, lignin fractions obtained from 'lignin-first' processes were tested as a mixture of lignin monomers and oligomers. Notably, it was shown that separation of lignin

monomers and oligomers may not be necessary for the successful incorporation of lignin fraction in polymeric materials.

To sum up, the origin of the overall good performance of tested lignin fractions in polymeric and carbonous materials, as well as in antioxidant additives can be related to their advantageous physico-chemical properties. These findings are critical for the evaluation of the marketable applications, where these type of lignin fractions have a high chance to be successful. Up until now, lignin fractions originating from mild solvolysis, 'lignin-first' and fractionation processes were available only at the lab scale, but ongoing scaling-up activities open the possibility to explore other applications in polymeric materials and additives, and their evaluation by the industry. Keeping in mind their improved characteristics, it can be expected that more value-added applications can be developed using those fractions in the near future.