

Towards Thermoplastic Lignin Polymers: Progress in the Utilization of Kraft Lignin for the Synthesis of Heat Stable Polymer Melts

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Most efforts to utilize lignin have been limited by various factors that impart in it characteristics that define it as an unreliable precursor to polymer production. This is because lignin (and more specifically technical lignin) offers relatively unpredictable polymerization characteristics, depending upon its source and the degree of delignification to which the plant materials were subjected. More specifically, the highly functional character of lignin (i.e. rich in phenolic and aliphatic OH groups, as well as reactive benzylic carbons), induces a variety of potential polymerization sites and heat instability in such materials. Both factors promote gelation processes under polymerization conditions or when the temperature increases close to, and/or above the glass transition temperature (T_g). In addition, the relatively low molecular weight (a few thousands) for lignin derived from commercial pulping and biorefinery operations makes lignin unsuitable for higher end applications, such as high performance, heat stable engineering thermoplastic applications.

The work of our group at NCSU has focused at providing a detailed molecular understanding of the way the polymeric properties of kraft lignin and its derivatives are affected by their thermal treatments.

This information was then correlated with the polymeric properties of the materials (glass transition temperature (T_g), molecular weight characteristics, and thermal stability), for a series of selectively and progressively derivatized softwood kraft lignin samples [1]. Softwood kraft lignin was shown to be highly susceptible to thermally induced reactions that cause its molecular characteristics to be severely altered with the concomitant formation of irreversible crosslinking with no thermoplastic processing possibilities. However, by fully methylating the phenolic OH groups [2], from within the structure of softwood kraft lignin, the thermal stability of these materials was seen to be dramatically enhanced and their T_g's reduced [1]. Optimum thermal stability and melt cycling was observed with the fully methylated derivatives. The accumulated data is aimed at providing the foundations for a rational design of single or multi-component lignin-based thermoplastic materials with reproducible polymeric properties when thermally processed in a number of manufacturing cycles [1-3].

Furthermore, we have been able to create polyarylene (ether sulfone)-kraft lignin copolymers synthesized by a base catalyzed stepwise copolymerization of suitably functionalized, fractionated kraft lignin with 4,4'-Difluorodiphenyl Sulfone (DFDPS) in an aprotic solvent at elevated temperatures (Scheme 1) [3].

The benefits of incorporating DFDPS within kraft lignin are apparent in the TGA thermograms of the copolymer shown in Figure 1. Thermally stable polymer melts exceeding 300°C are apparently attainable [3].

Conclusions and Overall Outlook

This effort offers novel avenues at creating reactive lignin materials that are stabilized and rendered better suited for industrial applications. It provides methods for creating lignins of controlled and modulated characteristics, exhibiting thermal and polymerization stabilities. Such thermal properties and stable molecular weight distributions of lignins and copolymers produced from commercial lignins provides a means for beneficially modulating the properties of an otherwise intractable bio-polymer.

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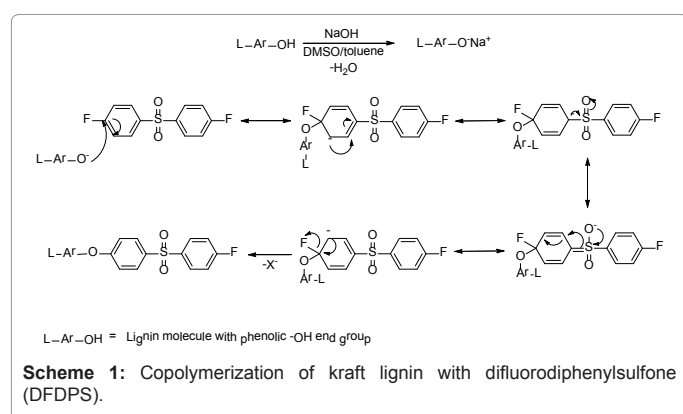
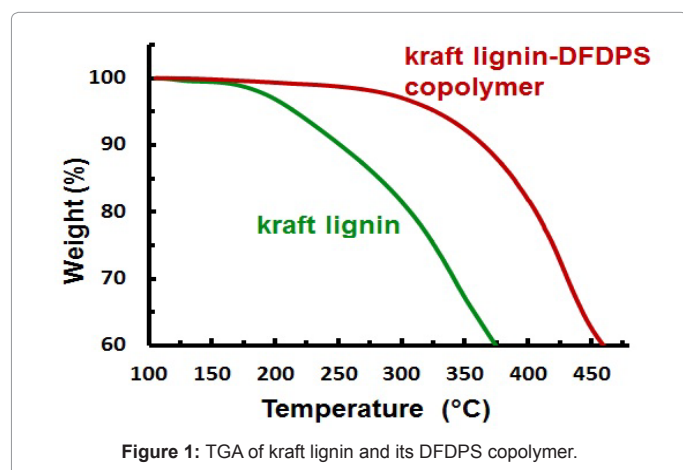
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