

Nanolignin enables the synthesis of semi-flexible polyurethane foams

Polyurethane (PU) is an important class of thermoset polymer with a \$70 bn/year market, providing materials for the construction, transportation, furniture, and packaging industries. PU materials are comprised of two main components, an isocyanate and a polyol. Both of these product classes are currently obtained from non-renewable petroleum resources, suggesting that the development of biobased alternatives is of utmost importance towards the national endeavor of net zero carbon emission by 2050.

Lignin, a major constituent of lignocellulosic biomass, is one of the most abundant natural biopolymers on Earth and is currently produced in large quantities as a byproduct in the pulp and paper industry. Being a renewable aromatic macropolyol, lignin holds promise as a substitute for fossil-derived feedstocks for polyurethane (PU) synthesis. There has been a considerable amount of previous work performed on developing lignin-based PU. Due to the heterogenous and complex structural properties, it remains a grand challenge to incorporate a high lignin content into a semi-flexible foam. There is an increasing push in the automotive industry to drive towards replacing traditional polyurethane (PU) foams with bio-derived polyurethane (BPU) foams with increasing bio-based content. Lignin-based PU foams are an area of active research and development.

Washington State University researchers, part of the NSF supported Industry-University Cooperative Research Center for Bioplastics and Biocomposites (CB²), recently developed a novel deep eutectic solvent (DES) extraction process that generates oligomeric lignin in high yield and nanoscale dimensions (100 nm in average particle size) from plant biomass. These nanolignin oligomers (nanoDESL) exhibit narrow molecular size distribution and controlled structural properties (e.g., ether linkages and functional group content), compared to traditional lignin materials.

The researchers recognized that oxypropylation of lignin, a process by which an alkyl chain consisting of poly(propylene oxide) was grafted onto the lignin backbone, is a key step in lignin-based PU synthesis. However, it has been a challenge to produce semi-flexible and flexible PU foams with oxypropylated lignin. In this project, the team found that polar aprotic solvents coupled with the appealing features of nanoDESL significantly promotes the oxypropylation reaction.

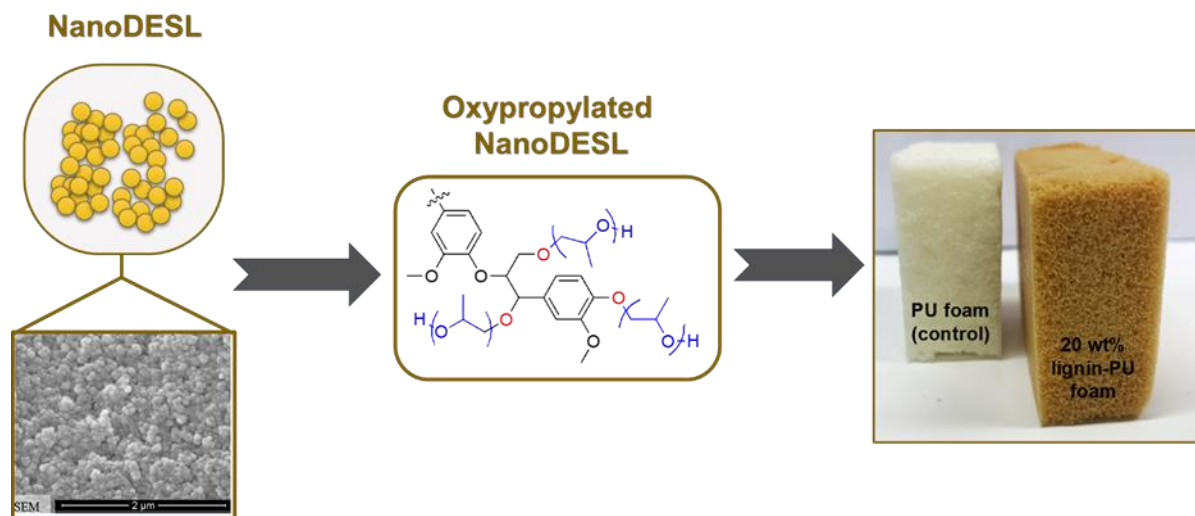
The team investigated the feasibility of producing semi-flexible PU foams with oxypropylated enanoDESL. The objective was to replace a significant amount of polyol with lignin whilst maintaining the key structural and mechanical characteristics. Figure 1 illustrates the major steps in PU synthesis to produce lignin-based PU (brown colored foam). This lignin-based PU contains ~20 wt% nano-DESL derived (or biobased) polyol and has shown comparable density as well as compressive force deflection value (CFDV) to the PU foam prepared using a standard formulation (white colored foam).

Dr. Alper Kiziltas, Technical Expert at Ford Motor Company commented that “This project target is to produce BPU foams that are comparable in cost to petroleum-derived PU foams. Cost and performance competitive lignin-based polyol from forest sources in the US can reduce exposure

to commodity markets and insulate from virgin material price fluctuations and shortages. Thus, the use of renewable, US-sourced, forest-based feedstock materials is economically appealing to both US manufacturers and agricultural producers and creates a value proposition of reduced carbon footprint and managed end-of-life.”

The CB² team is currently working to optimize the reaction procedure, with a goal to incorporate 40 wt% lignin-based polyol into semi-flexible foams. In addition, a series of nanoDESL samples will be prepared from different sources (such as woodchips, sawdust, rice straw, etc.) in order to develop a correlation between the lignin structural characteristics and the corresponding mechanical properties of PU foam, with an aim to further increase the achievable lignin content. The potential of nanoDESL-based polyurethane for adhesives, sealants, and coatings applications will also be explored. The team will also determine the biodegradability and environmental toxicity of lignin-based PU in comparison to the fossil-derived PU. Utilizing lignin as an alternative low-cost and sustainable resource for PU production not only promotes a circular economy, but may also lead to the development of greater economic opportunities and more sustainable end-of-life route for PU plastics.

Figure 1. Process diagram for the preparation of semi-flexible lignin-PU foam containing nanoDESL. The white and brown colored foams represent PU foam with control formulation and 20 wt% lignin derived polyol, respectively.



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