

## Nanolignin Enables the Synthesis of Semi-Flexible Polyurethane Foams

Polyurethane (PU) is an important class of thermoset polymer with a \$70 billion/yr market, providing materials for the construction, transportation, furniture, and packaging industries. PU materials are composed 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 for the national goal of net zero carbon emissions 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. As a renewable aromatic macropolyol, lignin is a promising substitute for fossilderived feedstocks for PU synthesis. A considerable amount of previous work has been performed to develop ligninbased PU. Due to the heterogenous and complex structural properties of lignin, 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 replace traditional PU foams with bio-derived polyurethane (BPU) foams.

Washington State Univ. (WSU) researchers, part of the NSF-supported Industry-University Cooperative Research Center for Bioplastics and Biocomposites (CB<sup>2</sup>), recently developed a novel deep eutectic solvent (DES) extraction process that generates oligomeric lignin at high yield and nanoscale dimensions from plant biomass. These nanolignin oligomers, which the researchers have dubbed nanoDESL, exhibit a narrower molecular size distribution and more controlled structural properties than traditional lignin materials.

The WSU researchers also optimized the oxypropylation of lignin, a process by which an alkyl chain of poly(propylene oxide) is grafted onto the lignin backbone to increase its reactivity and processability. In the past, researchers have tried to use oxypropylated lignin to make PU foams. However, it has been a challenge to maintain the desired flexibility characteristics of the resulting PU foams. In this project, the WSU team discovered that the introduction of polar aprotic solvents to the oxypropylation process, coupled with the appealing features of nanoDESL, significantly promote the oxypropylation reaction toward the synthesis of semi-flexible PU.

The team investigated the feasibility of producing semi-flexible PU foams with oxypropylated nanoDESL. The objective was to replace a significant amount of polyol with lignin while maintaining the key structural and mechanical characteristics of the PU. This lignin-based PU contains ~20 wt% nanoDESL-derived polyol



The Center for Bioplastics and Biocomposites developed a process for the preparation of semi-flexible lignin-based polyurethane (PU) foam using nanolignin oligomers (*i.e.*, nanoDESL). The brown foam represents PU made from 20 wt% lignin-derived polyol. and has a comparable density and compressive force deflection value (CFDV) to the PU foam prepared using a standard formulation.

Alper Kiziltas, Technical Expert at Ford Motor Company, commented: "Cost- and performance-competitive lignin-based polyol from forest sources in the U.S. can reduce exposure to commodity markets and insulate from virgin material price fluctuations and shortages. Thus, the use of renewable, U.S.-sourced, forest-based feedstock materials is economically appealing to both U.S. manufacturers and agricultural producers and creates a value proposition of reduced carbon footprint and managed end-of-life."

The CB<sup>2</sup> team is currently working to optimize the reaction procedure, with a goal of incorporating 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 the PU foam, with an aim to further increase the achievable lignin content. The potential of nanoDESL-based PU 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 a resource for PU production not only promotes a circular economy, but may also lead to the development of greater economic opportunities and a more sustainable end-of-life route for PU plastics. CEP

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