

Direct and Multistep Conversion of Lignin to Biofuels

Matyas Kosa

Though the rapid development of human society, concerns on the fossil fuel shortage, pollution, and end-of-life disposal issues are attracting the most attention nowadays. Therefore, more efforts from governments, industries, and research institutes have been paid to the sustainable development than it has ever been done before. Cellulose, lignin and hemicellulose are the major components of biomass and also the most abundant biopolymers in nature. They are widely available, renewable, biodegradable, non-edible, and have low stable market prices which are competitive with petroleum-derived polymers. Moreover, their unique structures have huge potentials to be explored. Not only being used as a raw material in pulp and paper mills, cellulose has been found to have a lot of superior properties when hydrolyzed into cellulose nanowhiskers (CNWs), which can be applied to structural materials and nanocomposites synthesis. As a major waste from the paper-making process, lignin has lead to the prosperity of the biobased chemicals and macromolecules instead of being burned directly as a low value fuel, attributing to its unique phenolic structures.

The first study in the thesis investigates the reinforcing effect of CNWs in preparation of rigid polyurethane (PU) foam, one of the most diverse and widely used plastic materials with an ever-growing global market. The control foam was prepared by first mixing polyols, catalysts, and surfactant, and then adding blowing agent and diisocyanate under strong stirring. Freeze dried CNWs of up to 1 wt% were added by dispersing in dimethyl formamide (DMF) and then mixing with polyols followed by DMF removal under high vacuum. The resulting control foam and nanocomposite foams exhibited different density and closed cell size. Therefore, the mechanical properties of the prepared foams were compared based on the unit mass data. Tensile property, especially compressive property was enhanced with increasing CNWs addition as compared to the control. FT-IR spectra indicated CNWs acted as a crosslinking reagent in the PU synthesis, which is one of the reasons for the improvement of mechanical and dynamic mechanical properties of the nanocomposites.

The second study presents the application of Kraft lignin in preparation of rigid PU foams. A commercial softwood Kraft pine lignin was derived from its solid form into a liquid polyol through a chain extension reaction with propylene oxide under the catalysis of potassium oxide. The structure, composition, and properties of the lignin polyol were studied by different techniques including FT-IR, GPC, and NMR. It has proven that the Kraft lignin polyol has characteristics suitable for rigid PU foam preparation. Later, a series of formulation optimization experiments was set up by gradually replacing commercial polyols, which were used in the control foam preparation, with lignin polyol, in order to prepare a rigid PU foam with superior mechanical strength. The compressive study showed that the foam prepared with only one type of polyol, lignin polyol, possessed the optimal properties.

Based on the results of the previous formulation optimization study, the preparation of an ethanol organosolv lignin (EOL)-based rigid PU foam reinforced with higher content of CNWs (up to 5 wt%) was reported in the third study. EOL, which is largely produced by the biorefineries today, was used instead of Kraft lignin due to its higher purity, lower molecular weight, and less condensed structure compared to Kraft lignin, and its sulfur free characteristic. In order to improve the content of CNWs to a level above 1 wt%, its aqueous suspension was directly mixed with the EOL polyol followed by water removal under high vacuum. Instead of using freeze dried CNWs, which is difficult to be well dispersed in organic solvents, e.g., DMF, this method can easily improved the CNWs content in PU

formulation with a homogeneous dispersion of CNWs. With increasing CNWs contents, the closed cell size of rigid PU foams was decreased resulted in a slight increase of the density. However, the density was still in the value range of the commercial low density rigid PU foams. The prepared nanocomposites possessed significant improvements of both mechanical properties and thermal stability which were shown by the compressive testing, differential scanning calorimetry (DSC) analysis, and thermogravimetric analysis (TGA).