From Petroleum to Biobased Crude: A Thermoplastic Polyurethane from Lignin-oil without Isocyanates

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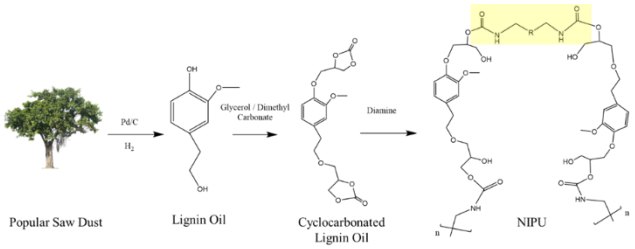
Abstract

The movement to transfer from petroleum-based products and materials to renewables does not necessarily have to bypass the use of oil. A new type of "black-gold" is readily abundant from the earth's most abundant source of aromatic carbon: lignin. While fractionation of petroleum yields fuels and chemicals for a diverse set of industries, lignin fractionation using targeted catalysts has demonstrated the ability to generate monomers and oligomers rich in functional groups for polymer synthesis. This study explores the use of lignin-oil, generated from reductive catalytic fractionation of popular wood, to a hydroxyl-rich mixture of aromatics that is used to synthesize a thermoplastic non-isocyanate polyurethane. The lignin-oil is first converted to a cyclocarbonated derivative using a benign synthetic sequence and further polymerized with a diamine to yield the non-isocyanate TPU. While more work is underway to optimize the reaction conditions and meet typical mechanical properties of commercial materials, initial analysis shows thermoplastic behavior and flexible properties consistent with traditional thermoplastic polyurethanes.



Graphical abstract depicting the synthetic steps toward the lignin-derived thermoplastic NIPU.

Introduction

To advance the modern biorefinery, lignin is an essential component. Composing up to 40% of biomass, lignin is an aromatic crosslinked polymer that acts as the "glue" to give structure and stability to the cellulose and hemicellulose component of trees and plants[1]. The aromatic units present in lignin's backbone are connected by a series of carbon-oxygen and carbon-carbon bonds that terminate in hydroxyl, ketone and carboxylic acid groups creating potential reactive positions for lignin to substitute for more common petroleum-derived precursors. While lignin has shown promise to be used in its unmodified form[2], its high molecular weight and heterogenous nature has created problems for its adaptation in industry for high-throughput applications. Chemical depolymerization of lignin to smaller more predicable molecules is one way to overcome this roadblock and introduce biobased building blocks that can be used to create renewable materials. Although lignin can be depolymerized through oxidative, reductive and/or acid/base techniques to name a few, the application of reductive catalytic fractionation (RCF) has proven to create high yields of monomers with narrow specificity[3]. RCF is a "lignin first" approach where biomass is fractionated to insoluble cellulosic components that can be recovered post-reaction, and an aromatic-rich lignin oil with high concentrations of low molecular weight monomers and oligomers. One particular method of RCF, using a Pd/C catalyst[4], has shown the ability to produce bi-functional phenyl propanol monomers, suitable for polymer synthesis, with yields up to 49% and a selectivity of 91%. The results of this method show promise to provide a feedstock for hydroxyl containing compounds that can participate in polyurethane synthesis.

Polyurethanes are typically manufactured from a polyol "part A" component and isocyanate "part B" component. However, due to the significant health-safety dangers associated with isocyanates, as well as the toxic synthetic pathway to their own synthesis[5], a non-isocyanate synthetic route was taken toward the biobased materials. Non-isocyanate polyurethanes (NIPUs) can be synthesized through polyaddition, chemical coupling, nucleophilic addition to carbamates, or the ring opening of cyclic carbonates with amines, to name a few[6]. The use of cyclic carbonates has shown to be a relatively facile reaction, creating no other chemical byproducts or intermediates[7]. The resulting polymer is also endowed with an additional hydroxyl group at each urethane bond, creating new sites for hydrogen bonding increasing the chemical resistance of the polymer. Stemming from recent success at employing green reagents in the insertion of cyclocarbonates on the backbone of unmodified kraft lignin[2,8], a similar approach was envisioned for the lignin-oil product synthesized from the RCF method using Pd/C. However, contrary to the use of multifunctional kraft lignin that led to crosslinked materials, the lignin-oil and its bi-functional nature was targeted as a thermoplastic material. Here, the initial results of a study employing cyclocarbonated lignin-oil towards the synthesis of thermoplastic NIPUs is reported and the thermal properties of the new polymer is explored.

Materials

Lignin oil was supplied by the National Renewable Energy lab in Golden, CO according to a published procedure[4]. Briefly, Popular wood sawdust was suspended in methanol in a Parr reactor to which was added the Pd/C catalyst. The vessel was sealed and pressurized with H_2 gas to 3 MPa and heated to 250°C. Once the reaction pressure increased to 12 MPa, the vessel was cooled to room temperature and depressurized. The insoluble cellulosic material was filtered and the methanol was evaporated to recover a brown lignin-oil. The oil was then extracted three times with dichloromethane (DCM) and water after which the DCM was removed using reduced pressure. Lignin monomer yields were measured from the Klaison lignin content using a gas chromatography (Agilent 6890 series) equipped with a HP5-column and a flame ionization detector (FID). Refer to a previous publication[4] for full details on lignin processing and measurement. Other chemicals used in the synthetic sequence were purchased from common chemical suppliers and used as received. The cyclocarbonation (CC) of lignin oil was accomplished using a previous protocol[2] with some revisions. Lignin oil was suspended in glycerol carbonate using a catalytic amount of K_2CO_3 and heated to 120°C for 45 minutes. After recovering with DCM, washing with water and drying, the lignin-oil product was reacted with dimethyl carbonate for 4 hours. The resulting compound was recovered in a similar manner and used without any further purification. Polymerization was achieved by the addition of 1,10-diaminodecane in a stoichiometric amount according to the concentration of cyclocarbonate groups present in the CC lignin-oil. The reaction was completed for 2 hours while stirring on a hotplate and then poured in a silicon mold and cured overnight at 105°C.

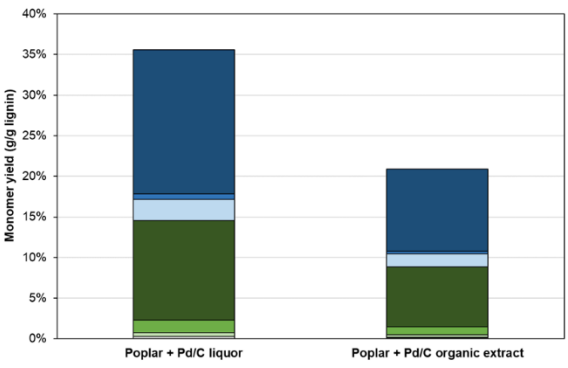
Results and Discussion

The lignin oil was obtained by the reductive catalytic fractionation of popular wood in methanol with a Pd/C catalyst. Runs were completed in a batch reactor at the National Renewable Energy Lab in Golden, CO. After the fractionation of biomass, the oil and cellulosic components were separated and the oil was extracted with dichloromethane to remove additional C-6 and C-5 sugar components. The catalyst was specifically chosen to generate aromatics with a hydroxyl group terminating the linear end of the molecule. For example, if Ru/C catalysts are used, the lignin-oil is more heavily concentrated with methyl-terminated linear end-groups[4] creating a mono-functional compound unsuitable for polymer synthesis. The monomers present in the oil as well as the targeted bi-functional aromatic structures are depicted in **Figure 1**. The final oil contained approximately 20.9% monomer by weight and 17.5% of the desired 4-propanolguaiacol and 4-propanolsyringol. The rest of the components in the oil have been determined to be low molecular weight dimers and oligomers[4]. Despite the low yield of the 4-propanol species, the oil still registered a total hydroxyl concentration of 7.3 mmol OH/g with a hydroxyl number of 409.5 mgKOH/g (**Table 1**). Although data for the exact chemical structures of the oligomeric components is still forthcoming, it is expected that the Pd/C catalyst will generate species with a functionality of at least 2 given its lower propensity to reduce alcohols.

Table 1. Chemical properties of precursors (CC = cyclocarbonate)

Precursor	OH / CC Content (mmol/g)	M_w
Lignin Oil	7.3 (OH)	136
CC Lignin Oil	3.3 (CC)	258

The lignin oil was subjected to a two-step reaction toward converting the terminal hydroxyl groups to cyclocarbonates (CCs). First, glycerol carbonated was added in a solvent free procedure to extend and convert the phenolic and aliphatic hydroxyl groups to a 1,2-diol. Next, a transesterification reaction was completed using dimethyl carbonate to induce a ring-closing of the 1,2-diol to create



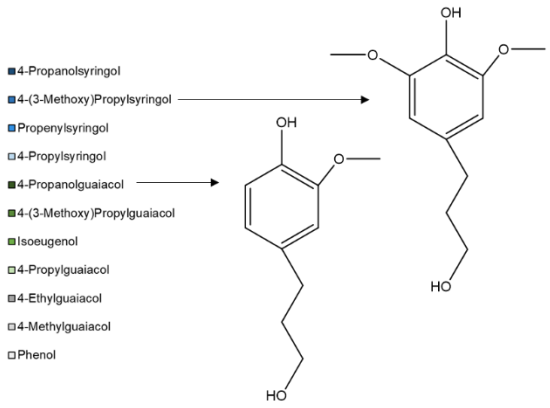


Figure 1. Monomer yield of lignin oil processed from popular wood over Pd/C catalyst. The two monomers of highest concentration that are targeted for NIPU synthesis are displayed to the right.

the CC species. An average of three runs using quantitative C-13 NMR revealed a CC content of 3.3 mmol/g oil. Compared to the nascent hydroxyl content of 7.3 mmol/g, a disparity can be observed as each OH group should theoretically be converted to a CC. To help elucidate the changes that occurred during the CC reaction, GPC was completed for the extracted oil and cyclocarbonated derivative. The results showed that M_w nearly doubles after the CC reaction (**Table 1**) pointing to addition reactions between monomers. Several side reactions are possible during the reaction with glycerol and dimethyl carbonate due to the prevalence of nucleophilic oxygen groups and electrophilic carbonyl centers on the CCs. FTIR confirms the presence of linear carbonate peaks at 1735 cm^{-1} (**Figure 2**), a product of polycarbonate condensation. The molecular weight analysis therefore predicts that on average each component of the lignin-oil combines with one other component to reduce the available hydroxyl content by half. The CC content therefore corresponds to an approximate conversion of 92% of available hydroxyl groups to CC (3.3 CC : 3.6 OH), given the molecular weight increase.

Polymer Synthesis

The high concentration of cyclocarboante groups present in the functionalized lignin-oil situates the precursor as a good candidate for ring-opening polymerization with an appropriate diamine. 1,10-diaminodecane was chosen for the polymerization reaction given its availability to be synthesized from castor oil, a biobased material. The extent of the reaction was monitored by FTIR, observing the consumption of the CC peak at 1795 cm^{-1} in favor of the urethane signal at ~ 1700 cm^{-1}. Representative spectra can be found in **Figure 2** where a complete conversion of the CC peak to urethane carbonyls is observed. The polyurethane can also be detected by the rise in the OH peak at ~3300 cm^{-1}, a product of the ring-opening reaction where a new hydroxyl group is generated from the urethane bond (see **graphical abstract**). The increase in the signal for methylene groups is a result of the aliphatic nature of the diamine backbone seen at 2900 cm^{-1} and 2800 cm^{-1}.

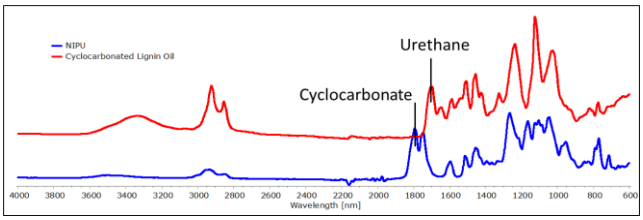


Figure 2. FTIR of cyclocarbonated precursors and the polymerized product.

It is worth noting that a full conversion of the CCs to urethane bonds was achieved a relatively mild conditions (105°C for 12 hours). In the past, NIPUs have suffered from low reactivity and the presence of side reactions leading to unreacted precursors and high concentrations of urea groups, respectively[7,9]. In terms of the urea signal normally observed ~ 1670 cm^{-1}, a small shoulder can be observed in **Figure 2**, however its intensity is overshadowed by the urethane peak at higher wavenumber. The samples also gave evidence of a fast curing process, where a screening of samples showed conversions of the CC signal in as little as 3 hours. The small molecules present in the reaction mixture show promise for fast kinetics, adding to the viability of the reaction scheme. Polymer samples demonstrated physical properties similar to flexible polyurethanes. While mechanical testing has not been completed, the rather tough materials showed promise for high tensile strength and ultimate strain (**Figure 3**) avoiding the pitfall of brittleness that is often observed in lignin-based materials. As will be seen in the thermal properties below, the NIPUs did not show evidence of crosslinking but rather behavior consistent with polymer chains with multiple phases.

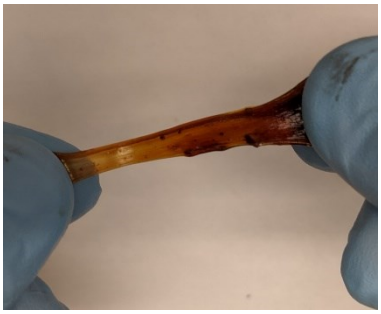


Figure 3. Picture of RCF-NIPU samples undergoing strain

Thermal properties

The synthesis of a thermoplastic polyurethane is difficult given the propensity of most lignin derivates to undergo crosslinking at elevated temperatures. While thermoplastic polymers from lignin have been synthesized in the past, these examples have relied upon the addition high concentrations of long-chained petroleum-derived molecules[10] (such as polybutadiene), limiting the sustainability of the protocol. The rational for using reductive catalytic fractionation centered on the ability to produce low molecular weight bi-functional molecules that would not crosslink but allow polymer flow above T_m. It must be observed that the lignin-oil is rather heterogeneous in nature, composed of monomers, dimers and oligomers that will affect the overall properties of the polymer. In fact, the dynamic scanning calorimetry (DSC) trace for the cured polymer (**Figure 4**) predictably shows a rather broad melting endotherm, characteristic of a multiphase material centered at 160°C. A broad glass transition region is also observed after 10°C, which may possibly point to low molecular weight species in the polymer composition.

Thermogravimetric analysis (TGA) was completed to assess the stability of the polyurethane in a nitrogen atmosphere. The weight loss over time, as well as the first-derivative are seen in **Figure 5**. The results show

a typical two-step degradation pathway consistent with thermal dissociation of the urethane bonds followed by higher temperature degradation of the precursors themselves. The polymer recorded a 5% weight loss at 168°C as well as a 10% weight loss at 202°C.

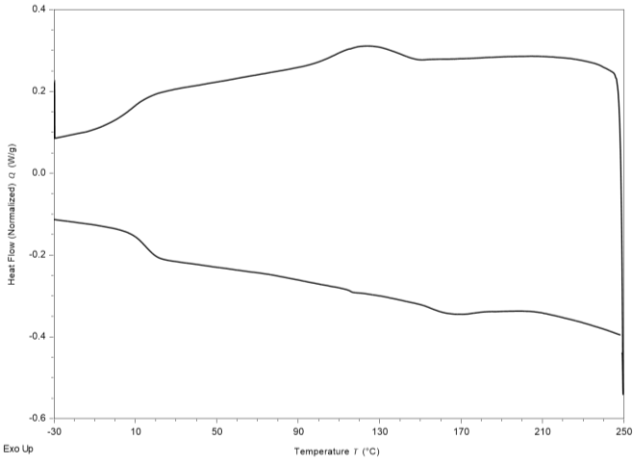


Figure 4. DSC trace of the first cooling and second heating cycle of the lignin-oil NIPU.

Polymer samples were conditioned for several days at atmospheric conditions which could have resulted in water uptake result in an increased weight-loss event above 100°C. However, the rather low thermal stability of the polymer lends more evidence to the conclusion that the current materials are low molecule weight samples that require further optimization to reach the standards of typical thermoplastic polyurethanes. Further work is in progress to create more homogeneous distributions of precursors in the RCF to create better conditions for high molecular weight polymers.

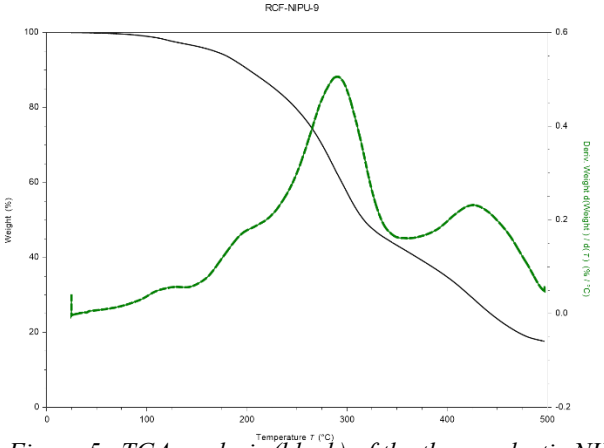


Figure 5. TGA analysis (black) of the thermoplastic NIPU including the first derivative of weight loss (green).

Conclusion

This initial study probing the use of lignin-oil for the synthesis of a thermoplastic non-isocyanate polyurethane pointed to success and challenges. On the one hand, the mixture of monomers and oligomers present in RCF lignin-oil did not prevent a successful functionalization and polymerization to give properties recognizable as a TPU. The high hydroxyl content of the oil led to a sufficient concentration of cyclocarbonate groups to induce polymerization without crosslinking. On the other hand, the rather low Tg and decomposition temperatures point to polymers of low molecular weight. Further optimization is needed for the cyclocarbonation step to limit polycarbonate condensation, a side reaction introducing linear carbonate linkages that may be attacked by the diamine and cause chain scission. It may also be possible to further narrow the precursor distribution by selective solvent extraction begin with more homogeneous feedstocks. However, this initial study gave a positive proof of concept to spur additional efforts.

Acknowledgements

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