Bio-based Polyurethane Foams Made from Microwave Liquefaction of Biomass

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BIO-BASED POLYURETHANE FOAMS MADE FROM MICROWAVE LIQUEFACTION OF BIOMASS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The School of Renewable Natural Resources

by

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B.S., Sichuan Agricultural University, 2013
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ABSTRACT

Polyurethane (PU) foam is one of the most versatile construction insulations due to its low density, low thermal conductivity, and high mechanical performance. However, it is still highly dependent on petro-based chemicals, i.e. polyol and isocyanate. In this work, biomass, such as rape straw, switchgrass, and yaupon holly (*Ilex vomitoria*) were liquefied using microwave energy to produce bio-based polyol in order to substitute petro-based polyol in the production of PU foam. Cellulose nanocrystals (CNCs) were also extracted from liquefaction solid residue. They were then applied to reinforce high bio-content PU foam. Moreover, lignin was fractionated from bio-polyol by adding distilled water, and then it was used as filler to reinforce PU foam. In addition, the microwave liquefaction conditions of woody underbrush were optimized to obtain the maximum conversion yield.

The overall results indicated that higher liquefaction temperature was beneficial to obtaining higher energy consumption efficiency as heated by microwave irradiation. Moderate liquefaction conditions could result in a high content of hydroxyl group products, while severe reaction conditions could produce a high yield of levulinic ester products. The rapid decomposition of hemicellulose and lignin during liquefaction process contributed to the decrease of activation energy ($E_a$), whereas the recondensation/repolymerization reaction could remarkably increase $E_a$. Most of lignin and hemicelluloses in the solid residues from 180°C/7.5 min were removed by liquefaction. The retained hemicelluloses and impurities were then eliminated by 2% NaOH and 5% H$_2$O$_2$ treatments. With high-intensity ultrasonic nanofibrillation treatment, CNCs with an average diameter of 12.59 nm were obtained from chemical purified samples. PU foam with 40% bio-polyol could be remarkably reinforced by 4% CNCs because the hydroxyl-rich structure in CNCs increased the crosslinking density. As compared with PU
foam without CNCs, the Young’s modulus and compressive stress in the 4% CNCs reinforced bio-foam increased by 590% and 150%, respectively. The foam with 10% lignin fractionated from bio-polyol had the highest apparent density of 0.061g/cm³, best mechanical strength, and superior thermal stability. The optimized parameters of the microwave liquefaction of underbrush can be summarized as follows: 1) particle size was controlled in the range of 16- to 40-mesh; 2) both the glycerol to EG ratio and liquid to solid ratio were set at 3:1; and 3) the liquefaction process was conducted at 160 °C for 10 min and catalyzed by 1.5% H₂SO₄. The optimal liquefaction conversion yield was 94.9%.
CHAPTER 1. INTRODUCTION

1.1. BACKGROUND

With the growing concern of environmental protection and rapid depletion of fossil fuel, the utilization of renewable lignocellulosic biomass, for example, rape straw, switchgrass, and yaupon holly (*Ilex vomitoria*), has attracted an increasing worldwide attention. Large quantities of rape straw are annually produced as an agro-waste from the edible oil industry. The common use of rape straw is to produce value-added products such as composites [1], bio-ethanol [2], and bio-oil [3]. Switchgrass (*Panicum virgatum*) is considered as a promising crop for a large region of the United States [4]. It has been used over other crops for conversion to bio-energy within the United States, and was identified by the US Department of Energy as a model herbaceous energy crop [5]. Highly abundant woody underbrush could provide ample bio-fuels for catastrophic wildfires that pose a threat to forest health and safety. Therefore, the removal and utilization of woody underbrush could support the goal of reducing catastrophic wildfires by reducing forest fuel loading levels and improving overall forest health. Yaupon holly is one of the most widespread woody underbrush species in the southeastern United States [6] that has great potential to be used as a raw material to produce bio-foam insulation *via* liquefaction.

1.1.1. Microwave Liquefaction

Liquefaction is one of the most promising thermochemical conversion routes to convert lignocellulosic biomass into valuable chemicals [7-8]. Through liquefaction, the high molecular weight components of biomass are broken down to low molecular weight gases, liquids, and liquefied residues. Generally, the gases are omitted because the yield of gaseous products is negligible. The liquid portion is the most commonly utilized liquefaction product. It can be applied to produce wood adhesive [9], bio-based polyurethane (PU) foam [10], methyl levulinate
[11], etc. However, there are a few reports about the utilization of the liquefied residues. The conventional one is to add it into polymer composites as a reinforcing agent [12]. The latest utilization method is to isolate cellulose nanofiber from liquefied residues [13-14].

The liquefying agent is vital to the efficiency of liquefaction. Solvents such as glycerol, water, and alcohol have been used to liquefy lignocellulosic biomass [15]. Alcohol remarkably enhances biomass liquefaction because it dissolves carbohydrates and lignins [7, 16]. Due to its low boiling point, methanol can be easily recovered from bio-oil by rotary evaporation. This feature has a great potential to increase the bio-substitution rate of polyol to produce PU foam.

Microwave heating has been successfully applied in the liquefaction of lignocellulosic biomass [15, 17]. Microwave heating offers the advantage of extremely rapid heating throughout the volume of the reaction mixture because it penetrates and produces a volumetrically distributed heat source [18].

1.1.2. Polyurethane Foam

Polyurethane foam is one of the most versatile construction insulations because of its low density, low thermal conductivity, and high mechanical performance. It has been widely used in automotive industry, insulating panel, and construction, etc [19]. Currently, the PU foam industry is still highly dependent on petro-based chemicals due to its two major feedstocks, i.e. polyol and isocyanate. With the growing concern of environmental protection and rapid depletion of fossil fuel, numerous efforts have been focused on the substitution of petro-based polyols with bio-based polyols such as vegetable oil [20] and bio-polyol derived from the liquefaction of lignocellulosic biomass [10]. It has been demonstrated that the bio-foams from the liquefaction of lignocellulosic biomass are comparable with petro-based ones [21]. Until now, a large variety of lignocellulosic biomass such as bamboo [22], wheat straw [23], and soybean
straw [24] have been liquefied into liquid polyols for the preparation of PU foams.

1.1.3. Cellulose Nanocrystals

Cellulose nanocrystals (CNCs) have high reinforcing capabilities because of their unique characteristics including high tensile strength, high Young’s modulus, high flexibility, and low coefficient of thermal expansion [25-28]. Previous studies have confirmed that agro-wastes such as cotton stalks [29], soybean hulls [30], rice straw [31], banana peel [32], and wheat straw [33] are important sources for the isolation of nanocrystals.

In the native cellulose fiber, CNCs are bonded by intermolecular forces and hydrogen bonds to each other [34]. The isolation of CNCs involves pretreatment to remove non-cellulose components, followed by fibrillation of the bundles of microfibrils. Concentrated sodium hydroxide and sulfuric acid combining with acidified sodium chlorite are the most commonly used pretreatment method to purify cellulose from plants [35]. However, there are still problems such as long treatment time and environmental pollution because of the use of concentrated alkali or acid and sodium chlorite. The microwave-assisted liquefaction catalyzed by acid could remarkably eliminate lignin and hemicelluloses with a high cellulose content retaining in the liquefied residue [13]. It suggests a great potential to extract CNCs from liquefaction solid residues.

As a promising composite modifier, CNCs have positive effects on physico-mechanical performance of the PU nanocomposites [36], whether the fraction is low (lower than 1.5%) [37-40] or high (up to 10%) [41-42]. This fact suggests a good potential to use CNCs for reinforcing high bio-content bio-foams.

1.2. OBJECTIVES

The objectives of this work are:
1) To optimize the microwave liquefaction conditions of biomass to obtain high quality biopolyol with low energy consumption.

2) To determine the pyrolysis characterizations of liquefaction solid residues, aiming at the further utilization of solid residue in the future.

3) To extract cellulose nanocrystals from liquefaction solid residue using a combination of green chemical purifications with ultrasonic treatment.

4) To produce high bio-content polyurethane foam from microwave liquefaction bio-polyol, and then reinforced by the cellulose nanocrystals extracted from liquefaction solid residue.

5) To reduce the preparation cost of polyurethane foam by adding lignin fractionated from bio-polyol.

6) To produce polyurethane foam insulation from the liquefaction of woody underbrush.

1.3. ORGANIZATION OF DISSERTATION

Chapter 1 provides an overall introduction of the research work and the structure of this dissertation.

Chapter 2 describes the optimization of microwave liquefaction of biomass in the consideration of energy consumption.

Chapter 3 presents the thermal properties of liquefaction solid residues determined by thermogravimetric analysis.

Chapter 4 introduces the extraction and characterization of cellulose nanocrystals from microwave liquefaction solid residue.

Chapter 5 presents the production and characterization of high bio-content polyurethane foam using microwave liquefaction bio-polyol and cellulose nanocrystals extracted from the solid residue.
Chapter 6 describes the fraction of lignin from bio-polyol and the characterization of lignin based polyurethane foams.

Chapter 7 presents the optimization of microwave liquefaction conditions of woody underbrush and the characterization of its resulting polyurethane foams.

1.4. REFERENCES


CHAPTER 2. MICROWAVE-ASSISTED LIQUEFACTION OF RAPE STRAW TO PRODUCE BIO-POLYOLS

2.1. INTRODUCTION

Alternative fuel and chemicals derived from lignocellulosic biomass, such as agro-waste, have attracted the attention of researchers worldwide because of the continuing depletion of fossil fuels [1]. As an agro-waste from the edible oil industry, large quantities of rape straw are produced annually, particularly in China [2]. Rape straw has great potential in the production of value-added products, such as composites [3], bioethanol [4], and stock-feed [5].

Several studies have investigated the conversion of lignocellulosic biomass into heavy liquid oil via pyrolysis and direct liquefaction [6-7]. The advantage of direct liquefaction is that the reaction occurs at a relatively low temperature and consumes less energy than pyrolysis [8].

The liquefying agent is vital to the liquefaction of lignocellulosic biomass. Solvents such as glycerol, water, and alcohol have been used to liquefy lignocellulosic biomass [9]. Alcohol remarkably enhances biomass liquefaction because it dissolves carbohydrates and lignins [10-11]. Due to its low boiling point, methanol can be easily recovered from bio-polyol by rotary evaporation.

Microwave heating has been successfully applied in the liquefaction of lignocellulosic biomass [9, 12]. Microwave heating offers the advantage of extremely rapid heating throughout the volume of the reaction mixture because it penetrates and produces a volumetrically distributed heat source [13]. Parameters such as liquefaction temperature and reaction time on

the liquefaction conversion yield have been extensively studied in previous investigation [14-15]. Despite the high conversion yield of microwave liquefaction, the energy consumption efficiency during this process and the quality of the liquefied products with respect to various liquefaction parameters have not yet been investigated thoroughly.

Bio-polyol obtained from liquefaction of lignocellulosic biomass is a versatile chemical source for the production of polyurethane foam [15]. Furthermore, methyl levulinate has been successfully prepared from liquefaction bio-polyol [16]. Several analytical techniques can be used to characterize bio-polyol components. Gas chromatography coupled with mass spectrometry (GC-MS) is the most frequently used method to analyze the chemical components of bio-polyols [17], due to its versatility, as well as the availability of a large library of mass spectra for compound identification. The characterization of chemical components of bio-polyols with respect to reaction condition provides insights to the changes of bio-polyols during liquefaction.

In this work, chemical components and structures of the bio-polyols obtained from different liquefaction reactions were analyzed by Fourier transform infrared spectroscopy (FT-IR) and GC-MS. The specific objective of this study is aimed to optimize the microwave liquefaction of rape straw from the point of high conversion yield and low energy consumption and to evaluate their changes in bio-polyol with respect to the liquefaction condition. The results in this study will provide an efficient pathway in preparation of bio-polyols from lignocellulosic biomass via microwave liquefaction.

2.2. MATERIALS AND METHODS

2.2.1. Materials

The rape straw collected in Sichuan Province, China, was ground into 20 to 40 mesh and
oven-dried at 105 °C until it reached a constant weight. The chemical compositions of rape straw were as follows: α-cellulose (36.72%), hemicelluloses (32.67%), Klason lignin (13.66%), alcohol-toluene extractives (4.46%), and ash content (8.27%). The holocellulose, α-cellulose, lignin content, alcohol-toluene extractives, and ash content were determined according to ASTM standards D 1104-56 (1971) [18], D 1103-60 (1971) [19], D 1106-96 (1996) [20], D 1107-96 (1996) [21], and D 1102-84 (2001) [22], respectively. The hemicellulose content was established as reported by Zhang et al. (2012) [23]. All chemicals, including sulfuric acid (H₂SO₄) and methanol, were purchased from commercial sources and used without further purification.

2.2.2. Methods

2.2.2.1. Microwave-assisted Liquefaction

The liquefaction of rape straw was performed in a Milestone MEGA laboratory microwave oven (Shelton, CT, USA) equipped with an ATC-400FO automatic fiber optic temperature control system (Figure 2.1). A typical run was carried out with 2 g of rape straw, 12 g of methanol, and 0.36 g of sulfuric acid. The mixed reactants were sealed in 100 mL Teflon reaction vessels with a magnetic stirring bar. The output power of the microwave energy was auto-adjusted based on the temperature feedback from the sensor under the maximum power of 700 W. The sealed vessels were subjected to microwave irradiation. The reaction temperature was increased from room temperature to the desired temperature (i.e., 140 °C, 160 °C, and 180 °C) within 5 min and then maintained for 0 to 10 min. An ice bath was applied to quench the finished reaction. After cooling, the liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper to separate the liquid and the solid residue. The liquid portion was evaporated at 65 °C under vacuum to remove the methanol. The gaseous products were vented because the yield of gaseous products was
negligible. The residue remaining on the filter paper was oven-dried for determining the conversion yield by Eq. 2.1.

\[
\text{Conversion yield (\%)} = (1 - \frac{\text{weight of residue}}{\text{weight of raw rape straw}}) \times 100
\]  

(2.1)

![Diagram of microwave-assisted liquefaction reaction system](image)

Figure 2.1. Diagram of microwave-assisted liquefaction reaction system

The unit energy consumption is defined as the energy needed to convert one gram of rape straw into bio-polyols. The energy requirement was calculated as the average microwave power multiplied by time. The average microwave power during the whole process was read on the electric control panel of the system. The energy consumption for each reaction was calculated as the total energy requirement for this reaction divided by the weight of the rape straws liquefied.

2.2.2.2. Characterization of Bio-polyols

The chemical structures of the bio-polyols from different liquefaction conditions were performed using a Nicolet Nexus 670 FT-IR equipped with a Thermo Nicolet Golden Gate MK II Single Reflection ATR accessory (Madison, WI, USA). A droplet of the bio-polyol was covered flatwise on the detection window. Each sample was analyzed in the range of resolution from 400 to 4000 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\), and a total of 32 scans were collected.
The general profiles for the bio-polyols were gained using electron-ionization-mass spectrometry (EI-MS). The products were analyzed on a mass spectrometer (Agilent 5975C VL MSD, Santa Clara, CA, USA), and the products were separated into their components using a gas chromatograph (Agilent 7890A) equipped with a fused capillary column (DP-5, L = 30 m, i.d. 0.32 mm, film thickness 0.25 µm) with 5% phenyl and 95% dimethylpoly-siloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min. The conditions for the detection were as follows: the injection mode had a split rate of 35; the column was held at 50 °C for 2 min and then heated to 250 °C at the rate of 10 °C/min; and the injector temperature was 250 °C. The identification of the components was confirmed using total ion chromatograms, as well as fragmentation patterns.

2.3. RESULTS AND DISCUSSION

2.3.1. Liquefaction Reaction

The effect of liquefaction temperature on the conversion yield of rape straw at five reaction times is depicted in Figure 2.2. To investigate the efficiency of the microwave with respect to temperature, the catalyst content was maintained at 3% of the weight of methanol. Liquefaction was initiated at the beginning of the process. The conversion yield increased dramatically as the liquefaction temperature increased from 140 °C to 180 °C. The increase in conversion yield during the initial period at low temperature (140 °C and 160 °C) was mainly due to the rapid degradation of the easily accessible rape straw cell wall components, such as lignin, hemicelluloses, and amorphous cellulose [23].
The conversion yield greatly increased with increasing liquefaction time, especially from 5 to 10 min. After 10 min, the conversion yield slightly decreased, and the color of the liquefied residue changed from grey to dark-brawn, and even black at 15 min. It was difficult for the solvent to penetrate into the crystalline region of the cellulose, which slowed the reaction and decreased the conversion yield. Moreover, severe conditions (high temperature and/or long time) could induce the recondensation/repolymerization of the already liquefied lignin and hemicellulose fragments [9]. Additionally, side reactions of the decomposed cellulose may yield insoluble substances [24]. Furthermore, the silica and silicates in the ashes may inhibit further liquefaction of the crop residues and cellulose [25]. Therefore, the resistance of cellulose, ash, and the recondensed fragments contributed to the decrease in conversion yield with long periods of microwave irradiation. Because recondensation/repolymerization took place after a prolonged reaction time, the energy consumed at that period may have been wasted. Therefore, energy
consumption analysis was essential to avoid energy waste and to ensure the high quality of the end product.

2.3.2. Energy Efficiency Evaluation

Though the maximum conversion yield of 86.54% was observed at 180 °C for 10 min, this did not mean that the reaction reduced energy consumption. As shown in Figure 2.3, higher liquefaction temperature resulted in lower energy consumption, except for the comparison between 160 °C/15 min and 180 °C/15 min. Microwave pretreatment opens water pathways in woody material, dramatically increasing its permeability and accelerating moisture migration in wood [26]. Microwaves induce heat at the molecular level by direct conversion of electromagnetic energy into heat, resulting in a fast heating rate [27]. Therefore, the energy consumption of microwave-assisted liquefaction would be lower than from conventional heating. As compared with conventional liquefaction, microwave-assisted liquefaction could save more than 85% energy consumption [28]. Hence, it is safe to state that the microwave-assisted liquefaction is a time and energy saving method to convert renewable biomass into bio-polyol.

Additionally, high pressure induced by high temperature in the sealed reaction system also enhances the conversion yield [23]. Consequently, high liquefaction temperature resulted in higher conversion yield and required lower energy consumption during the liquefaction regardless of liquefaction time.

The energy consumption of the 180 °C/15 min reaction was higher than that of the 160 °C/15 min reaction. This result suggests that recondensation/repolymerization took place at 180 °C/15 min, which decreased the extent of liquefaction. Because the excess energy was consumed in recondensation/repolymerization rather than decomposition, the energy was wasted. Therefore, the energy consumption evaluation of the liquefaction process could have also been
used as an indicator of the occurrence of recondensation/repolymerization.

Figure 2.3. Energy consumption as a function of liquefaction temperature and time (Other conditions: methanol/rape straw, 6/1; sulfuric acid, 3%)

2.3.3. FT-IR Spectra

Figure 2.4 presents the FT-IR spectra of the bio-polyols from different liquefaction conditions. The broad band at around 3330 cm\(^{-1}\) was related to the characteristic stretching vibration of hydroxyl groups [29], indicating that all bio-polyols contained a remarkable amount of hydroxyl groups. The absorption peaks at 1710 to 1740 cm\(^{-1}\) corresponded to carbonyl or ester groups [30]. As shown in the Figure 2.4, the intensity at 1740 cm\(^{-1}\) in the bio-polyols spectra increased from 160 °C/15 min to 180 °C/15 min, which could have been caused by oxidation and methanol esterification with increasing temperature, because the oxidation of hydroxyl groups could have formed the carbonyl groups [31]. Methanol esterification reaction may have also occurred during liquefaction [11], which could have increased the intensity of carbonyl groups. The extremely strong intensity at 1740 cm\(^{-1}\) from the 140 °C/15 min reaction was attributed to the rapid decomposition of hemicelluloses into C5 sugars with high content of hydroxyl groups. The intensified peak at 1409 cm\(^{-1}\) from 140 °C/15 min to 180 °C/15 min, which arose from the
plane deviational vibration of hydroxyl group in carboxylic groups, further evidenced the oxidation reactions during liquefaction [32].

Figure 2.4. FT-IR transmittances of bio-polyols from different treatments: (a) 140 °C/15 min; (b) 160 °C/15 min; (c) 180 °C/7.5 min; (d) 180 °C/10 min; (e) 180 °C/15 min

The characteristic peaks of aromatic ring at 1650 and 1450 cm\(^{-1}\) and benzene ring at 1363 cm\(^{-1}\) and 1210 cm\(^{-1}\) tended to be weaker with extended liquefaction, indicating that the decomposed lignin at the initial liquefaction stage underwent recondensation/repolymerization [33-34]. The intensity of 1210 cm\(^{-1}\) decreased as the liquefaction proceeded, demonstrating that the lignin derivatives participated in a cross-link reaction. The absorbance at 1150 cm\(^{-1}\) was due to the ether bond in cellulose [35], which was weakened with prolonging reaction times and increasing liquefaction temperatures, suggesting that the cellulose participated in recondensation/repolymerization. The intensity peak at 1088 cm\(^{-1}\) corresponding to the stretching vibration of C-O from polysaccharide gradually decreased as liquefaction proceeded [34]. This result was confirmed by the GC-MS analysis of bio-polyols as discussed below.
2.3.4. GC-MS Analysis

The chemical components of the bio-polyols obtained from the 140 °C/15 min, 160 °C/15 min, 180 °C/7.5 min, 180 °C/10 min, and 180 °C/15 min reactions are shown in Tables 2.1 and 2.2. Bio-polyols were mainly composed of C5 and C6 sugars, esters, furan derivatives, carbonyl compounds, and aliphatic hydrocarbons.

Table 2.1. Main components of bio-polyols (by area/%) from different treatments

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C5 Sugars</th>
<th>C6 Sugars</th>
<th>Aromatics</th>
<th>α-D-ribopyranoside, methyl</th>
<th>Esters</th>
<th>Levulinate Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C/15 min</td>
<td>46.30</td>
<td>14.43</td>
<td>4.52</td>
<td>33.11</td>
<td>15.18</td>
<td>0.50</td>
</tr>
<tr>
<td>160 °C/15 min</td>
<td>28.25</td>
<td>19.74</td>
<td>7.20</td>
<td>15.38</td>
<td>18.47</td>
<td>2.69</td>
</tr>
<tr>
<td>180 °C/7.5 min</td>
<td>19.97</td>
<td>17.84</td>
<td>7.22</td>
<td>8.67</td>
<td>21.79</td>
<td>6.53</td>
</tr>
<tr>
<td>180 °C/10 min</td>
<td>11.11</td>
<td>14.17</td>
<td>8.48</td>
<td>3.05</td>
<td>31.74</td>
<td>14.65</td>
</tr>
<tr>
<td>180 °C/15 min</td>
<td>7.19</td>
<td>7.17</td>
<td>8.35</td>
<td>1.50</td>
<td>43.27</td>
<td>21.71</td>
</tr>
</tbody>
</table>

As shown in Figure 2.5, GC-MS chromatograms are divided approximately into four zones within the retention time. The impurities mainly consisted of furfural, acetic acid, and ethanol, etc. The carbonyl compounds in the bio-polyols were primarily composed of esters, sulfuric acid derivative, furan derivatives, aliphatic hydrocarbons, succinic acid derivatives, and a small amount of C6 sugars, and aromatics. C5 sugars, C6 sugars, and aromatics were derived from hemicelluloses, cellulose, and lignin via liquefaction, respectively. Glycosidic bonds and dominant linkages between cellulose and hemicelluloses underwent methanolation under acidic condition, resulting in the release of C5 and C6 derivatives. Similarly, aromatics derivatives were released through cleaving the linkages of β-O-4, 4-O-5, and dibenzodioxocin units [10-11]. The presence of C5, C6 sugars, and aromatics in bio-polyols demonstrated the decomposition of hemicelluloses, cellulose, and lignin.

The total amount of C5, C6 sugars, and the aromatic derivatives remarkably decreased from 65.25% to 22.71% (area %) from 140 °C/15 min to 180 °C/15 min (Table 2.1). Ten types of C5

18
sugars derivatives, such as methyl 2-O-methyl-β-d-xylopyranoside, methyl α-D-rhamnopyranoside, methyl α-D-ribopyranoside, etc., were identified, accounting for 46.30% at 140 °C/15 min. This was remarkably reduced to 7.19% (area %) as the liquefaction temperature increased to 180 °C. This result suggested that the decomposition rate of the C5 sugars outweighed their generation. As shown in Table 2.1, the C5 sugar derivatives of methyl α-D-ribopyranoside was about 33.11% at 140 °C/15 min, which declined to 1.5% at 180 °C/15 min (area %). Its isomeric form of methyl β-D-ribopyranoside was also detected. The reduction of methyl α-D-ribopyranoside made a primary contribution to decreasing of C5 sugars. Eight kinds of C6 sugars derivatives, such as levoglucosenone, D-allose, and 3-Methylmannoside were detected. The total content of C6 sugar derivatives increased from 14.43 (140 °C/15 min) to 19.74 (160 °C/15 min), then decreased to 7.17% (area %) with increasing temperature to 180 °C (Table 2.1). This result indicated that the decomposition of cellulose mainly took place at the reaction condition of 140 °C/15 min, and that the decomposition outweighed its recondensation/repolymerization before 160 °C for 15 min.

The aromatic derivatives, such as benzoic acid 4-hydroxy-3-methoxy- methyl ester, 2-fluorobenzoic acid, 3,5-difluorophenyl ester, aspidinol, etc., were randomly distributed on the chromatograms (Table 2.2). The content of the aromatic derivatives generally increased from 4.52% at 140 °C/15 min to 8.48 % (area %) at 180 °C/10 min, and then slightly decreased to 8.35% at 180 °C/15 min (Table 2.1). The increase of aromatic derivatives revealed the decomposition of lignin, while the slight reduction in aromatics content was probably due to recondensation/repolymerization. For the preparation of polyurethane foams, the hydroxyl group of bio-polyols is a key index for quality control and the formulation determination. The content of the hydroxyl group was mainly attributable to the amount of the C5, C6, and aromatics and
their derivatives because each of those components can provide 2-5 hydroxyl groups. The GC-MS demonstrated that the content of C5, C6, and aromatics were remarkably decreased by exceeding the reaction time, which led to the possible decline of hydroxyl substances. Therefore, severe liquefaction reaction conditions should be avoided if the bio-polyols will be used in the production for preparation of polyurethane foam.

The ester content in bio-polyols remarkably increased from 15.18 (140 °C/15 min) to 43.27% (180 °C/15 min) (Table 2.1), which was primarily attributed to the increase of pentanoic acid, 4-oxo- methyl ester (a type esterification product of levulinic acid with methanol). This levulinate is an important chemical with numerous potential applications, such as a fuel additive used to improve petroleum stability, low-temperature fluidity, and flash point [24]. Hence, in this case, to obtain a high yield of levulinate ester, the liquefaction should be subjected to a severe reaction condition.

Other oxygenated by-products, such as furfural, methyl 2-furoate, furan, and succinic acid derivatives, increased as the liquefaction processed (Table 2.2). The furan derivatives that dehydrated from xylose originated from further decomposition of hemicelluloses [36]. The further decomposition of cellulose and hemicelluloses may also have generated organic acids, such as acetic acid [37-38]. The organic acids were esterified with methanol under acidic conditions, resulting in the increase of esters. Hence, it was speculated that the severe liquefaction caused the further decomposition of C5 and C6 sugars. Furthermore, dimethyl sulfate was also detected, which implied that sulfuric acid was involved in esterification.
Figure 2.5. GC-MS chromatograms of bio-polyols from different treatments: (a) 140 °C/15 min; (b) 160 °C/15 min; (c) 180 °C/7.5 min; (d) 180 °C/10 min; (e) 180 °C/15 min
Table 2.2. Components of bio-polyols from different treatments

<table>
<thead>
<tr>
<th>Peak</th>
<th>Chemical</th>
<th>Area (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>1</td>
<td>Ethanol</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>Tetramethyl silicate</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>Undecane</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td>o-Ethylhydroxylamine</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>Butanoic acid, 3-methyl-2-[(phenylmethoxy)iminoo]-, trimethylsilyl ester</td>
<td>0.64</td>
</tr>
<tr>
<td>5</td>
<td>Acetic acid, dimethoxy-, methyleles</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>3-Aminopyrazine 1-oxide</td>
<td>0.36</td>
</tr>
<tr>
<td>7</td>
<td>Cyclopropanecarboxylic acid, 2-methyl-2-methoxy, methyl ester</td>
<td>0.07</td>
</tr>
<tr>
<td>8</td>
<td>Cyclotrisiloxane, hexamethyl-</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td>Furfural</td>
<td>0.44</td>
</tr>
<tr>
<td>10</td>
<td>3-Methoxy-3-methyl-1-pentene</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Cyclopropanecarboxylic acid, 2-methyl-2-methoxy, methyl ester</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Acrolein,dimethyl acetal</td>
<td>0.06</td>
</tr>
<tr>
<td>13</td>
<td>2-Butenedioic acid (E)-, dimethyl</td>
<td>0.20</td>
</tr>
<tr>
<td>14</td>
<td>Sulfuric acid, dimethyl ester</td>
<td>0.90</td>
</tr>
<tr>
<td>15</td>
<td>Pentanoic acid, 4-oxo-, methyl ester</td>
<td>0.50</td>
</tr>
<tr>
<td>16</td>
<td>Methyl 2-furoate</td>
<td>0.30</td>
</tr>
<tr>
<td>17</td>
<td>Butanedioic acid, dimethyl ester</td>
<td>0.32</td>
</tr>
<tr>
<td>18</td>
<td>4-Hydroxyphenylacetic acid, ethyl</td>
<td>0.06</td>
</tr>
<tr>
<td>19</td>
<td>Succinic acid, heptyl 2-propyl ester</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>1H-Imidazole, 2-methyl-</td>
<td>0.08</td>
</tr>
<tr>
<td>21</td>
<td>Cyclopentasiloxane, decamethyl-</td>
<td>0.05</td>
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<tr>
<td>22</td>
<td>2(5H)-Furanone, 5-methyl-</td>
<td>-</td>
</tr>
<tr>
<td>23</td>
<td>Succinic acid, heptyl 3-methylbut-2-yl ester</td>
<td>-</td>
</tr>
<tr>
<td>24</td>
<td>1,3-Dioxolane-4,5-dimethanol, 2,2-</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>Furan</td>
<td>1.16</td>
</tr>
<tr>
<td>26</td>
<td>5H-Imidazole-4-carboxylic acid, 5-3-dodecyl ester</td>
<td>-</td>
</tr>
<tr>
<td>27</td>
<td>Phenol, 2-methoxy-</td>
<td>-</td>
</tr>
<tr>
<td>28</td>
<td>1-Pentanethiol, 4-methyl-</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>2,4(1H,3H)-Pyrimidinedione, dihydro-</td>
<td>0.40</td>
</tr>
<tr>
<td>30</td>
<td>1-(2-Thiethyl)-1-propanone</td>
<td>0.13</td>
</tr>
<tr>
<td>31</td>
<td>Methane, iodo-</td>
<td>0.26</td>
</tr>
<tr>
<td>32</td>
<td>Levoglucosenone</td>
<td>0.41</td>
</tr>
</tbody>
</table>

22
<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Name</th>
<th>Molar Mass (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34</td>
<td>3-Acetoxy-3-hydroxypropionic acid, methyl ester</td>
<td>3.02</td>
</tr>
<tr>
<td>35</td>
<td>Methyl tetradecanoate</td>
<td>0.12</td>
</tr>
<tr>
<td>36</td>
<td>Pentanediolic acid, 2-oxo-, dimethyl ester</td>
<td>-</td>
</tr>
<tr>
<td>37</td>
<td>5-Amino-3H-[1,2,3]triazole-4-carbo</td>
<td>1.03</td>
</tr>
<tr>
<td>38</td>
<td>Glycolaldehyde dimethyl acetal</td>
<td>0.10</td>
</tr>
<tr>
<td>39</td>
<td>Succinic acid, ethyl 2-(2-methoxyethyl)heptyl ester</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>2-Fluorobenzoic acid, 3,5-difluorophenyl ester</td>
<td>0.13</td>
</tr>
<tr>
<td>41</td>
<td>1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone</td>
<td>0.08</td>
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<tr>
<td>42</td>
<td>Phenol, 4-methoxy-2-nitro-</td>
<td>0.96</td>
</tr>
<tr>
<td>43</td>
<td>Isopropylimidazole-2-thione</td>
<td>-</td>
</tr>
<tr>
<td>44</td>
<td>Hexadecanoic acid, methyl ester</td>
<td>1.13</td>
</tr>
<tr>
<td>45</td>
<td>2H-Pyran-2-one, 4-hydroxy-6-methyl</td>
<td>-</td>
</tr>
<tr>
<td>46</td>
<td>Methyl-2,4-di-O-methyl-α-D-glucopyranoside</td>
<td>0.25</td>
</tr>
<tr>
<td>47</td>
<td>Citric acid, trimethyl ester</td>
<td>1.92</td>
</tr>
<tr>
<td>48</td>
<td>Octadecanoic acid, methyl ester</td>
<td>0.43</td>
</tr>
<tr>
<td>49</td>
<td>9-Octadecenoic acid, methyl ester(E)-9,12-Octadecadienoic acid (Z,Z)-methyl ester</td>
<td>0.66</td>
</tr>
<tr>
<td>50</td>
<td>Methyl-2-O-methyl-β-D-xylopyranoside</td>
<td>0.31</td>
</tr>
<tr>
<td>51</td>
<td>Methyl-α-D-rhamnopyranoside</td>
<td>0.65</td>
</tr>
<tr>
<td>52</td>
<td>Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester</td>
<td>0.67</td>
</tr>
<tr>
<td>53</td>
<td>α-D-ribopyranoside, methyl</td>
<td>1.5</td>
</tr>
<tr>
<td>54</td>
<td>α-D-ribopyranoside, methyl</td>
<td>21.84</td>
</tr>
<tr>
<td>55</td>
<td>2H-Pyran-3,4,5-triol, tetrahydro-2-methoxy-6-methyl</td>
<td>3.41</td>
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<td>56</td>
<td>2,4'-Dihydroxy-3'-methoxyacetophenone</td>
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<td>57</td>
<td>α-D-lyxofuranoside, methyl</td>
<td>1.55</td>
</tr>
<tr>
<td>58</td>
<td>α-D-Riboxyranoside, methyl</td>
<td>7.77</td>
</tr>
<tr>
<td>59</td>
<td>α-D-D-xyloturanoside, methyl 2,5-di-O-methyl</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>Methyl(methyl 4-O-methyl-α-D-mannopyranoside)uronate</td>
<td>7.44</td>
</tr>
<tr>
<td>61</td>
<td>Methyl-4-O-methyl-α-D-glucopyranoside</td>
<td>-</td>
</tr>
<tr>
<td>62</td>
<td>Benzoic acid, 4-hydroxy-3,5-dimethoxy-, hydrazide</td>
<td>1.00</td>
</tr>
<tr>
<td>63</td>
<td>α-D-xyloturanoside, methyl</td>
<td>0.56</td>
</tr>
<tr>
<td>64</td>
<td>Methyl 3-O-methyl-β-D-xylopyranoside</td>
<td>-</td>
</tr>
<tr>
<td>65</td>
<td>α-D-glucopyranoside, methyl</td>
<td>0.64</td>
</tr>
</tbody>
</table>
2.4. CONCLUSIONS

In this study, the acid-catalyzed liquefaction of rape straw in methanol using microwave energy was conducted to produce bio-polyols. The conversion yield remarkably increased with increasing liquefaction temperature reaction time; whereas, it decreased at 180 °C/10 min. A higher liquefaction temperature was beneficial to obtaining higher energy consumption efficiency as heated by microwave irradiation. The recondensation and/or repolymerization reactions at severe liquefaction conditions may have led to energy waste. The FT-IR spectra suggested that oxidation reactions of hydroxyl groups and methanol esterification occurred during liquefaction. GC-MS of bio-polyols analysis demonstrated the decomposition of hemicellulose, cellulose, and lignin during liquefaction; further decomposition of C5 and C6 sugars caused the reduction of hydroxyl groups and the increase of levulinate ester in bio-polyols. The main chemical components of bio-polyols were directly related to liquefaction conditions. Moderate liquefaction conditions could result in a high content of hydroxyl group products, while severe reaction conditions could produce a high yield of levulinic ester products, regardless of energy consumption efficiency.
2.5. REFERENCES


[26] S. Panthapulakkal, M.J. Sain, Investigation of structural changes of alkaline-extracted wood


CHAPTER 3. THERMAL DECOMPOSITION CHARACTERISTICS OF MICROWAVE LIQUEFIED RAPE STRAW RESIDUES USING THERMOGRAVIMETRIC ANALYSIS

3.1. INTRODUCTION

With the growing concern of environmental protection and rapid depletion of fossil fuel, the utilization of lignocellulosic biomass, a type of degradable and renewable resource, has attracted an increasing worldwide attention. Especially, in China, a large quantity of rape straw is produced annually as agro-waste. Liquefaction is one of the widely investigated methods to convert lignocellulosic biomass into valuable chemicals of fuels in recent years [1-2]. Through liquefaction, the high molecular weight components of biomass are broken down to low molecular weight gases, liquids, and liquefied residues. Generally, the gases are omitted because the yield of gaseous products is negligible. The liquid portion is the most commonly utilized liquefaction product. It can be applied to produce wood adhesive [3], bio-based polyurethane foam [4], methyl levulinate [5], etc. However, there are a few reports about the utilization of the liquefied residues. The conventional one is to add it into polymer composites as a reinforcing agent [6]. The latest utilization method is to isolate cellulose nanofiber from liquefied residues [7-8]. A potential utilization method of the liquefied residue should be to pyrolyze it into value added products.

Pyrolysis is one of the promising thermochemical conversion routes, playing an important role in biomass conversion. The end products of pyrolysis of gases and liquids can be used as

fuel due to their high calorific value [9, 10]. Information on pyrolysis kinetics is vital to evaluate biomass as a feedstock for fuel or chemical production. It is also crucial in the control of thermochemical conversion processes [11]. The study of the thermal decomposition characteristics of condensed wood liquefied residues was used to clarify the condensation reaction mechanism during liquefaction [12]. The evaluation on pyrolysis properties of agro-waste, such as corn stalk can be found in previous study [13]. However, there is no study on the thermal decomposition characteristics of liquefied residues from agro-waste. Therefore, it is essential to study the fundamentals of thermal decomposition properties of the liquefied rape straw residue.

Thermogravimetric analysis (TG) can quantify mass change and thermal decomposition of the samples [14]. It has been extensively used in the research on pyrolysis of biomasses, such as polar wood [14], corn stalk [15], macroalgae [16] microalgae [17], cellulose nanofibers and nanowishkers [18], tar from gasification [19], and pseudocomponents of biomass (i.e. cellulose, hemicelluloses and lignin) [20]. These studies help clarify our understanding of pyrolysis kinetic.

The main chemical components in biomass including hemicellulose, lignin and cellulose are the basic factors to interpret the pyrolysis properties. A previous study indicated that the mass loss of hemicellulose, cellulose and lignin mainly happened at 220-315 °C, 315-400 °C, and 160 to 900 °C, respectively [21]. However, hemicellulose is the most susceptible chemical component to liquefaction, followed by the lignin and cellulose [22]. Therefore, the main chemical components in liquefied residues will be inhomogeneity with the change of liquefaction conditions. It will result in the difference of pyrolysis properties of liquefied residues from different liquefaction conditions.
Thus, in this study, the thermal decomposition characteristics of microwave liquefied residues from different liquefaction conditions were investigated using thermogravimetric analysis at three different heating rates (5, 20, 50 °C min\(^{-1}\)) under an inert nitrogen atmosphere. Kinetic parameters, including apparent activation energy \(E_a\) and pre-exponential factor (expressed as \(\ln A_a\)), were determined by the model reported by Kissinger 1957 [23]. The pyrolysis properties of liquefied residue with conversion were also studied using the Kissinger method to provide fundamental pyrolysis parameters for the integrated utilization of liquefied residue.

3.2. MATERIALS AND METHODS

3.2.1. Materials and Chemicals

Rape straw from Sichuan province (Southwest of China) was milled in a knife mill to pass through a 20-mesh and maintain in 40-mesh sieve. Then the milled sample was oven dried at 105°C until constant weight. The holocellulose, \(\alpha\)-cellulose, lignin content, alcohol-toluene extractives and ash content of raw rape straw were determined according to ASTM standards D 1104-56 (1971), D 1103-60 (1971), D 1106-96 (1996), D 1107-96 (1996) and ASTM D 1102-84 (2001), respectively. The hemicellulose content was established in accordance with the method reported in previous study [24]. The chemical components of rape straw were as following: \(\alpha\)-cellulose (36.72%), hemicellulose (32.67%), Klason lignin (13.66%), alcohol-toluene extractives (4.46%), and ash content (8.27%). All reagent grade chemicals, including sulfuric acid (95-98%) and methanol, were purchased from commercial sources and used without further purification.

3.2.2. Microwave Liquefaction

Liquefaction of rape straw was performed in a Milestone MEGA laboratory microwave oven (Shelton, CT, USA) equipped with an ATC-400FO automatic fiber optic temperature control
system. A typical run was carried out with a loading of 2 g of rape straw, 12 g of methanol, and 0.36 g of sulfuric acid, i.e., so that the concentration of H$_2$SO$_4$ was 3%. The mixed reactants were sealed in a 100 mL Teflon reaction vessel with a magnetic stirring bar. The output power of the microwave energy was auto-adjusted based on the temperature feedback from the sensor under maximum power of 700 W. The sealed vessels were subjected to microwave irradiation. The reaction temperature was increased from room temperature to the desired temperature (i.e., 140 °C, 160 °C and 180 °C) within 5 min, and then maintained for 2.5, 5, or 10 min. An ice bath was applied to quench the reaction when it was done. After cooling, the liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper to separate the liquid and the solid residue. The solid residue contents from a series of liquefaction conditions are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Liquefaction conditions</th>
<th>140 °C/15 min</th>
<th>160 °C/15 min</th>
<th>180 °C/7.5 min</th>
<th>180 °C/10 min</th>
<th>180 °C/15 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue content (%)</td>
<td>44.22</td>
<td>30.15</td>
<td>23.44</td>
<td>13.46</td>
<td>16.78</td>
</tr>
</tbody>
</table>

3.2.3. Thermogravimetric Analysis

![Figure 3.1. Raw material and liquefied rape straw residues](image-url)
(1: rape straw; 2: 140 °C/15 min; 3: 160 °C/15 min; 4: 180 °C/7.5 min; 5: 180 °C/10 min; 6: 180 °C/15 min)

The TG analysis measurements of raw rape straw and liquefied residues (Figure 3.1) were conducted with a thermal analyzer Q50 TG (TA Instruments, New Castle, USA) to simultaneously obtain thermogravimetric data. As the potential purpose of this study is to explore the pyrolysis utilization of liquefied residues instead of its combustion properties, the TG analysis was only performed under an inert nitrogen atmosphere. Each sample, about 3 mg, was placed in a platinum pan, and then heated from 30 to 800 °C with constant heating rates of 5, 20 and 50 °C min$^{-1}$ under a flow of 40 mL min$^{-1}$ of high purity nitrogen atmosphere (99.999%).

3.2.3. Non-Isothermal Thermogravimetric Kinetics

In this study, $\alpha$ is defined as the conversion of sample expressed as normalized mass loss of decomposed sample, as Eq. 3.1,

$$\alpha = \frac{W_o - W_t}{W_o - W_f} \quad (3.1)$$

where $W_o$ is the initial sample mass, $W_t$ represents the actual mass at time $t$ and $W_f$ stands for the final sample mass after pyrolysis.

The conversion rate of solid sample to volatile product is commonly based on a single-step kinetic equation [19, 25], as Eq. 3.2,

$$\frac{d\alpha}{dt} = k(T_i) f(\alpha) \quad (3.2)$$

where $d\alpha/dt$, $t$, $T_i$, $k(T_i)$, $f(\alpha)$ are the conversion rate, time, absolute temperature, rate coefficient and the reaction model, respectively. $k(T_i)$ and $f(\alpha)$ are determined as Eq. 3.3 and 3.4, respectively.

$$k(T_i) = A_\alpha \exp\left(-\frac{E_\alpha}{RT_i}\right) \quad (3.3)$$
where $A_\alpha$ is the pre-exponential factor (min$^{-1}$), $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$) and $E_\alpha$ is the activation energy (kJ mol$^{-1}$).

$$f(\alpha) = (1 - \alpha)^n$$  \hspace{1cm} (3.4)

where $n$ is the reaction order. The most common reaction models for solid-state kinetic are organized in four categories that are nucleation, geometrical, diffusion and reaction order. The detailed description of reaction order was reported by Tadini et al. [26].

Combining equations (3.2), (3.3) and (3.4), the reaction rate can be written as Eq. 3.5,

$$\frac{d\alpha}{dt} = A_\alpha \exp\left(-\frac{E_\alpha}{RT_i}\right)(1 - \alpha)^n$$  \hspace{1cm} (3.5)

The constant heating rate $\beta$ is expressed as Eq. 3.6,

$$\beta = \frac{dT_i}{dt}$$  \hspace{1cm} (3.6)

As the conversion rate is a function of temperature, and the temperature is related to the heating time, the conversion rate can be described by Eq. 3.7,

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT_i} \cdot \frac{dT_i}{dt} = \beta \frac{d\alpha}{dT_i}$$  \hspace{1cm} (3.7)

Substituting expression (3.7) into equation (3.6), the sample decomposition can be expressed as Eq. 3.8,

$$\frac{d\alpha}{dT_i} = \frac{A_\alpha}{\beta} \exp\left(-\frac{E_\alpha}{RT_i}\right)(1 - \alpha)^n$$  \hspace{1cm} (3.8)

A model-free non-isothermal function is obtained by transforming Eq. 3.9 in accordance to the method reported by Kissinger 1957.

$$\ln\left(\frac{\beta}{T_i^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \frac{E_\alpha}{RT_i}$$  \hspace{1cm} (3.9)
Model-fitting and model-free methods are used to obtain the thermal degradation kinetic parameters under non-isothermal conditions. The former is insufficient in kinetic studies due to the limited applicability of single heating rate data, whereas, the model-free approach based on multi-heating rates and isoconversional data is more helpful in the study of kinetic parameters (19, 27-28).

The most used methods mentioned in previous publications to calculate the kinetic parameters are Ozawa-Flynn-Wall (OFW), Kissinger, Kissinger-Akahira-Sunose (KAS), and Starink (15, 26, 29). The OFW provides the lowest accuracy because it is based on a crude approximation, while the others could give more accurate kinetic parameters [26]. The Kissinger method was used previously to study thermal degradation kinetics of liquefied residues [12]. It is also recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) for conducting kinetics computation on thermal analysis data [16]. In the present study, the classic Kissinger method was only considered to be used as the computational method to calculate the activation energy and the pre-exponential factor by plotting \( \ln(\beta/T_i^2) \) against \( 1/T_i \) for different liquefaction conditions or different pyrolysis conversions (\( \alpha \)). The \( E_\alpha \) and \( A_\alpha \) can be obtained from the slope and intercept of a straight line [30].

3.3. RESULTS AND DISCUSSION

3.3.1. Thermal Decomposition Characteristics

The thermogravimetry/derivative thermogravimetric analysis (TG/DTG) curves of the raw rape straw and liquefied residues are shown in Figure 3.2 and Figure 3.3. The first stage of mass loss (<150°C) was attributed to the removal of absorbed moisture and light volatile components. After this peak, the DTG cure of raw rape straw showed three decomposition regimes: (1) the first decomposition shoulder peak at about 180-275 °C was attributed to thermal depolymerization
of hemicelluloses or pectin; (2) the primary decomposition peak in the temperature range of 280-390 °C corresponded to cellulose decomposition [21]; (3) peak from 410 to 585 °C corresponded to lignin degradation [9]. As compared with raw rape straw, liquefied residues lacked the shoulder peak corresponding to the hemicellulose decomposition. This was explained by the removal of hemicellulose at the initial liquefaction stage because it is the most susceptive to liquefaction among the main chemical components of fiber cell wall [22]. Furthermore, all of the liquefied residues had lower maximum decomposition temperatures, as indicated from the shift of major DTG peaks to lower temperature in comparison with raw material, suggesting that liquefied residues have higher reactivity. Although lignin is susceptive to liquefaction and decompose easily during liquefaction [22], the DTG cure of liquefied residue from 140 °C/15 min presented a broad function peak of lignin at around 520 °C. This suggested that a little lignin remained in the liquefied residue.
Figure 3.2. TG curves of rape straw and liquefied residues from different liquefaction conditions at the heating rate of 5 °C min\(^{-1}\) (a), 20 °C min\(^{-1}\) (b), and 50 °C min\(^{-1}\) (c) 
(1: rape straw; 2: 140 °C/15 min; 3: 160 °C/15 min; 4: 180 °C/7.5 min; 5: 180 °C/10 min; 6: 180 °C/15 min)
Figure 3.3. DTG curves of rape straw and liquefied residues from different liquefaction conditions at the heating rate of 5 °C min⁻¹ (a), 20 °C min⁻¹ (b), and 50 °C min⁻¹ (c)
(1: rape straw; 2: 140 °C/15 min; 3: 160 °C/15 min; 4: 180 °C/7.5 min; 5: 180 °C/10 min; 6: 180 °C/15 min)
Unlike the raw rape straw, the liquefied residues were observed to have a shoulder at about 350°C, which is attributed to the degradation of α-cellulose [31], except for the one from 180 °C/15 min. There were a few of peaks (around 740°C) presented on the DTG curves of the liquefied residues, but that from 180 °C/15 min. Those peaks might be attributed to the decomposition of charred residues. It could be the result of the breakdown of C-C and C-H bonds of the char [32]. A similar result was reported by Ceylan et al. [11]. This result suggested that the char obtained from 180 °C/15 min has the highest thermal stability under a high temperature (>700°C). This was further evidenced by the higher char content in comparison with the ones from other liquefaction conditions. With the increasing of liquefaction temperature and time, the char at 770 °C, obtained from liquefied residue, increased remarkably regardless of the heating rate (Table 3.2). One possible reason was that the formation of insoluble substances at severe liquefaction conditions increased the thermal stability. It was demonstrated that the insoluble substance mainly consisted of humins and unreacted cellulose [33], or
recondensation/repolymerization resultant of hemicellulose and lignin fragments [12]. The formation of insoluble substances also resulted in the increasing liquefied residue content, as shown in Table 3.1. Generally, the char content increased with the increasing of heating rate. It was attributed to the low thermal transfer efficiency at a high heating rate. This result was in agreement with a previous report [12]. A unique mass loss peak of liquefied residue at about 420 °C was observed from 180 °C/15 min. This might be attributable to the decomposition of a high degree of cellulose crystallinity. The removal of non-cellulose components during liquefaction could enhance the crystallinity index of cellulose and increase its thermal stability [6].

Table 3.2. Thermal parameters of rape straw and liquefied residues obtained from TG analysis

<table>
<thead>
<tr>
<th>Liquefaction residues</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Peak temperature (K)</th>
<th>Maximum decomposition rate (μg min⁻¹)</th>
<th>Char (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
<td>565.92</td>
<td>4.24</td>
<td>8.16</td>
</tr>
<tr>
<td>Rape straw</td>
<td>20</td>
<td>581.28</td>
<td>18.04</td>
<td>7.02</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>595.37</td>
<td>33.06</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>531.09</td>
<td>5.31</td>
<td>0.71</td>
</tr>
<tr>
<td>140 °C/15 min</td>
<td>20</td>
<td>545.77</td>
<td>31.04</td>
<td>16.38</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>565.49</td>
<td>55.60</td>
<td>10.37</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>535.34</td>
<td>5.34</td>
<td>14.64</td>
</tr>
<tr>
<td>160 °C/15 min</td>
<td>20</td>
<td>551.5</td>
<td>31.93</td>
<td>20.68</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>569.13</td>
<td>50.37</td>
<td>22.11</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>527.92</td>
<td>4.23</td>
<td>19.60</td>
</tr>
<tr>
<td>180 °C/7.5 min</td>
<td>20</td>
<td>552.80</td>
<td>28.16</td>
<td>28.65</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>564.02</td>
<td>43.96</td>
<td>31.34</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>518.96</td>
<td>2.32</td>
<td>30.08</td>
</tr>
<tr>
<td>180 °C/10 min</td>
<td>20</td>
<td>543.14</td>
<td>19.28</td>
<td>36.39</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>555.05</td>
<td>31.46</td>
<td>39.53</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>666.92</td>
<td>0.81</td>
<td>54.51</td>
</tr>
<tr>
<td>180 °C/15 min</td>
<td>20</td>
<td>682.69</td>
<td>4.24</td>
<td>65.16</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>705.17</td>
<td>7.97</td>
<td>56.73</td>
</tr>
</tbody>
</table>

The maximum thermal decomposition rate and temperature somewhat decreased with the increase in liquefaction temperature and time. It was related to the difference of chemical components among liquefied residues. The decomposition of hemicellulose and lignin at the
initial liquefaction stage contributed to the decreasing of the maximum decomposition rate and temperature. As can be seen in Table 3.2, the maximum decomposition temperatures shifted to higher temperature zones when increasing the heating rate from 5 to 50 °C min\(^{-1}\). The temperature resistance time in the samples shortened as the heating rate was increased, resulting in the retard of decomposition temperature [32]. Furthermore, the pool thermal conductivity of lignocellulosic biomass leads to a pool heat transfer [34]. The maximum thermal decomposition rate was also increased with the increase of heating rate. Ceylan and Topçu reported that the formation of volatile matter during hazelnut husk pyrolysis was slightly affected by increasing heating rate [11]. Additionally, a higher heating rate would increase the activation energy for hemicellulose and cellulose, and decrease that for lignin [8].

3.3.2. Non-Isothermal Thermogravimetric Kinetics

The kinetic analysis parameters of raw rape straw and liquefied residues were determined by the Kissinger method in Eq. 3.9 (Table 3.3). Figure 3.4 depicted the linear regression of \(\ln(\beta/T_\text{i}^2)\) versus \(1/T_\text{i}\). Three maximum decomposition rate temperatures from DTG profiles corresponding to three heating rates were fitted to determine activation energy and pre-exponential factor. This approach has proven to be an effective way to calculate the thermal degradation kinetic parameters from various materials [12]. Since the kinetic parameters were calculated from the maximum decomposition temperatures, the peak of lignin at around 520 °C observed from the DTG cure of liquefied residue from 140 °C/15 min would not affect the results of activation energy and pre-exponential factor. The coefficients \((R^2)\) corresponded to linear regression in Figure 3.4 was in the range of 0.955-0.993.
Figure 3.4. Kissinger plots of rape straw and liquefied residues
(1: rape straw; 2: 140 °C/15 min; 3: 160 °C/15 min; 4: 180 °C/7.5 min; 5: 180 °C/10 min; 6: 180 °C/15 min)

Table 3.3. The activation energy ($E_a$), pre-exponential factor ($\ln A_a$) and coefficients ($R^2$) of rape straw and liquefied residues obtained by the Kissinger method

<table>
<thead>
<tr>
<th>Liquefaction parameters</th>
<th>Fitted equation</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\ln A_a$ (lnmin$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rape straw</td>
<td>$y=33.63-25266.70x$</td>
<td>210.07</td>
<td>36.86</td>
<td>0.9933</td>
</tr>
<tr>
<td>140 °C/15 min</td>
<td>$y=24.52-18759.21x$</td>
<td>155.96</td>
<td>27.45</td>
<td>0.9625</td>
</tr>
<tr>
<td>160 °C/15 min</td>
<td>$y=25.82-19643.14x$</td>
<td>163.31</td>
<td>28.80</td>
<td>0.9826</td>
</tr>
<tr>
<td>180 °C/7.5 min</td>
<td>$y=22.01-17409.75x$</td>
<td>144.74</td>
<td>24.86</td>
<td>0.9858</td>
</tr>
<tr>
<td>180 °C/10 min</td>
<td>$y=21.73-16978.72x$</td>
<td>140.91</td>
<td>24.56</td>
<td>0.9904</td>
</tr>
<tr>
<td>180 °C/15 min</td>
<td>$y=28.42-26448.53x$</td>
<td>219.89</td>
<td>31.69</td>
<td>0.9551</td>
</tr>
</tbody>
</table>

A reaction with higher $E_a$ requires a higher energy to break down chemical bonds and results in a slower reaction [34]. As presented in Table 3.3, the $E_a$ of raw rape straw was higher than those for liquefied residues except for 180 °C/15 min. The $E_a$ of liquefied residues increased slightly at first from 155.96 to 163.31 kJ mol$^{-1}$ with the increasing of temperature from 140 to 160 °C for 15 min, and then decreased to 140.91 kJ/mol as the liquefaction condition was changed to 180°C/10 min. Finally, the $E_a$ for 180 °C/15 min noticeably increased to 219.89 kJ
mol\(^{-1}\). This suggests that liquefying residue at 180 °C/10 min is preferable over other liquefaction conditions, because it requires the lowest activation energy.

The decomposition of hemicellulose, lignin and cellulose during liquefaction undermined the thermal stability of liquefied residues, thus the \(E_a\) of liquefied residues reduced as compared with raw rape straw. In contrast, the recondensation/repolymerization reaction occurring at 180 °C/15 min enhanced the thermal stability and hence increased the \(E_a\). Therefore, the increasing of \(E_a\) from 140 to 160 °C for 15 min was attributed to the rapid decomposition of hemicellulose and lignin that resulted in a relatively increasing cellulose content with high thermal stability. The pre-exponential factor had a similar variation pattern with apparent activation energy, ranging from 24.56 to 36.86 min\(^{-1}\).

Since the liquefaction condition of 180 °C/10 min provided the maximum liquefaction conversion yield with lowest content of liquefied residue and the minimum \(E_a\), it was used as an optimal liquefaction condition to further investigate the pyrolysis properties of liquefied residues with conversion. It was worth mentioning that there was little or no correlation between \(\ln(\beta/T_i^2)\) and \(1/T_i\) when the pyrolysis conversion was less than 0.15 and greater than 0.55, in this study. The lack of correlation would introduce an erroneous interpretation of the phenomena. The linear regression lines are shown in Figure 3.5, and the pyrolysis properties are presented in Table 3.4. The coefficients varied from 0.956 to 0.996 and the value of apparent activation energy was highly dependent upon conversion. The \(E_a\) gradually increased from 142.06 to 212.27 kJ mol\(^{-1}\) with the increasing of conversion from 0.15 to 0.45, and then remarkably increased to 540.95 kJ mol\(^{-1}\) as the conversion reached to 0.55. It implied that the pyrolysis of liquefied residue was a complex process consisting of different degradation mechanism with pyrolysis conversion. The
lnA\textsubscript{\alpha} increased with the increasing of conversion from 0.15 to 0.55, varying from 25.41 to 107.45 lnmin\textsuperscript{-1}.

Figure 3.5. Kissinger plots of liquefied residue from reaction condition of 180 °C/10 min at different pyrolysis conversion

Table 3.4. The $E\textsubscript{\alpha}$, ln$A\textsubscript{\alpha}$ and coefficients ($R^2$) of liquefied residues from liquefaction condition of 180 °C/10 min obtained by the Kissinger method

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Fitted equation</th>
<th>$E\textsubscript{\alpha}$ (kJ mol\textsuperscript{-1})</th>
<th>ln$A\textsubscript{\alpha}$ (lnmin\textsuperscript{-1})</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>$y=22.27-17087.40x$</td>
<td>142.06</td>
<td>25.41</td>
<td>0.9560</td>
</tr>
<tr>
<td>0.20</td>
<td>$y=24.46-18293.92x$</td>
<td>152.10</td>
<td>27.36</td>
<td>0.9619</td>
</tr>
<tr>
<td>0.25</td>
<td>$y=25.76-19174.69x$</td>
<td>159.42</td>
<td>28.71</td>
<td>0.9723</td>
</tr>
<tr>
<td>0.30</td>
<td>$y=27.11-20073.86x$</td>
<td>166.89</td>
<td>30.11</td>
<td>0.9762</td>
</tr>
<tr>
<td>0.35</td>
<td>$y=28.67-21092.99x$</td>
<td>175.37</td>
<td>31.72</td>
<td>0.9825</td>
</tr>
<tr>
<td>0.40</td>
<td>$y=31.44-22796.72x$</td>
<td>189.53</td>
<td>34.56</td>
<td>0.9870</td>
</tr>
<tr>
<td>0.45</td>
<td>$y=36.04-25585.56x$</td>
<td>212.72</td>
<td>39.28</td>
<td>0.9907</td>
</tr>
<tr>
<td>0.50</td>
<td>$y=49.04-33229.73x$</td>
<td>276.27</td>
<td>52.54</td>
<td>0.9946</td>
</tr>
<tr>
<td>0.55</td>
<td>$y=103.27-65064.76x$</td>
<td>540.95</td>
<td>107.45</td>
<td>0.9960</td>
</tr>
</tbody>
</table>

3.4. CONCLUSIONS

Thermogravimetric analysis of raw rape straw and liquefied residues indicated that the primary decomposition occurred in the temperature range of 280-390 °C. The hemicellulose decomposition peak was absent at the DTG curves of liquefied residues. The liquefied residue
from 180 °C/15 min had the highest thermal stability under a high temperature (>700 °C) condition among all liquefied residues. The maximum decomposition temperatures of liquefied residues shifted to higher temperature zones as the heating rate increased from 5 to 50 °C mol⁻¹. It suggested that the decomposition processes were delayed with increasing heating rate. The rapid decomposition of hemicellulose and lignin during liquefaction contributed to the decrease of activation energy ($E_a$), whereas the recondensation/repolymerization reaction occurring at 180 °C/15 min remarkably increased $E_a$. The lowest $E_a$ was found in the liquefied residue from 180 °C/10 min. A noticeable increase in $E_a$ was observed in the liquefied residue from the 180 °C/10 min condition with pyrolysis conversion, which suggested a complex decomposition process with the increasing of pyrolysis temperature.

3.5. REFERENCES


CHAPTER 4. DILUTE ALKALI AND HYDROGEN PEROXIDE TREATMENT OF MICROWAVE LIQUEFIED RAPE STRAW RESIDUE FOR THE EXTRACTION OF CELLULOSE NANOCRYSTALS (CNCS)

4.1. INTRODUCTION

Nanocellulose has high reinforcing capabilities because of their unique characteristics including high tensile strength, high Young’s modulus, high flexibility, and low coefficient of thermal expansion [1-4]. Previous studies have confirmed that agro-wastes such as cotton stalks [5], soybean hulls [6], rice straw [7], banana peel [8], and wheat straw [9] are important sources for the isolation of nanocellulose. As an agro-waste from edible oil industry, large quantities of rape straw are annually produced, particularly in China. Though, value-added products such as composites [10], bioethanol [11], and bio-oil [12] have been produced from rape straw, no work has been reported on the isolation of CNCs from rape straw.

The plant cell wall is composed by cellulose and non-cellulose such as hemicelluloses, lignin, pectin, and inorganic substance [13]. In the native cellulose fiber, individual CNCs are bonded by intermolecular forces and hydrogen bonds to each other [14]. The isolation of CNCs involves pretreatment to remove non-cellulose components, followed by fibrillation of the bundles of microfibrils. Concentrated sodium hydroxide (NaOH) and sulfuric acid combining with acidified sodium chlorite (NaClO₂) are the most commonly used pretreatment method to purify cellulose from plants [15-16]. High intensity ultrasonication has been widely applied to fibrillate CNCs due to its high efficiency to separate the fibrils from purified cellulose [1-2].

Despite the successful isolation of CNCs from plant cell by the aforementioned processes, there are still problems such as long treatment time and environmental pollution because of the use of concentrated alkali or acid and the acidified sodium chlorite. In our previous studies, microwave-assisted liquefaction was applied in selectively liquefying non-cellulose components in bamboo to extract holocellulose fibers and nanofibers [16-18]. This is because microwave-assisted liquefaction catalyzed by acid could remarkably eliminate lignin and hemicelluloses with a high cellulose content retaining in the liquefied residue. After liquefaction with mild conditions, the residues were almost composed of cellulose; even with severe conditions, the residues still exhibited a cellulose structure, which suggests a potential to extract CNCs from liquefied residues. Hydrogen peroxide (H$_2$O$_2$), having been commonly applied for pulp bleaching, is a potential alternative for sodium chlorite because of its zero pollution. The HOO-group generated from H$_2$O$_2$ is the main oxygen compound for degrading lignin by reacting with quinine structures, double bonds or carbonyl group in lignin, forming the soluble fragments of lignin [19-20]. As reported in previous study, alkaline hydrogen peroxide is an interesting alternative chlorine-free method to extract nanocrystalline cellulose from agro-residue [21].

Thus, the objective of the study is to use dilute alkali and hydrogen peroxide to purify the microwave liquefied rape straw residues in order to achieve an efficient approach for the extraction of CNCs from liquefied residues. The liquefied residue from a proper liquefaction reaction was collected and characterized for further usage. The dilute sodium hydroxide (2%) and hydrogen peroxide (5%) were employed in the purification treatment. The chemical treated samples were then subjected to high-intensity ultrasonication for nanofibrillation. The extracted nanocrystals as well as samples from each stage in the whole process were characterized. This
study will provide a more environmental friendly approach for the isolation of nanocrystals and the integrated utilizations of rape straws.

4.2. MATERIALS AND METHODS

4.2.1. Materials and Chemicals

The rape straw was collected in Sichuan Province, China, air dried and ground into 20-40 mesh and then oven dried at 105°C until constant weight. All chemicals, including sulfuric acid (H$_2$SO$_4$), sodium hydroxide (NaOH), and 30% hydrogen peroxide (H$_2$O$_2$), were purchased from commercial sources without further purification.

4.2.2. Microwave Liquefaction

Liquefaction of rape straw was performed in a Milestone (Shelton, CT) MEGA laboratory microwave oven equipped with an ATC-400FO automatic fiber optic temperature control system. A typical run was carried out with the loading of 2 g of rape straw, 12 g of methanol, and 0.36 g of sulfuric acid. The mixed reactants were sealed in 100 mL Teflon reaction vessels with a magnetic stirring bar. The output power of the microwave energy was auto-adjusted based on the temperature feedback from the sensor under maximum power of 700 W. The sealed vessels were subjected to microwaves irradiation. The reaction temperature was increased from room temperature to the desired temperature (i.e. 140°C, 160°C and 180°C) within 5 min, and then maintained for 0 to 10 min. The ice bath was applied to quench the reaction when the reaction is finished. After cooling, the liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper to separate liquid and solid residue. The liquid portion was evaporated at 65°C under vacuum to remove methanol. The gaseous products were vented because the yield of gaseous products was negligible. The residue
remained on the filter paper was oven-dried and weighted for the calculation of liquefied residue content as the following Eq. 4.1.

\[
\text{Liquefied residue content (\%) } = \frac{\text{weight of residue}}{\text{weight of raw rape straw}} \times 100
\]  

4.1

The liquefied residue contents from various reactions are presented in Figure 4.1.

![Figure 4.1. Liquefied residue contents with respect to liquefaction temperature and time (Other conditions: methanol/rapeseed straw, 6/1; sulfuric acid, 3%).](image)

4.2.3. Extraction of CNCs from Liquefied Residue

The liquefied residue was added into 2% (w/v) NaOH solution with a solid to solvent ratio of 1:30 and maintained at 75°C for 1 h with constant stirring. The reaction was terminated by quenching with 10-fold ice water and the solution was centrifuged (6000 rpm at 5°C for 15 min) to collect the sediment. The sediment was vacuum-filtered and washed with distilled water until its pH was neutral. The solid remained on the filter paper was bleached by 5% H₂O₂ (solid/solvent, 1:30) at 75°C for 2.5 h, followed by centrifugation and vacuum-filtration. The bleaching treatment was conducted twice. The chemical treatments were used to remove the
phenolic compounds and eliminate traces of non-cellulosic components. The hydrogen peroxide could also partially hydrolyze the amorphous cellulose.

The bleached sample was soaked in deionized water (concentration 0.05 %) and subjected to ultrasonic fibrillation by high-intensity ultrasonic processor equipped with a cylindrical titanium alloy probe with a diameter of 15 mm. The process was performed at a frequency of 25 kHz with an output power of 750 W at 60% amplitude for 15 min. The ultrasonic treatment was carried out in ice bath throughout the process. The suspension obtained after ultrasonic treatment was centrifuged at rotate speed of 10000 rpm for 15 min at 5°C.

4.2.4. Characterization of Solid Residue and CNCs

4.2.4.1. SEM

A scanning electron microscope (SEM, JSM-6610 with 5-15 kV accelerating voltage) was used to examine the morphology of the samples. Test samples were prepared for SEM inspection by coating gold using a vacuum sputter coater before subjected to the SEM analysis.

4.2.4.2. FT-IR

Fourier transform infrared spectrometry (FT-IR) was used to study the chemical structure. The FT-IR analysis was performed on a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MK II Single Reflection ATR accessory. A small quantity of sample was covered flatwise on the detection window. Each sample was analyzed in the range of resolution from 400 to 4000 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\) and total of 32 scans were collected.

4.2.4.3. XRD

The X-ray diffraction pattern was measured using Bruker/Siemens D5000 X-ray automated powder X-ray diffractometer (Siemens Co., Wittelsbacherplatz, Munich, Germany) at ambient
The detections were performed at a scan speed of 0.2°/min over the 2θ from 5 to 40° with Cu-Ka radiation (λ=1.54 Å) at 45 kV and 40 mA.

4.2.4.4. TEM

The morphology of CNCs was evaluated using transmission electron microscopy (TEM, JEOL 100CX, JEOL, Inc., Peabody, MA, USA) with an accelerating voltage of 80 kV. A droplet of diluted CNCs suspension was deposited on glow-discharged thin carbon-coated copper grids. The diameters of the CNCs were calculated form TEM images using microscope image analysis system (Image J) by randomly measuring 100 fibers.

4.2.4.5. TG

The thermogravimetric and differential thermogravimetric (TG/DTG) analysis was conducted with a thermal analyzer Q50 TGA (TA Instruments, New Castle, DE) to simultaneously obtain thermogravimetric data. Each sample about 2 mg was conducted at 25 to 800°C with constant heating rate of 20°C/min under a flow of 60 mL/min of nitrogen atmosphere.

4.3. RESULTS AND DISCUSSION

4.3.1. Characterization of Liquefied Residues

4.3.1.1. FT-IR Spectra of Liquefied Residues

The FT-IR spectra of the raw rape straw and the liquefied residues from various liquefaction parameters are shown in Figure 4.2. The intensity of the broad peaks at around 3330 cm⁻¹ owing to the –OH stretching vibration [22], varied with respect to the liquefaction conditions, revealing the release of hydroxyl groups as the liquefaction parameter was maintained at 180°C/10 min (Figure. 4.2e). By prolonging the reaction time, the content of hydroxyl groups was significantly reduced as indicated by the low intensity peak at 3330 cm⁻¹. The prominent peaks at 1735 cm⁻¹ was due to either the vibrations of acetyl and uronic ester groups in hemicelluloses or ester
linkage of carboxylic group of the ferulic and p-coumaric acids of lignin and/or hemicelluloses [23]. It almost disappeared on the spectra of the liquefied residue from 160°C for 15 min (Figure. 4.2c). This result indicated the decomposition of hemicelluloses and lignin by breaking the carboxylic and ester bonds, rather than the disappearing of hemicelluloses and lignin [24]. However, it was intensified again in the spectra of residues from 180°C/10 min. One possibility for the re-presence of the peak at 1735 cm\(^{-1}\) was the esterification of the liquefied fragments.

![Figure 4.2. FT-IR transmittances of liquefied residues from different liquefactions: (a) raw rape straw; (b) 140°C/15 min; (c) 160°C/15 min; (d) 180°C/7.5 min; (e) 180°C/10 min; (f) 180°C/15 min (Other conditions: methanol/rape straw, 6/1; sulfuric acid, 3%)](image)

As shown in Figure 4.2, the peaks at 1596 and 1506 cm\(^{-1}\) corresponding to C=C skeletal vibration in aromatic rings, 1456 cm\(^{-1}\) arising from the C-H bending, the band at 829 cm\(^{-1}\) assigned to two adjacent hydrogen atoms on the benzene ring [24] and the absorbance at 1230 cm\(^{-1}\) assigned to vibration of guaiacyl ring were from lignin [25]. Those characteristic peaks of lignin decreased as the reaction prolonged, indicating that the degradation of lignin increased. However, the peaks at 1596, 1506 and 1456 cm\(^{-1}\) became intensive at 180°C/15 min.
The peak at 1370 cm\(^{-1}\) attributing to phenolic OH groups [26], remarkably increased as the temperature increased to 180°C for 7.5 min (Figure 4.2d), then rapidly decreased and disappeared with prolonging the reaction time (180°C/15 min) (Figure 4.2f).

The absorbance band at 1420 cm\(^{-1}\) arising from C-H\(_2\) symmetric bending, the band at 1162 cm\(^{-1}\) due to C-O-C asymmetric stretching, 1320 cm\(^{-1}\) assigned to CH\(_2\) rocking vibration, the bands at 1108 and 1050 cm\(^{-1}\) corresponding to C-O stretching, the C-O-C band at 1020 cm\(^{-1}\), and the CH deformation at 899 cm\(^{-1}\) were attributed to cellulose components [24,27]. Those bands became intensive at temperature of 180°C with less than 10 min, while the intensity significantly decreased with increasing the time. This was because liquefaction enhanced the intensity of the cellulose bands by decomposing the lignin and hemicelluloses before temperature of 180°C for 7.5 min, then cellulose begin to decompose resulting the decreasing or absence of its functional groups.

Specially, sulfate ester groups as evidenced by the bands at 1197 cm\(^{-1}\) corresponding to S=O vibration were introduced to the liquefied residue during the liquefaction due to the use of sulfuric acid as the catalyst [28].

4.3.1.2. SEM Images of Liquefied Residues

The microstructure of the samples was characterized by SEM images (Figure 4.3). The SEM images evidenced the gradual removal of cementing materials around the fiber bundles such as hemicelluloses, lignin, and pectin by liquefaction. Very well-organized fiber bundles were observed on the images of the raw rape straw, which had a tough surface with many fragments (Figure 4.3a). The mean diameter for the raw rape straw was around 246 ± 120.39 µm. As can be seen from Figure 4.3b, the bundles were reduced into small fiber bundles coupling with 2-3 single fibers at 140°C for 15 min, indicating the lignin in the middle lamella was
partially removed. When elevating the temperature to 160°C for 15 min (Figure 4.3c), small fiber bundles were broken down to small irregular fragments. Figure 4.3d (180°C/7.5 min) showed the significant effect of temperature on the liquefaction extent by presenting a relatively homogeneous texture and a huge surface exposed the multilayer structure of single fiber wall, which was caused by the collapse of compact structure of the fiber. The significant influence of time was confirmed by Figure 4.3e, which presents many uneven-sized spherical granule substances (2.26 ± 0.64 µm) on the surface. Generally, granule substance was ascribed to recondensed hemicelluloses/lignin derivatives. Besides, it may also attribute to the side-reaction by-product of acid-catalyzed hydrolysis of cellulose into levulinic acid [29]. Since the granule substance consisted mainly by humins and some unreacted cellulose [29], the yield of cellulose nanocrystals was speculated to be decreased by side-reaction. As the liquefaction prolonged to 15 min (180°C, Figure 4.3f), abundant of aggregate spherical granules with diameter of 3.42 ± 0.88 µm were formed. It was proposed that a somewhat carbonization reaction of sugar derivatives occurred.
Figure 4.3. SEM images of liquefied residues from different liquefactions and chemical treatments: (a) raw rape straw; (b) 140°C/15 min; (c) 160°C/15 min; (d) 180°C/7.5 min; (e) 180°C/10 min; (f) 180°C/15 min; (g) 2% NaOH for 1 h; (h) 5% H₂O₂ for 5 h
(Other liquefaction conditions: methanol/rape straw, 6/1; sulfuric acid, 3%)
4.3.2. Extraction of CNCs from Liquefied Residue

The liquefied residue with content of 23.44% from 180°C/7.5 min was used as raw material for the extraction of CNCs because the rape straw residue content was proper and still showed cellulosic structures as indicated by the FT-IR spectra and the SEM images. Chemical treatments were used to purify the residue for the extraction of CNCs. As compared with conventional liquefaction, microwave-assisted liquefaction could save more than 85% energy consumption [17], indicating that microwave heating has an energy advantage in liquefaction. By the referenced method [17], the energy consumption of rape straw liquefaction at 180°C for 7.5 min was $1.66 \times 10^5$ J (heating power of 378 W for 300 s plus maintaining power of 351 W for 150 s).

Figure 4.3g clearly shows that the spherical granules were exposed on the surface of the alkali treated samples, and the fibers became irregular and were much rougher in comparison with the liquefied residue. This is because of the removal of hemicelluloses. Generally, alkali can penetrate the inter-fiber region and cleave the $\alpha$-ether bonds between lignin and hemicelluloses, resulting in the removal of hemicelluloses and other impurities such as soluble lignin, pectin, and proteins [30-31]. The absence of band at 1735 cm$^{-1}$ on the FT-IR spectrum of the alkali treated residue gave the evidence that the retained hemicelluloses in the liquefied residue had been completely removed by the alkali treatment (Figure 4.4b). Furthermore, the weaker absorption at 1230 cm$^{-1}$ of alkali treated sample implied that most of the lignin in liquefied residue had been removed by treatment of 2% NaOH. With the removal of hemicelluloses and most of lignin, the purity of cellulose was enhanced remarkably, which was also reflected in the intensifying of the functional peak of absorbed water molecules at 1635 cm$^{-1}$ [32].
However, the dark-brown color of the liquefied residue remained unchanged after alkali treatment, suggesting that lignin fragments or carboxyl compounds introduced in the liquefaction process still existed, which formed a bridging bond with cellulose ester that prevents the separation of cellulose into individual fiber. Thus, it’s necessary to bleach the alkali treated sample for further purification. Hydrogen peroxide (5%) was used to bleach the alkali treated residue by eliminating the non-cellulose components. The surface and accessibility of cellulose were significantly increased with presenting an even, smooth, and flat surface (Figure 4.3h). The application of \( \text{H}_2\text{O}_2 \) promoted the lignin removal and carboxyl compounds elimination indicated by the color changing from dark brown to pure. This is mainly because the oxidation reaction between \( \text{H}_2\text{O}_2 \) and lignin fragments or carboxyl compounds would enhance the degradation of lignin [19-20].

The removal of non-cellulose components with 2% NaOH and 5% \( \text{H}_2\text{O}_2 \) treatments contributed to the increase of sulphate ester band intensity at 1197 \( \text{cm}^{-1} \) (Figure 4.4b; c). Two
absorption peaks at 1020 cm\(^{-1}\) and 894 cm\(^{-1}\) were observed in all the spectra which represented the typical structure of cellulose. They are attributed to C-O-C stretching vibrations and C-H deformation of cellulose, respectively, and confirmed the presence of cellulose in all samples [24]. After chemical treatments, only 26.27% of the liquefied residue was remained, suggesting that the liquefied residue contained a large amount of non-cellulose components. 39.42% of the non-cellulose components in the liquefied residue were removed first by 2% NaOH, and then 56.63% of the alkali treated residue was bleached by 5% H\(_2\)O\(_2\). This result also confirmed that the combination of alkali and hydrogen peroxide were efficient in eliminating the non-cellulosic compounds in the liquefied rape straws residues.

The purified samples were subjected to ultrasonic nanofibrillation process, and 80.56% of the purified samples were defibrillated into nanocrystals by ultrasonic treatment for 15 min. This result demonstrated that the ultrasonic was strong enough to defibrillate the chemical purified liquefied residue into nanocrystals. This was attributed to the ultrasonic treatment can break the hydrogen bonds and disintegrate microfibers into nanofibrils. Figure 4.4d elucidated that the chemical structure was not affected by the ultrasonic nanofibrillation process. Similar result was also observed on isolation of cellulose nanocrystals from banana peel using high-intensity ultrasonication [8].

As shown in the X-ray diffraction patterns of raw rape straw and the liquefied residue from 180°C/7.5min, the chemical purified cellulose and the nanocrystals obtained by ultrasonic treated for 15 min, all specimens exhibited diffractograms typical of cellulose I, with the main peaks at \(2\theta = 16.2^\circ, 22.5^\circ \) and \(34.5^\circ \) (Figure 4.5) [33]. This result indicated that the crystal structure of cellulose did not change during liquefaction, chemical and ultrasonic treatments. Those sharp peaks in the spectrum of liquefied residue (Figure 4.5b) were formed by the mineral matter such
as calcium sulfate and quartz. The result was in accordance with the liquefaction of corn stover [34]. The calcium sulfate was generated by the reaction of sulfuric acid and calcium oxide that is main components in ashes [35], beyond that, other sulphate crystals such as K$_2$SO$_4$ and Na$_2$SO$_4$ were formed during liquefaction [34]. In general, the quartz in the liquefied residue is derived from the naturally present SiO$_2$ in rape straw. Through most of hemicelluloses and lignin were removed after liquefaction, the main cellulose crystalline intensities at $2\theta = 16.2^o$ and $22.5^o$ were weakened in comparison with raw rape straw. One possible reason was that the recondensed lignin still be a highly amorphous polymer and remained in liquefied residue, resulting in a decline of crystallinity degree [36].

![Figure 4.5. X-ray diffraction patterns of residues from different treatments: (a) raw rape straw; (b) 180°C/7.5min; (c) 2% NaOH for 1 h; (d) 5% H$_2$O$_2$ for 5 h (e) ultrasonication for 15 min](image-url)
4.3.3. Characterization of CNCs

4.3.3.1. TEM Images of CNCs

The TEM images as shown in Figure 4.6 confirmed the existence of the CNCs. As shown in Figure 4.6a, individualized long fiber-like nanocrystals were observed. The diameter of the nanocrystals was 12.59 ± 6.08 nm. Meanwhile, opening up fiber-bundle was also observed in the TEM image, revealing that ultrasonic treatment did not completely separate the nanocrystals bundles (Figure 4.6b). Agglomeration of the individual nanocrystals was also found (Figure 4.6c). It might be resulted from the drying process of the suspension during the TEM observations, while no agglomeration was observed in the aqueous suspension was found even after quiescence for 72 h at 5°C. This may be attributed to the introduction of sulphate ester groups during the liquefaction (confirmed by FT-IR spectra), which could provide negative electrostatic layer on the nanocrystals surface resulting in stable colloidal suspensions [37]. Moreover, intense mechanical forces of water also enhance the dispersibility of nanocrystals in aqueous suspension [33]. Almost 40% of the nanocrystals had a diameter within range of 5-10 nm, nearly 54% of the nanocrystals had diameter between 10-25 nm, and only 7% of the nanocrystals had diameters higher than 25 nm or less than 10 nm (Figure 4.6d). Additionally, some granule substances were observed in the TEM image (Figure 4.6c). One plausible explain for this result was the micron-grade granule substances as presented in the above mentioned SEM images were also reduced into nano-scale spheres with diameter around 14.48 ± 4.92 nm by high-intensity ultrasonic waves, which provided strong mechanical oscillating power by producing violent shock within cavitation bubbles and the immediate surrounding area [2].
4.3.3.2. TG and DTG Cures

Thermogravimetric (TG) and differential thermogravimetric (DTG) cures of raw rape straw, liquefied residue (180°C/7.5 min), 2% NaOH treated, 5% H₂O₂ treated and ultrasonic treated samples were shown in Figure 4.7. A slight weight loss in the region of 40-120°C was due to the evaporation of the humidity of materials or the low molecular weight compounds [33]. Compared with raw rape straw, the liquefied residue was more susceptible to thermal decomposition and higher weight loss at relatively low temperature as shown in DTG curves. This is attributable to lignin, having a relatively thermal stability in comparison with hemicelluloses and cellulose, had been degraded during liquefaction [37]. Furthermore, for the liquefied residue, a weak weight loss peak was observed at 355°C in DTG cure, which was corresponded to the degradation of α-cellulose [39]. Moreover, it’s interesting to note that an
apparent decomposition peak in the liquefied residue TG cure occurred at 733.3°C, which might be attributed to degradation of granule substances that formed during liquefaction.

Figure 4.7. TG and DTG curves of residues from different treatments: (a) raw rape straw; (b) 180°C/7.5 min; (d) 5% H₂O₂ for 5 h (d) ultrasonication for 15 min
The maximum weight loss temperatures of the chemical treated and the ultrasonic treated samples occurred at 338.0 and 376.5°C, respectively. Compared with the chemical treated samples, the nanocrystals had higher weight loss temperature and lower weight loss rate, which indicated that the ultrasonic treatment could enhance the thermal stability of nanocrystals. The liquefied residue had the maximum char yield (21.46%) followed by chemical treated samples (9.63%). This variation pattern was attributed to the removal of non-cellulose during chemical treatments. Generally, the nanocrystals have minimum residue weight, because of the absence of non-organic components in the nanocrystals [15]. However, in this work, the minimum residual weight (4.61%) was observed from raw rape straw, rather than nanocrystals (6.82%). This was possible associated with the presence of nano-scale granule substances in CNCs. The high thermal stability of nanocrystals isolated from rape straw could expand its applicability for bio-composites.

4.4. CONCLUSIONS

Cellulose nanocrystals (CNCs) were successfully extracted from liquefied residues through treatments of dilute alkali and hydrogen peroxide combining high-intensity ultrasonication. Most of lignin and hemicelluloses in the liquefied residues from 180°C/7.5 min were removed during the liquefaction, resulting in cellulose as core structure, which was confirmed by the FT-IR spectra and SEM images. The retained hemicelluloses and impurities in the liquefied residue were eliminated by 2% NaOH and 5% H₂O₂ treatments. The surface and accessibility of the alkali treated samples were significantly increased by 5% H₂O₂ treatment. With high-intensity ultrasonic nanofibrillation treatment, CNCs with an average diameter of 12.59 nm were obtained from chemical purified samples. Thermogravimetric analysis demonstrated the CNCs had a good thermal stability.
4.5. REFERENCES


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CHAPTER 5. HIGH BIO-CONTENT POLYURETHANE (PU) FOAM MADE FROM BIO-POLYOL AND CELLULOSE NANOCRYSTALS (CNCS) VIA MICROWAVE LIQUEFACTION

5.1. INTRODUCTION

Rigid polyurethane (PU) foams are one of the most versatile polymer materials and have been used for construction insulation, due to their excellent thermal insulation and mechanical properties. Currently, the rigid PU industry is still highly dependent on petro-based chemicals due to its two major feedstocks including polyols and isocyanates. With the growing concern of environmental protection and rapid depletion of fossil fuel, numerous efforts have been focused on the substitution of petro-based polyols with bio-based polyols such as vegetable oil [1] and bio-polyol derived from lignocellulosic biomass [2].

Liquefaction is one of the most promising thermochemical conversion routes to convert lignocellulosic biomass into valuable chemicals [3-4]. Through liquefaction, the high molecular weight components of biomass are broken down to low molecular weight gases, liquids, and solid residues. In general, the gases are omitted because the yield of gaseous products is negligible. The liquid portion is the most commonly utilized liquefaction product [4]. It can be utilized to produce wood adhesive [5], methyl levulinate [6], and bio-based polyurethane (PU) foam [2]. It has been demonstrated that bio-foams from the liquefaction of lignocellulosic biomass are comparable with petro-based ones [7].

Even so, a major drawback was observed that a large amount of petro-based liquefaction solvents such as PEG-400, glycerol, ethylene glycol [7-9], were used to produce bio-polyol. This increases the production cost of polyols and consequently hinders future commercialization efforts. Furthermore, the conventional method to calculate the bio-polyol substitution rate, in fact, treats liquefaction solvents as bio-polyols, which results in a virtual high bio-content in bio-foams. To the authors’ knowledge, the true substitution rate of petro-based polyols with biopolyol (derived from biomass liquefaction) to make PU foam is in the range of 8-26% [2, 7-11]. There are two strategies to increase the true bio-polyol substitution rate. One is to increase the biomass share in the liquefaction system, which may compromise the biomass conversion yield [11]. The other one is to separate and recycle liquefaction solvents from bio-polyols. However, these conventional liquefaction solvents, as mentioned above, cannot be separated from biopolyols because of their high boiling point. Considering the above issues, a practicable method to break through the limit is to use a low boiling point liquefaction solvent. Although the bio-foam with high bio-content may have poor physico-mechanical properties, it is still worthy to explore the unknown bio-foam. In this work, therefore, low boiling point methanol will be used as the liquefaction solvent and will be recycled from the bio-polyol before producing bio-foams.

As for the liquefaction solid residue, the conventional use is to reinforce polymer composites as a filler [12]. Recently, our group started to isolate cellulose nanofibers and nanocrystals from solid residue [13-15]. However, there is still no effort being made to use these nano-scale products extracted from liquefaction solid residue. As a promising composite modifier, cellulose nanocrystals (CNCs) have high reinforcing capabilities owing to their high tensile strength, Young’s modulus, flexibility, and low coefficient of thermal expansion [16]; indeed, it has been demonstrated that the addition of CNCs do have positive effects on physico-
mechanical performance of the PU nanocomposites [17], whether the fraction is low (lower than 1.5%) [18-21] or high (up to 10%) [22-23]. This fact suggests a good potential to use CNCs for reinforcing high bio-content bio-foams. In terms of the research on modification of bio-foam from liquefaction, it’s major focus was on the increase of fireproof performance of PU foam [24]. But, there is no study on the use of CNCs in reinforcing liquefaction bio-polyol based PU foams.

The objective, in this work, is to produce high bio-content bio-foams from bio-polyol and CNCs via the microwave liquefaction of biomass. Rape straw was liquefied in methanol using microwave heating. The liquid portion after the removal of methanol was used as bio-polyol and the solid residue was used to extract CNCs. The bio-polyol was analyzed by gas chromatography coupled with mass spectrometry (GC-MS), $^1$H NMR, Fourier transform infrared spectroscopy (FT-IR) and rheometer. CNCs were characterized by transmission electron microscopy (TEM), FT-IR and solid state $^{13}$C NMR. The bio-foams and CNC reinforced bio-foams were analyzed using solid state $^{13}$C NMR, scanning electron microscopy (SEM), FT-IR and universal compression testing.

5.2. MATERIALS AND METHODS

5.2.1. Materials and Chemicals

Rape straw collected from Sichuan province, China, was air dried and ground into 20-40 mesh and then oven dried at 105°C until constant weight. The chemical components of rape straw are as following: $\alpha$-cellulose (36.72%), hemicellulose (32.67%), Klason lignin (13.66%), alcohol-toluene extractives (4.46%), and ash content (8.27%).

Methanol, sulfuric acid, sodium hydroxide, hydrogen peroxide, PEG-400 and glycerol were purchased from VWR International (Radnor, PA, USA). Polymeric methylene diphenyl
diisocyanate (pMDI) having 30-50% of 4,4′-methylenediphenyl diisocyanate and 50-70% of diphenylmethane diisocyanate was kindly supported by Huntsman Polyurethanes (Woodlands, TX, USA). The average functionality, NCO content and viscosity at 25°C of Rubinate M (the brand name of pMDI) are 2.7, 31.0% and 192 cps, respectively. Dow Corning 193 and dibutyltin dilaurate were used as surfactant and catalyst respectively for preparation of PU foams. Water was used as the eco-friendly blowing agent. All chemicals were used without further purification.

5.2.2. Preparation of Bio-polyol and CNCs

Liquefaction of rape straw was performed in a Milestone laboratory microwave oven (Shelton, CT, USA) equipped with an ATC-400FO automatic fiber optic temperature control system. A typical run was carried out with a loading of 2 g of rape straw, 12 g of methanol, and 0.36 g of sulfuric acid. The sealed vessels with reactants were subjected to microwave irradiation. The reaction temperature was increased from room temperature to 180 °C within 5 min, and then maintained for 2.5 min. After cooling, the liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper to separate the liquid portion and the solid residue. The liquefaction conversion yield was 77.6%.

The bio-polyol was obtained by the removal of methanol using a rotary evaporator. CNCs were extracted from solid residue in accordance with the method reported in our previous work [15]. The solid residue was treated by 2% NaOH for 1 h at 75°C, and then centrifuged to collect the sediment. The sediment was then bleached using 5% H₂O₂ for 5 h. Afterwards, the bleached sample was subjected to ultrasonic fibrillation by a high-intensity ultrasonic processor (Cole-Parmer CPX 750, Vernon Hills, IL, USA) for 15 min at 80% amplitude. CNCs suspension was obtained after centrifugation at 10000 rpm for 15 min. CNCs were freeze dried prior to reinforcing bio-foams.
5.2.3. Preparation of Bio-foams and CNC Reinforced Bio-foams

PU foams were prepared using a one-step method. For the reference foam, the polyol consisted of polyethylene glycol#400 and glycerol in mass ratio of 7:3, which was outlined by Li et al. [23]. A typical mixture of 3 g of polyol with or without bio-polyol, catalyst (dibutyltin dilaurate, 0.1 g), blowing agent (water, 0.2g) and surfactant (Dow Corning 193, 0.1g) was premixed thoroughly with a mechanical stirrer for 30 s, followed by adding 5.5 g of pMDI stirred with a high-speed agitator at a stirring speed of 3600 rpm. The foams were allowed to freely rise in open plastic cylindrical cups (about 450 mL capacity) and to cure overnight before test. The PU foams with 0, 5, 10, 15, 20, 25, 30, 35 and 40% of bio-polyol were named as PU0, PU5, PU10, PU15, PU20, PU25, PU30, PU35 and PU40, respectively. PU40 was further reinforced by 1, 2, 3, 4, 5 and 6% (wt %) CNCs by directly mixing CNCs in polyol stirred with a high-speed agitator. A series of CNC reinforced bio-foams were named PU401, PU402, PU403, PU404, PU405 and PU406. Each formulation was made in three replications.

5.2.4. Characterization of Bio-polyol and CNCs

5.2.4.1. Chemical Analysis of Bio-polyol

GC-MS analysis of bio-polyol was performed on a mass spectrometer of Agilent 5975C VL MSD (Santa Clara, CA, USA), and the products were separated into their components using a gas chromatograph of Agilent 7890A (Santa Clara, CA, USA) equipped with a fused capillary column (DP-5, L = 30 m, i.d. 0.32 mm, film thickness 0.25 µm) with 5% phenyl and 95% dimethylpoly-siloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min. The conditions for the detection were as follows: the injection mode had a split rate of 35; the column was held at 50 °C for 2 min and then heated to 250 °C at the rate of 10 °C/min;
and the injector temperature was 250 °C. The identification of the components was confirmed using total ion chromatograms, as well as fragmentation patterns.

The $^1$H NMR spectroscopy of bio-polyol was performed with a Bruker Avance 400 instrument (Karlsruhe, Germany). The $^1$H NMR spectrum of bio-polyol was acquired in dimethyl sulfoxide-d$_6$ (DMSO-d$_6$) at a concentration of 40 mg/mL. $^1$H NMR was recorded using a 1-s relaxation delay, an acquisition time of 3.28 s and 64 scans.

The FT-IR spectrum of bio-polyol was performed on a Nicolet Nexus 670 spectrometer (Middleton, WI, USA) equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of sample was covered flatwise on the detection window. The scanning range of wavenumbers was from 4000 to 600 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and total of 32 scans were collected.

5.2.4.2. Rheological Properties of Bio-polyol

The rheological properties of bio-polyol were measured using a stress-controlled rheometer of AR 2000 (New Castle, DE, USA) equipped with a DIN concentric cylinder geometry, which consists of a rotator with diameter of 28.03 mm and a stainless steel cup with diameter of 30.38 mm. The rheological curves were obtained by measuring the viscosity or shear stress as a function of shear rate in the range of 0.1 to 1000 s$^{-1}$ at 25°C.

The rheological data of bio-polyol were fitted to two different rheological models. One of the most popular and efficient models to fit the relation between shear stress and shear rate is the Herschel-Bulkey model [25], and has the following form (Eq. 5.1):

$$\tau = \tau_0 + K \dot{\gamma}^n$$

(5.1)

where $\tau$ is the shear stress, $\tau_0$ is the yield stress, $K$ is the flow consistency coefficient, $\dot{\gamma}$ is the shear rate, and $n$ is the flow behavior index. This model has been successfully used in describing
the rheological properties of bio-polyol obtained from the liquefaction of cellulose [26]. Since this model cannot give a unique fit for a given data set, the rheological properties of bio-polyol was also analyzed using an improved model, i.e., Sisko [27], as given below (Eq. 5.2):

\[
\tau = \mu_\infty \dot{\gamma} + K \dot{\gamma}^n
\]  

(5.2)

where \(\mu_\infty\) is the viscosity at infinite shear rate, \(K\) is the flow consistency coefficient, and \(n\) is the flow behavior index. This model performed well in describing the rheological properties of complex fluids over the entire range of shear rate, for example, in drilling fluids [28].

5.2.4.3. Morphology of CNCs

Transmission electron microscopy (TEM, JEOL 100CX, Peabody, MA, USA) with an accelerating voltage of 80 kV was used to evaluate the morphology of CNCs. A droplet of diluted CNCs suspension was deposited on glow-discharged thin carbon-coated copper grids. The diameter and length of CNCs were measured by randomly selections 100 fibers.

5.2.4.4. Chemical Analysis of CNCs

The chemical analysis of CNCs was characterized by FT-IR and solid state \(^{13}\)C NMR (Bruker Avance 400 WB, Rheinstetten, Germany). The CP/MAS experiments were performed with a relaxation delay of 2.0 s and a contact time of 2.0 ms. Magic angle spinning (MAS) was achieved at a rate of 12 kHz.

5.2.5. Characterization of Bio-foams and CNC Reinforced Bio-foams

5.2.5.1. Cell morphology of bio-foams and CNC reinforced bio-foams

Cell morphology of PU foams was analyzed by a scanning electron microscopy (SEM, JSM-6110 LV, Tokyo, Japan). Prior to analysis, the samples were gold coated. Images of cross-section of PU foams were obtained. The average cell diameter was calculated from 50 measurements.
5.2.5.2. Densities of bio-foams and CNC reinforced bio-foams

The densities of PU foams were determined by dividing the weight of specimens (30 × 30 × 30 mm$^3$) by the calculated volume, according to ASTM D 1622-08.

5.2.5.3. Thermal conductivity of bio-foams and CNC reinforced bio-foams

Thermal conductivity of PU foams was determined by using a KD2 Pro (Pullman, WA, USA). The original PU foam samples, in cylindrical cups, without further processing, were used to determine thermal conductivity. A 10 minute read time was performed to minimize the contact resistance errors. Ten replicates were conducted for each group.

5.2.5.4. Mechanical properties of bio-foams and CNC reinforced bio-foams

An eXpert 2610 universal mechanical test analyzer (Norwood, MA, USA) was used to measure the compressive properties of the foams, according to the ASTM D 695. Samples were placed between the two parallel plates and compressed at 10 mm/min. The Young’s modulus was calculated by the slope of tangent of linear portion in the stress-strain profile in accordance to the method described in previous reports [7, 29]. The compressive stress was taken from the stress-strain curves at deformation of 10%. Ten replicates were measured for each group.

5.2.5.5. Chemical analysis of bio-foams and CNC reinforced bio-foams

The chemical analyses of PU foams were also characterized using FT-IR and solid state $^{13}$C NMR.

5.3. RESULTS AND DISCUSSION

5.3.1. Characterization of Bio-polyol

5.3.1.1. Chemical Analysis of Bio-polyol

A black bio-polyol liquid was obtained after the microwave liquefaction of rape straw. Its chemical components and structures were further analyzed using GC-MS, $^1$H NMR, and FT-IR.
The GC-MS chromatogram displays that the bio-polyol mainly consisted of carbohydrate derivatives, including C5 (20.0%, by area), C6 sugars (17.8%), aromatics (7.2%), and other chemical components (23.4%) such as aliphatics, esters, and ethers (Figure 5.1). The main chemical components were further confirmed by $^1$H NMR analysis (Figure 5.2). For instance, the resonances of carbohydrate functionalities were located from 4.5 to 6.0 ppm in $^1$H NMR [30, 31]. Aromatic protons signals were observed in the region of 6.0-8.5 ppm [31-33] and at weak peak of 5.3 ppm [34]. The protons resonating between 3.0 to 4.5 ppm, represented protons on carbon atoms next to an aliphatic alcohol (i.e., hydroxyl group), ether and ester [30, 32]. Resonances between 0.5 and 3.0 ppm were caused by aliphatics protons [35].

Figure 5.1. GC-MS chromatogram of bio-polyol via microwave liquefaction
Figure 5.2 $^1$H NMR spectrum of bio-polyol (in DMSO-d$_6$)

Figure 5.3. FT-IR spectra of preparation of bio-polyol and CNC via microwave liquefaction
From the chemical structures identified by GC-MS, C5 sugars could provide 3 hydroxyl groups, C6 sugars have 2 to 5 hydroxyl groups, and all the aromatics were observed to have only one alcoholic hydroxyl group. This result suggested that C5 and C6 have a strong ability to cross link with pMDI indicating that the bio-polyol is a hydroxyl-rich source, which was further evidenced by the FT-IR spectra from the broad absorbance band of hydroxyl groups at 3330 cm\(^{-1}\) [36], shown as presented in Figure 5.3. Using the titration method, the hydroxyl number in bio-polyol was determined for 222.4 mg KOH/g.

C5, C6 sugars and aromatics were derived from hemicelluloses, cellulose and lignin, respectively. Their existence in bio-polyol suggested that the main chemical components in rape straw underwent a decomposition process during liquefaction. Methanolysis catalyzed by acid could break down the glycosidic bonds and dominant linkages between hemicellulose and cellulose, releasing C5 and C6 sugars. The produced aromatics were likely contributed by the breakdown of the β-O-4, 4-O-5, and dibenzodioxocin units in lignin structure [3, 32]. The observation of esters in the bio-polyol may be ascribed to the oxidation of hydroxyl group [37] and the methanol esterification reactions [3-4].

5.3.1.2. Rheological Properties of Bio-polyol

Figure 5.4 shows the viscosity and shear stress of bio-polyol with respect to shear rate. The viscosity was strongly dependent on the shear rate. A nonlinear reduction on viscosity of bio-polyol was found at the low shear rate region. The decrease tendency was attributed to the increase of liquid flow arrangement by increasing shear rate [26]. The disproportionality of viscosity at low shear rate indicated that bio-polyol could be categorized as a non-Newtonian liquid [38-39], which was further confirmed by the mathematical models analysis.
Figure 5.4. Rheological properties of bio-polyol via microwave liquefaction

The estimated mathematical models are shown in Figure 5.4. As expected, a slightly larger $R^2$ was observed in the model of Sisko, in comparison with Herschel-Bulkey, indicating that the Sisko is more appropriate for describing the rheological properties of bio-polyol. However, the Herschel-Bulkey could give the yield stress ($\tau_0 = 0.98$) directly, which reflects the minimum stress before the fluid starts to move [28]. In this study, it needed at least 0.98 Pa to move bio-polyol. Normally, the fluid can be categorized into three types based the value of flow behavior index. They are Newtonian ($n=1$), pseudoplastic (non-Newtonian) with a shear thinning behavior ($n < 1$), and dilatant (non-Newtonian) with shear thickening behavior ($n > 1$) [40]. The flow behavior indexes ($n$) obtained from two models were lower than 1. This result further confirmed that the bio-polyol is a pseudoplastic (non-Newtonian) fluid. It was demonstrated in previous research that pseudoplastic bio-polyol was suitable to produce PU foam [26].
5.3.2. Preparation and Characterization of Bio-foams

The bio-polyol was applied for the preparation of bio-foams, and the morphology and physico-mechanical properties of the resulting foams were evaluated. It was visually observed that the bio-foam became much darker with increasing the bio-polyol amount. This finding was also reported by Xie et al. (2015) [10] and dos Santos et al. (2017) [41]. This result could be ascribed to the addition of aromatics derived from the lignin.

5.3.2.1. Morphology of bio-foams

![SEM images of bio-foams and CNC reinforced bio-foams](image)

Figure 5.5. SEM images of bio-foams and CNC reinforced bio-foams
The SEM images of the cross-section surfaces of the bio-foams are depicted in Figure 5.5. The cell diameter of the bio-foam containing 20% bio-polyol dramatically decreased by 90% in comparison with the reference foam as shown in Table 5.1. The hydroxyl groups in bio-polyol have lower reactivity than that of petro-based foams, resulting in the prolongation of cream and tack free time [42]. This slowed down the merging of fine air bubbles (CO$_2$) in the matrix. Since fine air bubbles act as nucleation sites in the preparation of polyurethane foams [29], it could be understood that the low merging speed of fine air bubbles resulted in the fine cells in the bio-foam with 20% bio-polyol (PU20) in comparison with PU0. In contrast, further increasing the bio-polyol content from 20 to 40% in polyol mixture resulted in a remarkable increase of cell diameter by 460%, and the cells became open and heterogeneous. Abdel Hakim et al. (2011) attributed the tendency of increasing cell diameter to the enhancement of number of cross links between the polyurethane macromolecules [42].

Table 5.1. Cell diameter, physico-mechanical properties of the bio-foams and CNC reinforced bio-forms

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cell diameter (mm)</th>
<th>Density (kg·m$^{-3}$)</th>
<th>Thermal conductivity (mW·m$^{-1}$·K$^{-1}$)</th>
<th>Young's modulus (kPa)</th>
<th>Compressive stress (δ10% kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU0</td>
<td>4.1±1.1</td>
<td>26.8±1.6</td>
<td>40.4±1.7</td>
<td>272.1±67.6</td>
<td>25.3±2.5</td>
</tr>
<tr>
<td>PU5</td>
<td>3.9±0.8</td>
<td>26.1±1.0</td>
<td>39.9±1.8</td>
<td>258.3±65.1</td>
<td>24.8±3.5</td>
</tr>
<tr>
<td>PU10</td>
<td>3.3±0.7</td>
<td>20.7±1.3</td>
<td>38.1±1.9</td>
<td>151.4±15.6</td>
<td>12.1±1.4</td>
</tr>
<tr>
<td>PU15</td>
<td>0.5±0.1</td>
<td>21.0±1.5</td>
<td>38.0±1.2</td>
<td>500.3±81.7</td>
<td>35.7±4.8</td>
</tr>
<tr>
<td>PU20</td>
<td>0.5±0.2</td>
<td>21.2±1.3</td>
<td>37.2±2.9</td>
<td>637.4±95.0</td>
<td>40.7±3.6</td>
</tr>
<tr>
<td>PU25</td>
<td>0.6±0.3</td>
<td>22.1±2.1</td>
<td>37.2±1.7</td>
<td>592.1±81.1</td>
<td>37.3±4.8</td>
</tr>
<tr>
<td>PU30</td>
<td>1.9±0.4</td>
<td>23.3±2.3</td>
<td>39.7±1.9</td>
<td>197.8±36.8</td>
<td>14.3±2.1</td>
</tr>
<tr>
<td>PU35</td>
<td>2.4±0.5</td>
<td>23.1±3.0</td>
<td>39.6±0.8</td>
<td>171.7±43.9</td>
<td>12.0±1.7</td>
</tr>
<tr>
<td>PU40</td>
<td>2.8±0.8</td>
<td>24.2±2.6</td>
<td>39.8±1.9</td>
<td>172.7±46.4</td>
<td>11.6±1.8</td>
</tr>
<tr>
<td>PU401</td>
<td>3.1±0.7</td>
<td>26.6±2.0</td>
<td>41.1±1.4</td>
<td>327.2±46.4</td>
<td>17.8±1.7</td>
</tr>
<tr>
<td>PU402</td>
<td>0.9±0.3</td>
<td>24.7±2.6</td>
<td>36.1±1.9</td>
<td>459.2±28.2</td>
<td>22.0±1.3</td>
</tr>
<tr>
<td>PU403</td>
<td>0.3±0.1</td>
<td>24.8±1.1</td>
<td>35.8±1.9</td>
<td>681.4±132.9</td>
<td>22.3±2.9</td>
</tr>
<tr>
<td>PU404</td>
<td>0.2±0.1</td>
<td>24.2±0.7</td>
<td>34.4±0.8</td>
<td>1186.6±163.3</td>
<td>28.7±4.5</td>
</tr>
<tr>
<td>PU405</td>
<td>0.2±0.1</td>
<td>23.3±2.3</td>
<td>34.4±1.3</td>
<td>976.6±137.4</td>
<td>26.6±3.2</td>
</tr>
<tr>
<td>PU406</td>
<td>0.2±0.1</td>
<td>20.6±0.8</td>
<td>34.0±1.1</td>
<td>857.8±114.5</td>
<td>25.6±3.5</td>
</tr>
</tbody>
</table>
5.3.2.2. Physico-mechanical Properties of Bio-foams

The physico-mechanical properties including density, thermal conductivity, Young’s modulus and compressive stress of bio-foams are summarized in Table 5.1. The densities of bio-foams were lower than that of the reference foam (PU0). Table 5.1 also shows the density increased from 20.7 to 24.2 kg·m\(^{-3}\) with increasing the bio-polyol content from 10 to 40%. This may be attributed to the increase of cross linking density of bio-foams macromolecules [42]. Thermal conductivity is the key thermal property that governs insulation applications of PU foams. It is closely related to the foam density, cell orientation, the ratio of open to closed cells, and the thermal conductivity of trapped gas [43]. The thermal conductivity values of bio-foams was in the range of 37.2 to 40.4 mW·m\(^{-1}\)·K\(^{-1}\), with peaks at both 0% and 40% bio-polyol content. These values were comparable with those of corn stover derived foam ranging from 32.2 to 38.9 mW·m\(^{-1}\)·K\(^{-1}\) [9]. In general, they were satisfactory enough to be used as insulation foam in which the thermal conductivity varies between 23.3 and 50.5 mW·m\(^{-1}\)·K\(^{-1}\) [7, 44]. The minimum thermal conductivity value was observed at bio-foam with a bio-polyol content of 20% (PU20), probably because of the lower radiant heat transfer rate through the gases trapped in smaller cells [42]. Therefore it could be said that the application of bio-polyol was somewhat beneficial in producing low thermal conductivity insulation foams.

From the Table 5.1, compared with PU0, a dramatic decrease of mechanical properties was found in the PU10, which was probably attributed to the remarkable reduction of density. It was note worthy that the maximum values for mechanical properties of bio-foams were observed in the PU20. This result was ascribed to the fine and homogenous cell structures of foam. However, with further increasing the bio-polyol content from 20 to 40%, both the Young’s modulus and compressive stress decreased by 70%. These results could be explained by the complex chemical
reactions involved in the preparation of bio-foams. The stronger mechanical properties in PU20 was probably ascribed to multi-hydroxyl structures of C5 and C6, which could act as chain extenders to increase the density of three-dimensional cross linkages by reacting with multi-isocynate groups. In addition, the smaller cell sizes lead to stronger cell walls due to reduced moments of inertia of the smaller individual cell walls. The reduction of mechanical properties of PU40 may be attributed to the increase of aromatics that have only one hydroxyl group in the polyol mixture, which was consumed in the reaction with isocyanate. In this case, the crosslinking process between hydroxyl and isocyanate will be terminated at the aromatics point due to the lack of additional hydroxyl groups in the aromatics. In other words, it can be inferred that the aromatics, in fact, act as a chain-cutting agent, resulting in a low crosslinking density. Moreover, liquefaction bio-polyol acted as a hard segment in PU foam, rather than soft segment, and consequently, the higher hard segment content made the foam more brittle [45]. Generally, the compressive properties of foams are influenced by both apparent density and crosslinking density [46].

Although the physico-mechanical properties of PU foam could be enhanced by replacing 20% of petro-based polyol with bio-polyol, the high bio-content foam (PU40) did not show a satisfactory physico-mechanical performance. Hence, it is necessary to modify the PU40 in order to make high bio-content foam with improved physico-mechanical performance. Cellulose nanocrystals (CNCs) have a high surface area, specific strength and modulus, and low coefficient of thermal expansion [16]. Moreover, it is also a source of hydroxyl groups, which makes it a good candidate to react with isocyanate groups. Considering these merits of CNCs, the addition of CNCs into the bio-polyols may have potential in the reinforcement of bio-foams.
5.3.2.3. Effect of CNCs on The Preparation of Bio-foams

The CNCs were extracted from liquefied solid residue; the extraction process was reported in our previous work [15]. As shown Figure 5.6, it was clear that the CNCs were rod-shaped with an average length, diameter, and aspect ratio of 161.9 ± 38.8 nm, 10.8 ± 2.3 nm, and 15.2 ± 4.9. From the FT-IR spectrum of the CNCs (Figure 5.3), it was noteworthy that a new peak of sulfate ester group at 1197 cm\(^{-1}\) was introduced; this was because of sulfuric acid used in the liquefaction reaction [47]. The introduction of the sulfate ester group could contribute to stabilizing the CNC suspension because it could provide a negative electrostatic layer on the CNCs surface [48].

![TEM image of CNCs extracted from liquefaction solid residue](image)

**Figure 5.6.** TEM image of CNCs extracted from liquefaction solid residue

The addition of CNCs resulted in whiter foams with smaller cell diameter (Figure 5.5). A similar finding was reported in the literature [22]. In comparison with the reference (PU40), the cell diameter became larger by adding 1% CNCs. From Table 5.1, the cell diameter decreased from 3.1 to 0.2 mm by increasing the CNCs content from 1 to 6%. This result was consistent with the observation of Faruk et al. (2014) [49]. The reason was that the CNCs acted as
nucleation sites to facilitate the cell nucleation process and resulted in a finer cell structure [22, 49]. With increasing the addition of CNCs content from 1 to 6%, the density decreased from 26.6 to 20.6 kg·m\(^{-3}\). A possible explanation could be that the CNC enhanced the formation of three-dimensional crosslinked polyurethane groups in bio-foams as a result of the increase of foam volume. The thermal conductivity values slightly decreased with increasing CNCs content. The result was attributed to the formation of closed cells covered by a thin polyurethane membrane in PU404 and PU406. It was also worthy to note that the 1% CNCs undermined the thermal conductivity. This result was attributed to the larger cell size and lower closed cell content, because the CNCs could interfere with the development of cell windows [21]. From Table 5.1, it is evident that the mechanical properties increased remarkably with the addition of 4% CNCs, reaching the highest values. As compared with PU40, the Young’s modulus and compressive stress in 4% CNCs reinforced bio-foam increased by 590% and 150%, respectively. It was also noteworthy that these values were superior to those of the petro-based reference foam (PU0). This incidence could be attributable to the CNCs having a good dispersion in the bio-foam matrix at a low concentration, resulting in an increased foam structure [19, 22]. In contrast, when further increasing the CNCs content, the mechanical properties began to decline, probability due to the poor dispersion of CNCs in the foam matrix [22-23].

The reinforcement of CNCs in nanocomposite foam was ascribed to the CNCs enhancing the formation of larger cell strut area which contributed to improving the mechanical strength of PU foam [22-23]. CNCs could function as a polyol and react with isocyanate [50-51], due to the existence of hydroxyl groups in their chemical structure. It was worthy to note that these hydroxyl groups are bonded to the glucose with separate dimensional directions. This feature of CNCs makes it possible to form three-dimensional crosslinked polyurethane groups, leading to
the increase of cell strut area and crosslinking density. Apart from this, the interactions between CNCs and polyurethane hard segments (urethane and urea) could reinforce the cell wall strength [20, 52]. Improved mechanical properties could result partly from some inherent properties of CNCs, such as the high crystallographic structure and mechanical properties [18, 53]. It should be noted that foams with higher CNCs content were more ductile, owing to the CNCs acting as plasticizer during the preparation of PU foam [54].

5.3.3. Reaction Mechanism

In order to understand the reactions occurring in the bio-foams preparation and to clarify how CNCs achieved the reinforcement during the process, the chemical structures of the reference foam, bio-polyol containing foam, and the CNC reinforced bio-foam was characterized using FT-IR and NMR.

5.3.3.1. FT-IR Spectra

FT-IR spectra of PU0, PU40 and PU404 are shown in Figure 5.7. All samples showed typical infrared spectra of PU foams. For instance, the presence of urethane linkages could be observed from peaks of 3490 cm\(^{-1}\) (free N-H), 3330 cm\(^{-1}\) (hydrogen-bonded N-H), 1218 cm\(^{-1}\) (C-N) and 1064 cm\(^{-1}\) (C-O) [20, 23, 55]. The shoulder at the peak of 1615 cm\(^{-1}\) evidenced the occurrence of urea linkages [42]. The bands at 1510 cm\(^{-1}\) and 1597 cm\(^{-1}\) were derived from aromatics of pMDI [23]. Apart from this, the characteristic absorbance of NCO group appeared at 2277 cm\(^{-1}\). In this study, an excessive amount of pMDI was used deliberately to ensure that hydroxyl components could completely react with NCO groups. Moreover, it was possibly attributed to the decomposition of uretoneimine structure in PU crosslinkages [56].
Figure 5.7. FT-IR spectra of the bio-foams and CNC reinforced bio-foams

It was noteworthy that the carbonyl region was split into two peaks. The major at 1708 cm\(^{-1}\) is associated with the hydrogen-bonded carbonyls and the secondary one at 1729 cm\(^{-1}\) is caused by the non-hydrogen bonded carbonyl. The characteristic absorbance had been normalized by referring to phenyl band at 1597 cm\(^{-1}\). The classic carbonyl hydrogen-bonding index can be determined by calculating the ratio of the normalized absorbance intensity at 1708 cm\(^{-1}\) to that at 1729 cm\(^{-1}\) [55]. The hydrogen-bonding index slightly increased from 1.19 (PU0) to 1.25 (PU40), and then declined to 1.22 (PU404). The substitution of 40% of petro-based polyol with bio-polyol resulted in the decrease of total hydroxyl value in the polyol mixture, and thereby, leading to a low urethane density with a good mobility, which, in turn, probably increased the possibility of foam hydrogen bonding with other urethane chains. The reduction of hydrogen-bonding index when incorporating CNCs was well in line with the literature [18, 57]. A convincing reason is
that some CNCs could function as covalent bond to the PU molecular chains during polymerization, limiting its mobility and decreasing its ability to hydrogen bond to other urethane chains [18]. This result confirmed that CNCs serve as cross-linking agents during the preparation of PU foam. In addition, the normalized band of hydrogen-bonded N-H (3330 cm$^{-1}$) of PU404 was stronger than that of PU40, suggesting that CNCs indeed enhance the cross-linking reactions.

5.3.3.2. Solid State $^{13}$C NMR Analysis

$^{13}$C NMR spectra and assignments of CNC, PU0, PU40 and PU404 are shown in Figure 5.8. The urethane linkages and urea linkages were detected in all PU foams. The former was reflected from the peak at 154.2 ppm and the latter was deduced from the peak at 118.4 ppm [58, 59]. The difference between the chemical shifts of C=O groups of urethane (154-155 ppm) and urea (156 ppm) is only 1 to 2 ppm [58], and thereby the urea single peak might be overlapped in the urethane characteristic peak. However, it can be deduced from the single peak at 118.4, which belongs to the benzene ring bonded with urea linkage [59]. The peaks at 136.6 ppm, 129.1 ppm, and 40.1 ppm were assigned to pMDI [44, 59-60], and the peaks at 70.1 ppm and 63.4 ppm corresponded to PEG 400 and glycerol, respectively [33, 61]. The peak at around 35.6 ppm and 16.8 ppm could be related to the methylene aliphatic carbons [62-63]. Those signals were observed from reference foam, as well as bio-foams with and without CNCs, suggesting the basic structures are somewhat similar in all foams.

However, in comparison with reference foam, a new peak at 52.4 ppm was found from the spectra of bio-foams, which belongs to $\beta-5'$ unit in lignin [64]. The detection of typical lignin signal demonstrated the successful introduction of bio-based resources during the preparation of bio-foams. In order to analyze the role of CNCs in reinforced bio-foam, the CNCs features were
characterized by solid state $^{13}$C NMR. The spectrum of the CNCs represented characteristic signals of glucose rings which were C1 (104.9 and 95.5 ppm), C2 (74.4 ppm), C3 (74.4 ppm), C4 (88.5 and 84.3 ppm), C5 (74.4) and C6 (62.6 ppm) [54, 65]. Those peaks disappeared in the spectrum of CNC reinforced bio-foam, indicating that the hydroxyl group in CNCs indeed reacted with isocyanate in pMDI. This reaction enhanced the formation of three-dimensional crosslinked polyurethane groups in bio-foam, therefore, increasing the physico-mechanical performance of PU foam.

![Solid state $^{13}$C NMR](image.png)

Figure 5.8. Solid state $^{13}$C NMR of CNCs, bio-foam and 4% CNC reinforced bio-foam

5.3.3.3. Reaction Scheme

The occurrence of urethane and urea links in CNCs reinforced bio-foam were confirmed by the analysis of FT-IR and solid state $^{13}$C NMR. C5, C6 sugars and aromatics in bio-polyol as well as CNCs are sources of hydroxyl groups that could react with isocyanate to form urethane
links. In addition, the blowing agent, i.e. water, could react with isocyanate to form urea links and CO$_2$. By considering these issues, a proposed reaction scheme and possible chemical structure of CNC reinforced bio-foam was shown in Figure 5.9. It should be noted that C5, C6 sugars and CNCs could react with multi-isocyanate groups, resulting in a three-dimensional crosslinked structure. Thereby, the crosslinking density was developed by the increase of chemical crosslinkages. Aromatics, however, terminated the extension of crosslinking.

![Reaction Scheme and Possible Chemical Structure](image)

Figure 5.9. Proposed reaction scheme and possible chemical structure of CNC reinforced bio-foam

5.4. CONCLUSIONS

Bio-polyol and CNCs were successfully prepared from the liquid portion and solid residue of microwave liquefied rape straw. GC-MS, $^1$H NMR and FT-IR demonstrated that the bio-polyol is a hydroxyl-rich source, suggesting it is suitable to make PU foam. By replacing 20% of petro-based polyol with bio-polyol, the foam cell became more homogenous and finer, resulting in a low thermal conductivity and high mechanical performance, while, further increasing bio-polyol content from 20 to 40%, the cell diameter was increased by 460% and both the Young’s modulus and compressive stress decreased by 70%. However, the 40% bio-polyol foam could be
remarkably reinforced by 4% CNCs because the hydroxyl-rich structure in CNCs increased the crosslinking density resulting in the increase of physico-mechanical performance of bio-foam. The reinforcement behavior of CNCs in the preparation of bio-polyol foams were evidenced by solid state $^{13}$C NMR and FT-IR analysis. As compared with reference (PU40), the Young’s modulus and compressive stress in the optimal 4% CNCs reinforced bio-foam increased by 590% and 150%, respectively.

5.5. REFERENCES


410-5.


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CHAPTER 6. CHARACTERIZATION OF BIO-BASED POLYURETHANE FOAMS EMPLOYING LIGNIN FRACTIONATED FROM MICROWAVE LIQUEFIED SWITCHGRASS

6.1. INTRODUCTION

As an important engineering material, polyurethane foam (PU foam) has been widely used in automotive industry, insulating panel, and construction, etc [1]. Currently, the research on the alternative of petroleum-based polyol, a main chemical component to manufacture PU foam with eco-friendly bio-polyol sources such as biodiesel residues has attracted an increasing attention [2], due to the rapid depletion of fossil fuels.

Vegetable oil composed of triglycerides of long chain fatty acids has great potential for the synthesis of polyols. In recent years, a series of vegetable oils have been successfully applied in the preparation of bio-based PU foams, such as modified oils from soybean and castor oils [3-5]. Meanwhile, chemical platforms derived from non-food resources was also modified and used as alternative components to achieve highly functional bio-based foams. Lignocellulosic biomass composed of cellulose, hemicellulose, and lignin is a valuable and worldwide accessible bioresource which can provide alternative chemicals via proper conversion processes. Recent achievements in biomass thermochemical conversion techniques have stimulated great interests in the integrated utilizations of lignocellulosic biomass for the production of hydroxyl-rich bio-polyols. The achieved bio-polyols by liquefaction have high hydroxyl functionalities and great promising properties in the production of PU foams [6]. A large variety of lignocellulosic

biomass such as bamboo [7], wheat straw [8], and soybean straw [9] have been liquefied into liquid polyols for the preparation of PU foams. Instead of converting lignocellulosic biomass into bio-polyols as a core reactant in the synthesis of foams, other researchers directly added bio-derived materials such as wood pulp fiber [10] and nanoparticle lignin [11] into matrix materials as reinforcing filler in the bio-foams.

Lignin is composed of three different types of phenylpropane units. It is a three dimensional amorphous phenolic polymer which fills the space between cellulose and hemicellulose and cross links with hemicellulosic polysaccharides [12]. Lignin generally features an irregular structure with a highly condensed cross-linked polymer network providing the biomass with mechanical strength as well as rigidity to resist external forces [13]. However, lignin from pulping or biorefinery industries is currently an underutilized waste product. About 225 million tons of lignin generation is expected from the cellulosic alcohol industry in the United States in the near future, and only 2% is used for value-added applications [14]. In order to address the resource waste problem and to enhance the commerciality of the bioethanol industry, a number of studies have been conducted to use lignins as raw feedstocks for production of bio-based materials. Lignin was added into poly lactic acid (PLA) matrix to fabricate PLA-lignin composites for use as packaging materials [15]. The liquefied lignin was applied for the substitution of petro derived ployol to prepare flexible polyurethane foams [16]. Organosolv and Kraft lignin were used as hydroxyl sources to replace polyols for the production of PU foams [17-18]. Meanwhile, some chemical strategies such as oxypropylation [19], urethane modification [20], and liquefaction [21] were also used to modify lignin macromolecules, and the modified lignin was incorporated into the polyurethane matrix for production of high bio-content materials. Although, recent research work on lignin-based foam has achieved great
progress, some of these synthesized foams couldn’t show comparable properties to commercial ones. Thus, intensive work is still needed to find efficient ways to transform lignin into highly functional materials for market applications.

In the past decades, research for alternate fuel resources to meet the ever-increasing energy demand and to avoid dependence on fossil fuel has attracted the attention of researchers worldwide. Switchgrass (*Panicum virgatum*), which occurs naturally from 55°N latitude to central Mexico [22] is considered as a promising crop for a large region of the United States. Switchgrass shows promise due to its high productivity, suitability for marginal land quality, low water and nutritional requirements, environmental benefits, and flexibility for multipurpose uses [23]. It has been used over other crops for conversion to bioenergy within the United States, and was identified by the US Department of Energy as a model herbaceous energy crop [24]. Nowadays, fast pyrolysis and enzymatic hydrolysis has been used as common strategy for energy conversion employing switchgrass [25-26]. Recent research on alkaline pretreatment of switchgrass for lignin removal and sugar retentions for economic valuable cellulosic ethanol production was reported by Karp *et al* [27]. Meanwhile, liquefaction was also applied in the integrated utilizations of switchgrass for bio-based epoxy resins [28]. In our previous study, we optimized a system to selectively liquefy the lignin in lignocellulosic biomass for production of carbohydrate polymers. In order to verify the commercial potential of this novel biomass utilization process, the lignins from the selective liquefaction process were recovered and the physicochemical properties of the lignin samples were examined [15]. Previous results showed that the recovered switchgrass lignin retained its original core structure, high thermal stability, and good solubility in common organic solvents. Thus, in order to verify whether the recovered lignin had potential for PU foam, lignins were introduced into the PU matrix for the preparation
of lignin containing semirigid PU foams. The specific objective of this study was to investigate the influence of lignin on the morphological, mechanical, and thermal properties of the synthesized foams. The aim of this research was to provide a new approach for the utilizations of biorefinery industrial lignins.

6.2. MATERIALS AND METHODS

6.2.1. Materials and Chemicals

Switchgrass (*Panicum virgatum*) was harvested from agricultural land in central Louisiana, USA. The whole switchgrass straw including leaves was reduced to particles using a Thomas Wiley Laboratory mill. The particles were screened to collect particles that passed through a 20-mesh sieve and then retained on a 40-mesh sieve and then dried to a constant weight in an oven maintained at 80°C. The dried particles were stored in polyethylene bags and used without further treatment. All acids, glycerol, and methanol used were of reagent grade and obtained from commercial sources.

6.2.2. Microwave Liquefaction

Microwave selective liquefaction was carried out in a Milestone MEGA laboratory microwave oven. Mixed glycerol and methanol at a ratio of 2/1 (w/w) was used as the solvent at a solvent to switchgrass ratio of 4/1 (w/w). Sulfuric acid (1.75% of solvent weight) was used as the catalyst. A typical reaction mixture consisting of 2 g of switchgrass particles, 8 g of solvent, and 0.14 g of sulfuric acid were loaded in Teflon vessels with a magnetic stirring bar. The Teflon vessels were then placed on the rotor tray inside the microwave cavity. The temperature was monitored using an ATC-400FO automatic fiber optic temperature control system. Based on monitored temperature, the output power was auto-adjusted during liquefaction. In this study, the temperature was increased from room temperature to 120°C and then was kept constant for 4
min. The resulting reaction mixtures were dissolved in methanol and then vacuum-filtered through Whatman No. 4 filter paper.

The filtrated liquid was evaporated at 45°C under vacuum to remove methanol, and then distilled water [10/1 (w/w)] was added to the obtained liquid. The mixture was stirred thoroughly with a glass rod. Afterwards, the mixture was centrifuged at 5000 rpm for 10min. The precipitates were dried at 30°C for 12h. The samples were kept in ambient conditions for further usage.

6.2.3. Preparation of PU Foams

The control PU foam was prepared using a one-step method according to a previous used method [29]. A typical mixture of PEG-400/glycerol (8.0 g), catalyst (dibutyltine dilaurate, 0.16 g), blowing agents (water, 0.54 g), and surfactant (Dow corning 193, 0.16 g) was premixed thoroughly in a beaker with a mechanical stirrer for 15 s. Afterwards, 12.8 g of isocyanate ([NCO]/[OH] ratio, 0.6) was added to the pre-mixture and the combination was stirred with a high-speed agitator at a stirring speed of 3600 rpm. Immediately afterwards, the resultant mixture was poured into an open cylindrical mold and was allowed to freely rise at room conditions. The obtained foams were allowed to cure at room temperature for 1 h. For the preparation of lignin containing foams, desired lignin samples were dissolved in PEG/glycerol blend at the mass rate of 5, 10, and 15% (based on PEG/glycerol mixture), and then the mixture was compounded with other components following the same procedure for the control foam.

6.2.4. Characterization

The foam samples were crumbed into powder prior to the chemical structure analysis by using FT-IR. The FT-IR analysis was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. Data collection was
performed with a 4 cm⁻¹ spectral resolution and 32 scans were taken per sample. The surface morphology of the foam was observed using scanning electron microscopy (SEM, NeoScope JCM-5000, NiKon Instruments Inc.). Test samples were coated with gold using a vacuum sputter coater before subjected to the SEM analysis. TG/DTG analysis was conducted with a thermal analyzer, TGA (Q50, TA Instruments), to simultaneously obtain thermos gravimetric data. About 5 mg of powder sample was loaded on the platinum crucible and analyzed by the thermal analyzer. Pyrolysis was terminated at 800°C with a heating rate of 20°C/min under a flow of 60mL/min of nitrogen gas. The apparent density of the PU foam was measure at 23°C with 50% relative humidity according to ASTM D1622-03. The size of the specimen was 30mm × 30mm × 30mm (length × width × thickness). Five specimens were used for per sample and the average value was reported. The mechanical properties were characterized by the compressive strength and compressive modulus. The size of the specimen used for compressive strength was 30mm × 30mm × 30mm (length × width × thickness). The test was performed using an Instron testing machine (Instron 4465), with a load of 2 KN at a crosshead speed of 2.5 mm/min. Compressive strength at 10% strain and compressive modulus were performed according to ASTM D 1621-10. For each sample, five specimens were tested, and an average value was taken along with the standard deviation.

6.3. RESULTS AND DISCUSSION

6.3.1. Morphological Structures

The cross-section structure of the PU foam samples was characterized by SEM images. As presented in Figure 6.1, both the control (Figure 6.1a) and the lignin containing (Figure 6.1b-d) PU foams exhibited a honeycomb structure with closed cells. The control PU foams had almost regular cell size and distribution with a negligible quantity of broken cell walls. Despite the
broken cell walls, the pure polyol PU foams with a light yellow color had no significant
difference in cell structures from the ones with 5% lignin, indicating the influence of lignin on
the foam structure was insignificant with less than 5% lignin content in the foam. With the
introduction of lignin into the PU matrix, the PU foam color became brown and the cell diameter
tended to be larger.

![SEM images of (a) pure polyol, (b) 5% lignin, (c) 10% lignin, and (d) 15% lignin
content polyurethane foams](image)

Figure 6.1. SEM images of (a) pure polyol, (b) 5% lignin, (c) 10% lignin, and (d) 15% lignin
content polyurethane foams

The cell diameter and number of cells by surface area (n) of the PU foams were measured
and the values are listed in Table 6.1. From Table 6.1, the polyol PU foams had relatively small
cell diameter and high number of cells by surface area (n). The cell diameter of foams with 5, 10,
and 15% lignin were 523.1, 521.3, and 838.8 μm, respectively, and the number of cells by
surface area (n) was 1.82, 1.87, and 1.02 N/mm², respectively. According to the ANOVA
analysis, significant differences (p<0.01) in the cell diameter were found between 15% lignin
foam and the others. The result revealed that the addition of 15% lignin into the PU matrix had a
significant effect on the foam cellular structures. The alteration in the cell structure may be due to the fact that high lignin content affected the cell nucleation process in the preparation of PU foams [30]. Similar results were also found by Pan and Saddler [17], who reported that the increase of ethanol organosolv lignin ratio in petroleum-based polyol resulted in particularly large cells (bubbles). However, this finding regarding cell diameter was quite different from Luo et al [3]. This may be due to the character variations among the polyols and lignins employed in the foam preparation. A combination of PEG/glycerol blends and depolymerized switchgrass lignin were used as hydroxyl sources in this study whereas soy oil/lignin powder was used as the reaction feedstock in Luo’s research [3].

Table 6.1. Cell diameter and number of cells by surface area of different polyurethane foams

<table>
<thead>
<tr>
<th>Index</th>
<th>Lignin content (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (μm)</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>513.4±112.7</td>
<td>523.1±89.8</td>
<td>521.3±130.7</td>
<td>838.8±167.1</td>
</tr>
<tr>
<td>Number of cells by surface area (n) (N/mm²)</td>
<td>1.98</td>
<td>1.82</td>
<td>1.87</td>
<td>1.02</td>
</tr>
</tbody>
</table>

6.3.2. Chemical Structure

FT-IR spectra were used to character the chemical structures of polyol, lignin, MDI (Figure 6.2A), and the synthesized PU foams (Figure 6.2B). As shown in Figure 6.2B, the polyol was confirmed by the absorption bands at 3330 cm⁻¹ (OH stretching) and 2870 cm⁻¹ (C-H stretch). Switchgrass lignin was confirmed by the main characteristic bands at 1599 cm⁻¹ (aromatic ring vibration), 1510 cm⁻¹ (aromatic skeletal vibration), 1456 cm⁻¹ (C-H deformation), and 1220 cm⁻¹ (C-O stretching in phenol and ethers) [15]. An intensity band at 2240 cm⁻¹ attributed to the NCO group was found on the spectrum of MDI. The absorption bands of urethane moieties such as 3310 cm⁻¹ (NH stretching vibration), 1703 cm⁻¹ (C=O), 1599 cm⁻¹ (CO-NH variation), 1510 cm⁻¹
(NH bending vibration), and 1220 cm$^{-1}$ (O-CO stretching vibration) were identified in the spectra of the PU foams.$^{18}$ No absorption band was observed at 2240 cm$^{-1}$ assigned to NCO groups in the spectra of the PU foams, which indicated the isocyanate group was completely consumed with the production of urethane or urea linkages. Meanwhile, the intensity of both the peaks at 3330 and 2870 cm$^{-1}$ in the spectrum of the polyols were weakened and became broad. These results indicated the occurrence of the efficient chemical interactions between the polyols and MDI.

Figure 6.2. FT-IR spectra of (1) polyol, (2) Switchgrass lignin, and (3) MDI; (a) pure polyol, (b) 5% lignin, (c) 10% lignin, and (d) 15% lignin content polyurethane foams
Compared to the spectrum of the control foam, no extra band was introduced by the addition of lignin into the PU foam (Figure 6.2B). There was a slight position shift of carbonyl stretching vibration band from 1703-1707 cm\(^{-1}\) by increasing the amount of lignin in the PU. This result could allow the chemical interactions that occurred between the hydroxyl bonds from the lignin and the NCO groups [31]. From this result, it can be speculated that lignin was well miscible with the PU foam matrix at a molecular level. Moreover, the bands at 1599 and 1510 cm\(^{-1}\) which also corresponds to the aromatic structure of lignin presented no significant difference between the control and lignin containing foams, revealing that the main structure of lignin was not altered by the reactions.

### 6.3.3. Apparent Density and Mechanical Properties

The apparent density and mechanical properties of the PU foams are shown in Figure 6.3. The apparent density initially increased and then decreased by increasing the lignin content (Figure 6.3a). The apparent density for the foam with 10% lignin was the highest, increased by 14.2% relative to the control foam; while the foam with 15% lignin showed the lowest density of 0.047 g/cm\(^3\), which was 12.8% lower than the control foam. In general, for foams with similar cell wall thickness, density is known to decrease as cell size increases, which further influence mechanical properties [32]. Therefore, the low density for the 15% lignin foam is due to its large cell size as evidenced by the SEM image (Figure 6.1d). Though the 10% lignin foam had similar cell size to that for the control, its relatively high density was due to thicker cell walls (Figure 6.1c). As shown in Figure 6.3b and Figure 6.3c, by increasing the lignin content to 10%, the compressive strength and compressive modulus increased from 38 and 296 KPa to 63 and 485 KPa, respectively; with additional increase in the amount of lignin, the compressive strength and compressive modulus decreased to 53 and 410 KPa, respectively. The influence of lignin content
on mechanical properties of the foams was similar to that on density. This result also confirmed that density is a prominent parameter determining mechanical properties. It can be concluded that the incorporation of lignin into the PU matrix reinforced the PU foams.

Figure 6.3. Effect of lignin content on physical and mechanical properties (a) apparent density, (b) compressive strength, and (c) compressive modulus of the PU foams
Other researchers also observed an increase in compressive strength and compressive modulus by the introduction of less than 10% of lignin into foams \[18, 33\]. However, lignin was not reinforcement filler in the foam in the report of Xue \[30\], who argued that lignin was not completely miscible with the polyol, and the uneven mixture of lignin and polyol resulted in irregular cellular structure, and thus weakened the mechanical properties. According to other researches \[34-35\], the addition of 2wt% and 1.5wt% cellulose and wood flour into foams increased the compressive strength by 21% and 30%, respectively. In this study, the compressive strength was increased by 63% with the addition of lignin to the foam. For comparison, the lignin used in this study was significant in reinforcing the mechanical properties of foams with comparison to cellulose and wood flour. The significant reinforcement functionality of lignin in the foam may be because lignin is a three-dimensional polymer acting as a compatibilizer in the PU matrix, which resulted in good molecular order of the polyurethane network \[31\]. With higher lignin content (15%), the mechanical properties of the foam were decreased, probably due to the lignin macromolecules agglomerating into segments, which reduced the uniform distribution of lignin in the foam. This will result in significant changes in the cellular structure, and weaken the strength of the foam \[17\].

6.3.4. Thermal Stability

The thermal decomposition behavior of PU foams was evaluated by TG in nitrogen and the TG profiles are presented in Figure 6.4. All the samples had a narrow degradable temperature range of 350-450°C. The decomposition processes of both the control and lignin containing foams were divided into two stages corresponding to soft and hard segments, respectively \[36\], indicating the addition of lignin into the foams had no significant influence on the degradation mechanism.
Figure 6.4. TG and DTG cures of (a) pure polyol, (b) 5% lignin, (c) 10% lignin, and (d) 15% lignin content polyurethane foams

The thermal degradation temperatures and char yield are presented in Table 6.2. The control foam started to decompose at a relative low temperature.\( T_{\text{onset}} \) (defined as the temperature at the mass loss of 5%) significantly increased as the lignin content increased, revealing that lignin in the foam could elevate the initial decomposition temperature primarily because of the thermosoluble segments produced from interactions between lignin and the PU matrix. The maximum decomposition rate temperature (\( T_{\text{max}} \)) shifted to higher temperatures with the addition of lignin. Though \( T_{\text{max}} \) for the foam with 10% lignin was lower than the PU foam with 19% soluble ammonium polyphosphate (flame retardant) [37], it was greater than the control foam about 11°C.
As shown in Figure 6.4b, the foam with 10% lignin had particularly high degradation rate at the second peak temperature. This is probably due to the ability of lignin to reinforce the soft phase of the PU matrix resulting in the enrichment of the hard segments. These results indicate that the introduction of lignin into the foam could improve the thermal stability of the foams, and the foam with 10% lignin had the best thermal stability. A similar result was found in a study of PU foam made from lignin derivatives enriched bio-polyol [29].

Table 6.2. Temperature and residue yield of the PU foams with different lignin content

<table>
<thead>
<tr>
<th>Lignin content (%)</th>
<th>$T_{onset}$ (°C)</th>
<th>$T_{max}$ (°C)</th>
<th>Char yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>133</td>
<td>323</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>140</td>
<td>332</td>
<td>5.8</td>
</tr>
<tr>
<td>10</td>
<td>178</td>
<td>335</td>
<td>12.4</td>
</tr>
<tr>
<td>15</td>
<td>224</td>
<td>334</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Char yield showed an increasing trend as the lignin content in the foams increased. Char yield for the foam with 10% lignin content was more than 2 times that for the control. This is mainly due to the cross-linkage cellular structure and thermo stable nature of lignin. The difference in char yield among the control and lignin containing foams further confirmed that lignin acted as thermal filler in the PU foams.

6.4. CONCLUSIONS

The addition of less than 10% of lignin fractionated from microwave liquefied switchgrass into the PU matrix had no significant influence on the microstructures of the PU foam, while higher lignin content (15%) in the PU matrix resulted in foam with large cell size. FT-IR spectra indicated the occurrence of chemical interactions between lignin hydroxyl groups and NCO groups with the production of an extra hydroxyl bond. The foam with 10% lignin content had the highest apparent density of 0.061g/cm$^3$, best mechanical strength (compressive strength and compressive modulus), and superior thermal stability. Further increase of the lignin content in
the foam resulted in a decline in the apparent density and mechanical properties. The lignin obtained from liquefied switchgrass could be used as reinforcement filler in the preparation of semi-rigid polyurethane foams.

6.5. REFERENCES


CHAPTER 7. BIO-BASED POLYURETHANE FOAM INSULATION FROM MICROWAVE LIQUEFACTION OF WOODY UNDERBRUSH

7.1. INTRODUCTION

Insulation plays a key role in green housing due to its ability to conserve energy associated with heating and cooling, and it is growing in popularity for residential and commercial housing. Polyurethane (PU) foam is one of the most versatile construction insulations because of its low density, low thermal conductivity, and high mechanical performance. Currently, the PU foam industry is still highly dependent on petro-based chemicals due to its two major feedstocks, i.e. polyol and isocyanate. With the growing concern of environmental protection and rapid depletion of fossil fuels, numerous efforts have been focused on the substitution of petro-based polyols with bio-based polyols, such as vegetable oil [1] and bio-polyol, derived from lignocellulosic biomass [2-3].

Liquefaction is one of the promising thermochemical conversion routes to convert lignocellulosic biomass into valuable chemicals [4-5]. Through liquefaction, the high molecular weight components of biomass are broken down to low molecular chemical products. One major application of the liquefaction product is to produce the bio-based PU foam [3]. It has been demonstrated that the bio-foams from the liquefaction of lignocellulosic biomass are comparable with petro-based ones [6]. Until recently, a considerable amount of biomass have been liquefied to produce bio-based PU foams, such as agricultural wastes, e.g., wheat straw [7], corn bran [8], cornstalk [9], sugar-cane bagasse [10-11], soybean straw [12], and coffee grounds [6], as well as

woody materials, e.g. waste paper [13], bamboo [3], lignin [14-15], cork [16-17], wood powder [18], and wood bark [19]. However, currently there is no research on the production of PU foam from the liquefaction of low-diameter woody underbrush.

Highly abundant woody underbrush could provide ample biofuels for catastrophic wildfires that pose a threat to forest health and safety. Therefore, the removal and utilization of woody underbrush could support the goal of reducing catastrophic wildfires by reducing forest fuel loading levels and improving overall forest health. Moreover, the rapid growth and wide distribution of woody underbrush can continue to supply lignocellulosic biomass. Yaupon holly (*Ilex vomitoria*) is one of the most widespread woody underbrush species in the southeastern United States [20] that has great potential for use as a raw material to produce bio-foam insulation via liquefaction.

In this work, the microwave liquefaction parameters of yaupon holly were optimized using a single factor method, and the liquefaction products were analyzed by Fourier transform infrared (FT-IR) spectrometry. The optimal liquefaction product with solid residue would be used directly to produce bio-foam. The cross-section morphology of the bio-foams was imaged by scanning electron microscopy (SEM). The physico-mechanical properties, including density, thermal conductivity, thermal stability, and compressive properties of the resulting bio-foams, were evaluated to obtain the most promising PU foam from a series of isocyanate index formulas.

7.2. MATERIALS AND METHODS

7.2.1. Materials and Chemicals

The yaupon holly collected at the Bob R. Idlewild Research Station near Clinton, Louisiana, USA, was ground into 6- to 8-mesh, 8- to 16-mesh, 16- to 40-mesh, 40- to 60-mesh, and 60- to
80-mesh and oven-dried at 105 °C until it reached a constant weight. The chemical compositions of yaupon holly are as follows: α-cellulose (45.26%), hemicellulose (28.10%), Klason lignin (23.46%), alcohol-toluene extracts (4.01%), 1% sodium hydroxide (NaOH) solubility (27.53%), hot-water extracts (9.20%), and ash content (0.91%). The holocellulose, α-cellulose, lignin content, hot-water extracts, alcohol-toluene extractives, 1% NaOH solubility, and ash content of the raw material were determined in accordance to ASTM D1104-56 (1971) [21], ASTM D1103-60 (1971) [22], ASTM D1106-96 (1996) [23], ASTM D1110-96 (1996) [24], ASTM D1107-96 (1996) [25], ASTM D1109-84 (2001) [26], and ASTM D1102-84 (2001) [27], respectively. The hemicellulose content was established as reported by Zhang et al. (2012b) [28].

Glycerol, ethylene glycol (EG), methanol, and 98% sulfuric acid (H2SO4) were purchased from VWR International (Radnor, PA, USA). Polymeric methylene diphenyl diisocyanate (pMDI) with 30% to 50% of 4,4′-methylenediphenyl diisocyanate and 50% to 70% of diphenylmethane diisocyanate was kindly supported by Huntsman Polyurethanes (Woodlands, TX, USA). The average functionality, isocyanate (NCO) group content, and viscosity at 25 °C of pMDI (Rubinate M) are 2.7, 31.0%, and 192 cps, respectively. Dow corning 193 (Dow Corning Corporation, Midland, MI, USA) was used as a surfactant and the combination of dimethylcyclohexylamine (Jeff cat DMCHA) (Huntsman Corporation, Woodlands, TX, USA) with dibutyltin dilaurate (Pfaltz & Bauer, Waterbury, CT, USA) was used as a co-catalyst for the preparation of PU foams. Water was used as the eco-friendly blowing agent. All of the chemicals were used without further purification.
7.2.2. Methods

7.2.2.1. Microwave Liquefaction

Liquefaction of yaupon holly was performed in a Milestone laboratory microwave oven (Shelton, CT, USA) equipped with an ATC-400FO automatic fiber optic temperature control system. Glycerol and EG with the ratio from 1:1 to 5:1 were used as the liquefaction solvent. Pre-weighed yaupon holly by different liquid to solid ratios in the range of 2:1 to 6:1 and 98% sulfuric acid (percentage of solvent mass varying from 0.5% to 4.5%, wt/wt) were thoroughly premixed before cooking. The reaction temperature was elevated from room temperature to the desired temperature (120 °C to 200 °C) within 5 min, and then maintained for 2.5 min to 10 min. Four replicates were carried out for each liquefaction parameter. The ice bath was applied to quench the reaction when the reaction was done. After cooling, liquefied products were dissolved in 150 mL of methanol under constant stirring for 4 h and filtered through Whatman No. 4 filter paper (GE Healthcare, Chicago, IL, USA) to separate the liquid and solid residue. The liquid portion was evaporated at 65 °C under vacuum to remove methanol. The gaseous products were vented because the yield of gaseous products was negligible. The solid residue that remained on the filter paper was oven-dried and weighted for the calculation of liquefaction conversion yield as Eq. 7.1,

\[
\text{Conversion yield (\%) = } (1 - \frac{\text{weight of residue (g)}}{\text{weight of raw material (g)}}) \times 100
\]  

(7.1)

7.2.2.2. Acid and Hydroxyl Number of Bio-polyols

The procedure to determine acid number was shown as follows: A mixture of 1 g bio-polyol sample and 20 mL dioxane-water solution (4/1, v/v) was titrated with 0.1 mol/L NaOH to endpoint (pH 8.3). The blank titration was conducted using the same procedure. Acid number was
calculated as Eq. 7.2,

\[ AN = \frac{C-D}{W} \cdot N \cdot 56.1 \]  \hspace{1cm} (7.2)

The procedure to determine hydroxyl number was shown as follows: 1 g of bio-polyol and 10 mL of phthalic anhydride solution (dissolving 150 g phthalic anhydride in 900 mL of dioxane and 100 mL pyridine) were added into a 150 mL beaker. The beaker was sealed and put into a boiling water bath for 20 min. After cooling down, 20 mL of dioxane-water solution (4/1, v/v) and 5 mL of water were added to the beaker and then titrated with 1 mol/L NaOH to pH 8.3. Blank titration was conducted using the same procedure. Hydroxyl number was calculated as Eq. 7.3,

\[ HN = \frac{B-S}{W} \cdot N \cdot 56.1 + AN \]  \hspace{1cm} (7.3)

where \( AN \) and \( HN \) represent acid number and hydroxyl number (mg KOH/g), \( B \) and \( D \) are the volume of NaOH standard solution consumed in blank titration (mL); \( C \) and \( S \) are the volume of NaOH standard solution consumed in sample titration (mL); \( W \) is the sample weight (g); and \( N \) stands for the equivalent concentration of NaOH standard solution (mol/L).

7.2.2.3. Preparation of PU Bio-foams

The liquefaction products were used directly to produce PU foam without separating the solid and liquid portions. The PU foams were prepared by a one-step method. A mixture of 3.00 g liquefaction products, 0.30 g co-catalyst (Jeff cat DMCHA : dibutyltin dilaurate = 1:1 ), 0.20 g deionized (DI) water, and 0.20 g surfactant was thoroughly premixed in a plastic beaker with a mechanical stirrer for 1 min, followed by adding an established amount of pMDI (i.e., 5.80 g, 6.63 g, 7.46 g, and 8.29 g) with stirring at 1500 rpm for 3 min. The isocyanate index was set as 105, 120, 135, and 150, and calculated in accordance to previous literature as shown in Eq. 7.4
All the foam samples were allowed to freely rise and cure at ambient condition for 2 days before characterization.

\[
\text{Isocyanate index} = \frac{\frac{m_{\text{iso}} \cdot \%_{\text{NCO}}}{M_{\text{NCO}}}}{m_{\text{polyol}} \cdot \frac{OH\text{ number} + AN}{M_{\text{KOH}}} + m_{\text{H}_2\text{O}} \cdot Eq_{\text{H}_2\text{O}}} \cdot 100
\]  

(7.4)

In Eq. 7.4, \(m_{\text{iso}}\) is the mass of pMDI (g), \(\%_{\text{NCO}}\) is the quantity of NCO groups in pMDI (31.0%), \(M_{\text{NCO}}\) is the molecular weight of NCO group (0.042 g/mmol), \(m_{\text{polyol}}\) is the mass of the polyol (g), \(M_{\text{KOH}}\) is the molecular weight of potassium hydroxide (KOH) (56.1 mg/mmol), \(OH\text{ number}\) and \(AN\) are the hydroxyl number and the acid number of polyol, respectively (mg KOH/g), and \(m_{\text{H}_2\text{O}}\) is the mass of water used as blowing agent, while \(Eq_{\text{H}_2\text{O}}\) is the equivalent of OH groups in the water (111 mmol/g).

7.2.2.4. Characterization of Liquefaction Products

Fourier transform infrared spectrometry (Madison Instruments, Middleton, WI, USA) was used to study the chemical structure of the liquefaction products. The FT-IR analysis was performed on a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MK II Single Reflection ATR accessory. A small quantity of sample was covered flatwise on the detection window. Each sample was analyzed in the range of resolution from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) with a spectral resolution of 4 cm\(^{-1}\) and a total of 32 scans were collected.

7.2.2.5. Characterization of Bio-foams

Scanning electron microscopy (JSM-6610 LV, JEOL, Tokyo, Japan) was used to examine the morphology of the bio-foams. Prior to analysis, the samples were gold coated using a EMS 550 X sputter coater (Electron Microscopy Sciences, Hatfield, PA, USA). Images of the cross-
section of bio-foams were obtained. The average cell diameter was calculated from 50 measurements.

The density of the PU foams was determined by dividing the weight of the specimens (30 × 30 × 30 mm³) by the calculated volume, according to ASTM D1622-08 (2008) [29]. Ten replicates were carried out for each group.

The thermal conductivity of bio-foams was determined via a KD2 Pro (Decagon Devices, Pullman, WA, USA). A 10 min read time was used to minimize the contact resistance errors. Ten replicates were conducted for each group.

An eXpert 2610 universal mechanical test analyzer (ADMET, Norwood, MA, USA) was used to measure the compressive properties of the foams. Samples (10 × 10 × 10 mm³) were placed between the two parallel plates and compressed at 10 mm/min. The Young’s modulus was calculated by the slope of the tangent of the linear portion in the stress-strain profile in accordance to the method described in previous reports [6, 16]. The compressive stress was taken from the stress-strain curve at a deformation of 10%. Ten replicates were measured for each group.

The thermogravimetric and differential thermogravimetric (TG/DTG) analysis of bio-foams were conducted with a thermal analyzer Q50 TGA (TA Instruments, New Castle, DE, USA) to simultaneously obtain thermogravimetric data. Each sample (approximately 5 mg) was conducted at 30 °C to 800 °C with a constant heating rate of 20 °C/min under a flow of 40 mL/min of nitrogen atmosphere.

7.2.2.6. Statistical Analysis

Statistical analysis was conducted using SAS (version 9.1, SAS Institute, Cary, NC, USA). An analysis of variance (ANOVA) was performed to determine the significant differences (α = 0.05).
0.05) among the different levels within a single factor.

**7.3. RESULTS AND DISCUSSION**

**7.3.1. Optimization of Liquefaction Parameters**

The liquefaction conversion yield of yaupon holly with respect to particle size, glycerol to EG ratio, liquid solvent to solid ratio, sulfuric acid (H$_2$SO$_4$) concentration, liquefaction time, and liquefaction temperature are shown in Figure 7.1 to 7.6.

![Figure 7.1. Liquefaction conversion yield with respect to particle size](image)

(Other conditions: Glycerol:EG = 4:1, liquid:solid = 3:1, H$_2$SO$_4$: 1.5%, reaction time: 10 min, and temperature: 140 °C)

From Figure 7.1, all conversion yields of yaupon holly were higher than 82%, and the maximum value (89.9%) was observed from the category of 16- to 40-mesh. According to the ANOVA, no significant (p > 0.05) difference on the conversion yields was found among the different particle sizes. It is understood that smaller particle size can provide a benefit associated with a greater contact area between the biomass and solvent, which increases the conversion yield. However, if the particles are too fine (> 40-mesh in this case), they will tend to aggregate.
and it is hard to acquire a homogeneous mixing, resulting in a low conversion yield. Similar tendencies were reported from the liquefaction of cork and bamboo shoot shell [17, 30]. Hence, the optimal particle size, in this work, was 16- to 40-mesh.

Figure 7.2. Liquefaction conversion yield with respect to glycerol to EG ratio
(Other conditions: Particle size: 16- to 40-mesh, liquid:solid = 3:1, H2SO4: 1.5%, reaction time: 10 min, and temperature: 140 °C)

It has been reported that the co-solvents of glycerol and EG can effectively promote the liquefaction of biomass at atmospheric pressure [16]. With an increasing glycerol to EG ratio from 1:1 to 2:1 the liquefaction conversion yield significantly (p < 0.05) increased from 79.3% to 88.1%, and then slightly declined to 84.4% as the ratio reached 5:1 (Figure 7.2). It has been demonstrated that glycerol is very effective in enhancing the decomposition of biomass [11] because glycerol can reduce the surface tension of the liquefaction solvent and accelerate the diffusion of small molecules from liquefied biomass into the liquefaction solvent [28]. Therefore, to a certain extent, increasing the glycerol loading could obtain a higher conversion yield. In contrast, the reduction of conversion yield with further increase in glycerol loading was probably
attributed to the decrease of flowability of liquefaction solvent while adding less EG that has a lower viscosity as compared with glycerol. In that case, lower flowability could not have a great homogenous reactants mixture in the same stirring speed, thereby leading to a lower conversion yield. Even though the maximum conversion yield was observed at the glycerol to EG ratio of 2:1, considering the glycerol will be replaced by crude glycerol (i.e., a byproduct of the production of biodiesel) in the authors’ future work, a little higher glycerol loading (3:1) was deliberately selected as the optimal liquefaction solvent.

Figure 7.3. Liquefaction conversion yield with respect to liquid to solid ratio
(Other conditions: Particle size: 16- to 40-mesh, glycerol:EG = 3:1, H2SO4: 1.5%, reaction time: 10 min, and temperature: 140 °C)

Figure 7.3 illustrates the influence of solvent liquid to biomass solid ratio on the liquefaction conversion yield. The conversion yield exhibited a slight increase as the liquid to solid ratio increased from 2:1 to 5:1, and thereafter decreased minimally when the ratio reached 6:1. This result was in line with the finding reported by Jo et al. (2015) [31]. The ANOVA indicated that there was no significant difference in conversion yield with the change of liquid to
solid ratio. Insufficient liquefaction solvent could result in an insufficient contact between the biomass and solvent, which could lead to an incomplete liquefaction reaction. Moreover, insufficient solvent could also increase the viscosity of reaction system that will lead to recondensation/repolymerization reactions between the liquefied components, resulting in a lower liquefaction efficiency [32]. In contrast, the viscosity of the reaction system could be decreased by increasing the liquefaction solvent loading, and the liquefaction reaction would be promoted. However, an excessive liquefaction solvent will increase the solvent-related costs for bio-polyol synthesis. Overall, the liquid to solid ratio of 3:1 with a conversion yield of 88.0% was chosen in this work.

Figure 7.4. Liquefaction conversion yield with respect to H2SO4 concentration (Other conditions: Particle size: 16- to 40-mesh, Glycerol:EG = 3:1, liquid:solid = 3:1, reaction time: 10 min, and temperature: 140 °C)

It has been established that the liquefaction of biomass is mainly comprised of decomposition and solvolysis processes [5, 33], and the presence of catalyst is crucial to increase the liquefaction process and reduce the liquefaction temperature and time [34]. One of the most
Effective catalysts is sulfuric acid because it provides highly reactive protons (H\(^+\) ions) that are able to promote the hydrolytic reactions of glycosidic bonds, resulting in the dissolution of biomass [35]. As expected, the increase of H\(_2\)SO\(_4\) concentration had a positive effect on the liquefaction content of yaupon holly (Figure 7.4). The conversion yield significantly (p < 0.05) increased 102.3% as the H\(_2\)SO\(_4\) concentration increased from 0.5\% to 1.5\%. The maximum conversion yield (94.56\%) was obtained at the H\(_2\)SO\(_4\) concentration of 3.5\%. Thereafter, a reduction of conversion yield was observed at 4.5\% H\(_2\)SO\(_4\). This result was ascribed to the occurrence of recondensation/repolymerization among liquefied fragments with the excessive addition of sulfuric acid, resulting in an increase of insoluble residue [36-37]. Because no statistical difference on the conversion yield was found between the H\(_2\)SO\(_4\) concentration of 1.5\% and 3.5\%, the optimal H\(_2\)SO\(_4\) concentration was considered to be set at 1.5\%.

![Figure 7.5. Liquefaction conversion yield with respect to reaction time](image)

(Other conditions: Particle size: 16- to 40-mesh, glycerol:EG = 3:1, liquid:solid = 3:1, H\(_2\)SO\(_4\): 1.5\%, and reaction temperature: 140 °C)
Notably, approximately 88% of yaupon holly was liquefied at the initial rapid increase state within 10 min. At the slow increase stage from 10 min to 17.5 min, the conversion yield gradually increased to 94.2% (Figure 7.5). The rapid increase of conversion yield within 10 min was ascribed to the decomposition of hemicellulose, lignin, and amorphous zones of cellulose because they are susceptible to liquefaction process [28, 36]. The decomposition of the crystalline regions of cellulose made a contribution to the slow increase stage of liquefaction [38]. Microwave liquefaction is a time and energy saving strategy to convert biomass into useful products [5, 39]. Microwaves induce heat at the molecular level by direct conversion of electromagnetic energy into heat, resulting in a fast heating rate [40]. Accordingly, 10 min was used as the optimal liquefaction time.

Figure 7.6. Liquefaction conversion yield with respect to reaction temperature

(Other conditions: Particle size: 16- to 40-mesh, glycerol:EG = 3:1, liquid:solid = 3:1, H2SO4: 1.5%, and reaction time: 10 min)

The effect of liquefaction temperature on conversion yield is shown in Figure 7.6. It was obvious that the conversion yield increased significantly (p < 0.05) as the temperature increased
from 120 °C to 160 °C. With further increase in the reaction temperature, the conversion yield slightly dropped. In general, the liquefaction of biomass is a dynamic balance between reactions of decomposition of macromolecules and the recondensation/repolymerization of small liquefied fragments [41]. Thus, raising the temperature from 120 °C to 160 °C, the amount of activated macromolecules and their internal energy increased [42], which caused more and more chemical bonds to be broken. In this situation, the decomposition overweighed recondensation and/or repolymerization, which resulted in the increase of conversion yield [43]. While, in the severe reaction temperature, the degradation gradually decreased and the recondensation and/or repolymerization played a dominant role, which attributed to the decrease of conversion yield [32]. Thus, 160 °C would be the most desirable liquefaction temperature for yaupon holly within the studied range. Hereafter, three duplicates were run using the optimized liquefaction parameters and the optimal liquefaction conversion yield was 94.90%.

7.3.2. FT-IR Spectra of Liquefaction Products

Figure 7.7 presents the FT-IR spectra of the raw material, solid residue, bio-polyol, and liquefied yaupon holly (bio-polyol with solid residue). It was clear that the macromolecules in wood were broken down after liquefaction, which was evidenced from the observation of methyl and/or methylene (2935 cm$^{-1}$ and 2874 cm$^{-1}$) in solid residue [44]. The intensified -OH characteristic peak at around 3330 cm$^{-1}$ was observed on the spectrum of solid residue [45], which indicated that the hydroxyl groups in the raw materials were released through liquefaction. The strong hydroxyl group peaks in bio-polyol and liquefied yaupon holly were partially attributed to liquefaction solvent, *i.e.* glycerol and EG. The other part of hydroxyl sources were derived from the liquefaction of yaupon holly.
One of the hydroxyl sources is the liquefaction of hemicellulose, which can produce an abundance of C5 sugars with a multi-hydroxyl structure [5, 35]. The prominent peaks appeared on the spectra of bio-polyol and liquefied yaupon holly at 1730 cm$^{-1}$ corresponding to acetyl and uronic ester groups in hemicellulose [46], which suggested that the hemicellulose in the raw material was successfully liquefied and dissolved into bio-polyol. The liquefaction of cellulose is another hydroxyl source, which provides an abundance of C6 sugars that are rich in hydroxyl groups [5, 35]. The liquefaction of cellulose could be observed from the observation of cellulose characteristic peaks in bio-polyol and liquefied yaupon holly at 1420 cm$^{-1}$ (C-H$_2$), 1035 cm$^{-1}$ (C-O), and 899 cm$^{-1}$ (C-H) [44, 46]. The peaks at 1600 cm$^{-1}$ and 1500 cm$^{-1}$ (C=C in aromatic rings), 1456 cm$^{-1}$ (C-H in aromatic rings), and 1235 cm$^{-1}$ (guaiacyl ring) corresponded to lignin [46-47].
These peaks were discovered in the spectra of bio-polyol and liquefied yaupon holly, which indicated that the lignin in the raw material was successfully liquefied and dissolved into bio-polyol as well. Moreover, the lignin-derived hydroxyl group was also observed in the bio-polyol at a peak of 1370 cm\(^{-1}\) [48], which suggested that the liquefaction of lignin was also a hydroxyl source. The hydroxyl number of bio-polyol was 347.42 ± 8.61 mg KOH/g determined using a titration method. This hydroxyl number was closed to the value (343 mg KOH/g) from the liquefaction of cork at 150 °C for 80 min heated by conventional method [16].

### 7.3.3. Characterization of Bio-foams

Because the cell structure and pore size of PU foams are closely related to their thermal conductivity and mechanical properties [6], it is necessary to characterize the microstructure of bio-foams. The SEM images of the cross-section surfaces of the bio-foams with different isocyanate indexes are depicted in Figure 7.8. It was found that the foam cells became more regular and smooth with an increased isocyanate index from 105 to 150. Especially, bio-foams with an isocyanate index of 135 and 150 exhibited a formal honeycomb skeleton covered by a thin membrane, which was beneficial to increase the thermal insulation property. With an increased isocyanate index from 105 to 135, the pore diameter gradually increased from 161.5 µm to 242.1µm. In contrast, with further increase in the isocyanate index to 150, it decreased to 223.5µm. The increase of pore diameter was probably attributable to the increase of CO\(_2\) amount as the increase of isocyanate index. However, the decreasing pore size at PU150 was probably due to the increase of cell wall elasticity, which could contribute to restricting the CO\(_2\) blowing and expanding, resulting in a smaller pore diameter. As reported in literature, the increase of isocyanate index could increase the formation of allophanate crosslinks, which has a positive effect on the elasticity of cell wall [49]. As a whole, the pore diameter was comparable to that of
sugarcane bagasse-derived PU foam [10]. The SEM micrographs indicated that the variation of isocyanate index played an important role in the microstructure of the bio-foams.

Figure 7.8. SEM images of bio-foams as a function of isocyanate index
(a: 105; b: 120; c: 135; d: 150)
As shown in Table 7.1, the densities of bio-foams decreased with increased isocynate index from 105 to 135, and then increased as the isocynate index increased to 150. The density was highly dependent on the foam cell size. In general, foam with larger pore diameter will have a lower density and vice versa [50]. Besides, the density of cellular material is also related to its cell wall thickness. In this work, even though the pore diameter of PU150 was bigger than those
of PU105 and PU130, its density presented a greater value as compared with PU105 and PU130. The result was probably attributable to its thick wall structure. As reported, the densities of bio-foams made from liquefaction of biomass are in the range of 20.4 kg·m$^{-3}$ to 119.5 kg·m$^{-3}$ [6, 10-11, 16-17, 51]. In comparison to these foams, the bio-foams obtained in this work had a low density varying from 15.16 kg·m$^{-3}$ to 18.46 kg·m$^{-3}$.

Table 7.1. Physico-mechanical properties of bio-foams with respect to isocyanate index

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<th>Sample ID</th>
<th>Density (kg·m$^{-3}$)</th>
<th>Thermal Conductivity (W·m$^{-1}$·K$^{-1}$)</th>
<th>Young's Modulus (kPa)</th>
<th>Compressive Stress ($\delta_{10%}$ kPa)</th>
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<td>PU105</td>
<td>18.11 ± 2.04</td>
<td>0.035 ± 0.004</td>
<td>68.81 ± 9.17</td>
<td>6.13 ± 0.57</td>
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<td>PU120</td>
<td>18.00 ± 1.46</td>
<td>0.036 ± 0.003</td>
<td>79.41 ± 12.54</td>
<td>7.84 ± 0.85</td>
</tr>
<tr>
<td>PU135</td>
<td>15.16 ± 1.13</td>
<td>0.037 ± 0.002</td>
<td>125.87 ± 16.98</td>
<td>10.94 ± 1.21</td>
</tr>
<tr>
<td>PU150</td>
<td>18.46 ± 1.15</td>
<td>0.033 ± 0.002</td>
<td>176.66 ± 15.47</td>
<td>15.35 ± 1.09</td>
</tr>
</tbody>
</table>

Thermal conductivity is the key thermal property that governs insulation applications of PU foams. It is closely related to the foam density, cell orientation, the ratio of open to closed cells, and the thermal conductivity of trapped gas [52]. It was observed that the thermal conductivity value of bio-foams gradually increased from 0.035 W·m$^{-1}$·K$^{-1}$ to 0.037 W·m$^{-1}$·K$^{-1}$ with the increased isocyanate index from 105 to 135, and the minimum value (0.033 W·m$^{-1}$·K$^{-1}$) was obtained from PU150, as shown in Table 7.1. The result was ascribed to the variation of foam density. In general, thermal conductivity is inversely proportional to density of the PU foam, probably because of the lower radiant heat transfer rate through the gases trapped in small cells [10]. The thermal conductivity values were comparable with those of corn stover derived foam ranging from 0.032 W·m$^{-1}$·K$^{-1}$ to 0.039 W·m$^{-1}$·K$^{-1}$ [51]. It should be noted that they were satisfactory to be used as insulation foam in which the thermal conductivity varies between 0.0233 W·m$^{-1}$·K$^{-1}$ and 0.0505 W·m$^{-1}$·K$^{-1}$ [6, 15].
The compressive stress-strain curves of bio-foams were composed of three regions as shown in Figure 7.9. The first linear region (< 10%) corresponded to the elastic response of material with foam cell walls bending, followed by a so-called plateau-collapse region that the cell walls buckled and yielded, and finally, beyond 25% deformation, the compressive stress underwent a rapid increase process and the foams became densified because the cell walls were crushed together. Figure 7.9 also indicates that the isocyanate index had a dramatic effect on the mechanical properties of bio-foams. With increased isocyanate index, both the compressive stress at 10% strain and the slope of the linear region increased gradually, which suggested that the compressive properties were enhanced by adding more pMDI. The result was confirmed in Table 7.1. The excessive isocyanate groups (NCO) could be reacting with urethane and urea to form allophanate and biuret, which could provide stronger linkages than urethane bonds [53], resulting in rather strong mechanical properties. It was noteworthy that the maximum Young’s modulus (176.7 kPa) and compressive stress (15.4 kPa) obtained from PU150 were superior to
that of the bio-based polyurethane insulation foam derived from the liquefaction of coffee grounds, in which the Young’s modulus varied from 73.2 kPa to 88.6 kPa and the compressive stress ranged from 2.5 kPa to 7.3 kPa [6], suggesting that sufficient mechanical properties of polyurethane foam could be obtained from PU150 for the application of thermal insulation.

Figure 7.10 presents the TG and DTG curves of bio-foams under nitrogen. There were three distinctive regions of major weight loss for these bio-foams. The weight loss up to 150 °C was considered to be due to the evaporation of the moisture content and the release of volatile components. The DTG curves exhibited a fluctuant status between 140 °C and 230 °C, which were attributed to the reversible dissociation and reassociation reaction of the unstable urethane links [54]. This decomposition became irreversible around 230 °C and reached the maximum at approximately 330 °C. The second region of the significant weight loss was at approximately 400 °C, which might have been caused by the decompositions of polyol and liquefied wood components [19, 51]. Finally, the third region centered at approximately 490 °C was assigned to the degradation of lignin and other more difficult to break parts [55]. Moreover, it also corresponded to the degradation of pMDI. It was worthy to note that increasing the isocyanate index resulted in the increase of the maximum decomposition temperature from 324.42 °C to 336.34 °C. It was probably ascribed to the higher isocyanate index that could contribute to higher crosslink density, which could enhance the thermal stability of bio-foams [19]. The thermal stability and degradation behavior of bio-foams produced in this work were similar to those of sugarcane bagasse-derived PU foam [11].

Therefore, it could be said that the bio-polyol from the liquefaction of yaupon holly can be used directly to produce PU foam. It was recommended that the resulting low-density insulation
foam with low thermal conductivity can be produced using the isocyanate index 150, and it can be used as thermal insulation.

![Figure 7.10. TG and DTG curves of bio-foams as a function of isocyanate index](image)

**7.4. CONCLUSIONS**

In this work, yaupon holly was subjected to microwave liquefaction to produce bio-based polyurethane foam insulation. The optimized liquefaction parameters can be summarized as follows: 1) particle size was controlled in the range of 16- to 40-mesh; 2) both the glycerol to EG ratio and liquid to solid ratio were set at 3:1; 3) the liquefaction process was conducted at 160 °C for 10 min and catalyzed by 1.5% H₂SO₄. The optimal liquefaction conversion yield was 94.9%. The FT-IR spectra of liquefaction products confirmed the successful liquefaction of hemicellulose, cellulose, and lignin that are sources of hydroxyl groups. The hydroxyl number of bio-polyol was 347.4 mg KOH/g, which was determined using a titration method. The desired low-density bio-based PU foam was obtained by controlling the isocyanate index at 150. The density, thermal conductivity, Young’s modulus, and compressive stress of the resulting low-
density bio-foam were 18.5 kg·m$^{-3}$, 0.033 W·m$^{-1}$·K$^{-1}$, 176.7 kPa, and 15.4 kPa, respectively. It is noteworthy that this low-density bio-foam is suitable for use as construction insulation.

7.5. REFERENCES


ASTM International, West Conshohocken, USA.


CHAPTER 8. OVERALL CONCLUSIONS

8.1. MAIN CONCLUSIONS

In this work, biomass, such as rape straw, switchgrass, and yaupon holly (*Ilex vomitoria*), were liquefied using microwave heating to produce bio-based polyurethane foams.

The liquefaction of rape straw indicated that higher liquefaction temperature helped obtain better energy consumption efficiency when heated by microwave irradiation. GC-MS demonstrated the decomposition of hemicellulose, cellulose, and lignin during liquefaction. Generally, the main chemical components of bio-polyols were directly related to the liquefaction conditions. Moderate liquefaction conditions could result in a high content of hydroxyl group products, while severe reaction conditions could produce a high yield of levulinic ester products.

Thermogravimetric analysis of raw rape straw and solid residues indicated the solid residue from the 180 °C/15 min samples had the highest thermal stability under a high temperature (>700°C) condition among all solid residues. The rapid decomposition of hemicellulose and lignin during liquefaction contributed to the decrease of activation energy ($E_a$), whereas the recondensation/repolymerization reaction occurring at 180 °C/15 min remarkably increased $E_a$. The lowest $E_a$ was found in the solid residue from 180 °C/10 min.

CNCs were successfully extracted from solid residues through treatments of dilute alkali and hydrogen peroxide combined with high-intensity ultrasonication. Most of the lignin and hemicelluloses in the liquefied residues from 180°C/7.5 min were removed during the liquefaction, resulting in cellulose as core structure. The retained hemicelluloses and impurities in the solid residue were eliminated by 2% NaOH and 5% H$_2$O$_2$ treatments. With high-intensity ultrasonic nanofibrillation treatment, CNCs with an average diameter of 12.59 nm were obtained from chemically purified samples.
By replacing 20% of petro-based polyol with bio-polyol, the PU foam cell became more homogenous and finer, resulting in a low thermal conductivity and high mechanical performance, while, further increasing bio-polyol content from 20 to 40%, the cell diameter was increased by 460% and both the Young’s modulus and compressive stress decreased by 70%. However, the 40% bio-polyol foam could be remarkably reinforced by 4% CNCs because the hydroxyl-rich structure in CNCs increased the crosslinking density resulting in the increase of physico-mechanical performance of bio-foam. As compared with PU foam without CNCs, the Young’s modulus and compressive stress in the optimal 4% CNCs reinforced bio-foam increased by 590% and 150%, respectively.

The addition of less than 10% of lignin fractionated from microwave liquefied switchgrass into the PU matrix had no significant influence on the microstructures of the PU foam, while higher lignin content (15%) in the PU matrix resulted in foam with large cell size. The foam with 10% lignin content had the highest apparent density of 0.061 g/cm³, best mechanical strength (compressive strength and compressive modulus), and superior thermal stability. The lignin obtained from liquefied switchgrass could be used as reinforcement filler in the preparation of semi-rigid polyurethane foams.

The optimized parameters of the microwave liquefaction of underbrush can be summarized as follows: 1) particle size was controlled in the range of 16- to 40-mesh; 2) both the glycerol to EG ratio and liquid to solid ratio were set at 3:1; and 3) the liquefaction process was conducted at 160 °C for 10 min and catalyzed by 1.5% H₂SO₄. The optimal liquefaction conversion yield was 94.9%. The density, thermal conductivity, Young’s modulus, and compressive stress of the resulting low-density bio-foam were 18.5 kg·m⁻³, 0.033 W·m⁻¹·K⁻¹, 176.7 kPa, and 15.4 kPa,
respectively. It is noteworthy that this low-density bio-foam is suitable for use as construction insulation.

8.2. FUTURE WORK

The possible future works are presented here in the aspects of the work for each chapter (Chapters 2 to 7).

1) Because the liquefaction of biomass at a severe reaction condition can produce levulinic ester products, addictive in petroleum, microwave heating should be applied to boost the reaction temperature in minutes. Therefore, it is possible to prepare levulinic ester products in a rapid and energy-saving way.

2) The liquefaction process could unpack the plant cell structure, which will help reduce the energy consumption of pyrolysis of solid residue. So, people can optimize the liquefaction conditions in order to fully destroy the cell structure, in order to decrease energy consumption during pyrolysis.

3) CNCs extracted from solid residues do not have an uniform dimension; therefore, the CNCs’ quality control will be a possible future work.

4) Although CNCs reinforced PU foam has a high physico-mechanical performance, the use of high amount of CNCs will indeed increase the cost. The research on reducing CNCs content and increasing their distribution stability will be significant in the future.

5) More than 50 million tons of lignin is produced annually in the U.S. paper industry and yet only 2% of this material is used commercially. It has been demonstrated that lignin can be used as a reinforcement filler in the production of PU foam. The future work should be focused on the modification of lignin and increasing lignin content in PU foam matrix.
6) The production of PU foam from the liquefaction of woody underbrush should be investigated in a pilot scale to further realize the application of microwave liquefaction in the PU foam industry.
APPENDIX. PERMISSION LETTER

For chapter 3

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VITA

Xingyan Huang was born in Sichuan Province, China. He obtained the BS in Wood Science and Engineering from Sichuan Agricultural University, Sichuan, China, in 2013. He got his MS Silviculture from Sichuan Agricultural University as well with Dr. Jinqiu Qi as his advisor, in 2015, where he studied wood and bamboo anatomy, physical-mechanical properties and chemical properties. Since 2016, he has studied in the School of Renewable Natural Resources at Louisiana State University as a Ph.D candidate with Dr. Cornelis F De Hoop as advisor. His research focuses on the preparation, characterization, and application of polyurethane foams made from microwave liquefaction of biomass. He anticipates graduating with his Ph.D degree in December 2018.