Preparation of Bio-based Polyurethane Foams from Liquefied Cassava Bagasse and Polymeric Diphenylmethane Diisocyanate

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Cassava bagasse (CB) was liquefied using polyethylene glycol to prepare polyol. The liquefied cassava bagasse (LCB) was reacted with polymeric diphenylmethane diisocyanate (PMDI) to produce novel bio-based polyurethane foams (PUF) via a one-pot process. The results showed that the density of the LCB-PUF was in the range of 0.027 to 0.039 g/cm³. When the LCB was used to instead of polyether polyol with a replacement ratio rising from 20% to 100%, the compressive strength of the LCB-PUF decreased from 0.171 to 0.057 MPa. The TGA results indicated that a higher replacement ratio (≥60%) of the LCB had a negative effect on the thermal stability of LCB-PUF, and the PUF with heterogeneous walls and irregular pore shapes was mainly caused by the high replacement ratio of the LCB. In addition, the mechanical properties of the LCB-PUF were improved through the adjustment of the [NCO]/[OH] ratio and the foam additive content.

Keywords: Cassava bagasse; Liquefaction; Polyurethane foam; Compressive strength

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INTRODUCTION

Along with the fast depletion of fossil oil and environmental issues associated with the extensive use of fuels, it is desirable to develop eco-friendly and economical resources instead of the traditional petrochemical-based products. Cassava bagasse (CB) is a type of low-cost and earth-abundant biomaterial. Apart from small quantities of protein, lipid, and ash, CB mainly consists of 40 to 64% un-extracted starch, and 15 to 51% fiber, and its composition mostly depends on the type of cassava and the process of starch extraction (Zhang et al. 2016).

According to Food and Agriculture Organization (FAO) statistics, the global output of CB is expected to be approximately 266 million tons by 2020, 7 to 10% of which is used for industrialization (Pandey et al. 2000). To date, CB research has been mainly related to the development of value-added products, such as a single cell protein, bio-energy, biochemical, enzyme, antibiotics, bioactive secondary metabolites, etc. (Pandey and Soccol 1998; Ekop et al. 2019). However, due to the complicated composition of fermentation broth and the high cost of separation, the utilization of the CB is currently restricted (Zhang et al. 2013). Regarding the composite material, some studies show that CB can be used to produce a CB-kraft paper composite, cellulose whiskers, reinforcing
rubber, thermoplastic for food packaging, and biodegradable films, etc. (Pasquini et al. 2010; Carvalho et al. 2018).

Biomass liquefaction with polyhydric alcohols affords large molecules that can be subsequently polymerized to produce adhesives, plastics, and other polymers. For the liquefaction process of lignocellulosics, there are mainly two reactions occurring: decomposition and polycondensation reactions, where the composition of molecules extracted will be impacted by the choice of liquefying solvent and catalyst (Niu et al. 2011; Esteves et al. 2017). Compared to the other liquefied biomaterials such as pine wood, the liquefied CB being rich in starch is more suitable for producing novel bio-based polyurethane foam (PUF), which has prospective applications in packaging, construction, etc. (Lee and Lee 2018).

In the present work, the CB was liquefied into polyol, then it was further synthesized into an environmentally friendly bio-based composite. A convenient method that was conducted at low temperature and low pressure was designed and optimized to decrease the energy consumption and pollution during PUF production. Moreover, the CB was liquefied into the bio-based polyol and directly reacted with isocyanate to generate PUF, which could reduce production cost and the utilization of various types of polyurethane.

**EXPERIMENTAL**

**Materials**

The fresh CB was obtained from a cassava starch mill (Jiahua Starch Factory, Wuming, China), shattered into powder using a Wiley mill (60-mesh; Retsch, North Rhine-Westphalia, Germany), dried at 54 °C for 24 h, and then stored in an airtight container. Polyethylene glycol (PEG#400), glycerin, polysorbate (Tween-80), and H₂SO₄ (Tianjin Kemiu Chemical Reagent Co., Ltd., Tianjin, China) were of reagent grade and were directly used as liquefaction reagents. The 4110 (polyether polyol, hydroxyl number 430 mg KOH/g) and PM-200 (polymeric diphenylmethane diisocyanate (PMDI), -NCO content 30.2%) were purchased from Majjia Chemical Co., Ltd. (Guangzhou, China) and Yantai Wanhua Polyurethane Co., Ltd. (Yantai, China), respectively. The foam stabilizer SD-60 (Polyether siloxane), the foaming catalyst T-12 (DBTDL, dibutyltin dilaurate), and triethylene diamine were obtained from Siltech New Materials Co., Ltd. (Suzhou, China), Air Products & Chemicals (China) Inc. (Shenzhen, China), and Tianjin Guangfu Science & Technology Co., Ltd. (Tianjin, China), respectively. The HCFC-141b (Shanghai 3F New Chemical Materials Co., Ltd., Shanghai, China) and water were used as the blowing agents.

**Preparation of the LCB**

A three-necked flask equipped with an atmospheric condenser, a thermometer, and a motor-driven stirrer was used for liquefaction. A total of 10 to 20 g of the CB and 50 to 80 g of the liquefaction reagents were placed into the three-necked flask, where the liquefaction reagents included (in that order) 35 to 48 g PEG#400, 8 to 18 g glycerin, 0.1 to 0.3 g Tween-80, and 0.5 to 2.0 g sulfuric acid. The flask was heated to 130 to 190 °C and kept at that temperature for 30 to 180 min, with a stirring speed of 200 rpm. After reaction, the flask was immersed in cold water to terminate the reaction, and then the reacted mixture was neutralized with sodium hydroxide (48 wt%) using an automatic
titrator (AT-510; KEM (Kyoto Electronics Manufacturing Co., Ltd.), Kyoto, Japan) to obtain the liquefied cassava bagasse (LCB).

**Methods**

*Characterization of the LCB*

The moisture of polyol had a notable effect on the foaming process and morphology of the PUF. The Karl Fisher method equipped with a moisture content meter (EBU-610-KF; KEM, Kyoto, Japan) was used to determine the moisture content of the LCB samples. The detection of the residual CB was clearly described in a previous study (Yao et al. 1996). Approximately 5 g of the LCB was dissolved with 100 mL of dioxane/water solution (4/1, v/v) in a conical flask (250 mL). The insoluble residue was filtered using a solvent filter and an organic microporous membrane (0.45 μm). Then, the insoluble residue was dried to constant weight, and its content in the LCB mixture was calculated as follows,

\[
\text{Residue} (\%) = \frac{m_2 - m_3}{m_1} \times 100
\]  

(1)

where \( m_1 \) is the initial dry weight (g) of the CB in the LCB mixture and \( m_2 \) and \( m_3 \) are the dry weights (g) of the membrane with and without insoluble residue, respectively.

For the hydroxyl number of the LCB, 1 g of the LCB was esterified with 25 mL of phthalate agent (150 g phthalic anhydride, 24.2 g imidazole, and 1000 g dioxane) at 110 °C for 20 min, then added to 75 mL of dioxane/water solution (2/1, v/v). The mixture was titrated with sodium hydroxide (1 mol/L) to the equivalence point using an automatic potentiometric titrator (AT-510; KEM, Kyoto, Japan) (Kurimoto et al. 2000). The hydroxyl number (mg KOH/g) of the LCB was calculated using Eq. 2,

\[
\text{Hydroxyl number} = \frac{[(B - A)C \times 56.1]}{W}
\]  

(2)

where \( A \) is the volume (mL) of the sodium hydroxide solution required for titration of the LCB, \( B \) is the volume (mL) of blank solution, \( C \) is the normality (mg KOH/mL) of the sodium hydroxide, and \( W \) is the weight (g) of the LCB.

*Preparation of LCB-PUF*

The LCB mixtures and PMDI were reacted to prepare the foams by a one-pot process. A mixture consisted of 4110, LCB, SD-60, T-12, triethylene diamine, and traces of water was mixed uniformly in a paper cup at 500 rpm for 2 min, where the triethylene diamine was used as a collaborated foaming additive. Then the HCFC-141b and PMDI were added into the mixture and stirred (1500 rpm) at room temperature for copolymerization until the mixture formed a cream-like substance. The isocyanate index was calculated using Eq. 3,

\[
\frac{[\text{NCO}]}{[\text{OH}]} = \frac{M_{\text{PMDI}} \times W_{\text{PMDI}}}{M_{\text{LCB}} \times W_{\text{LCB}} + M_{4110} \times W_{4110} + W_{\text{water}} \times 1000/9}
\]  

(3)

where \( M_{\text{PMDI}} \) is the content (7.43 mmol/g) of isocyanate group in PMDI, \( M_{\text{LCB}} \) is the content (mmol/g) of the hydroxyl group in the LCB (hydroxyl number/56.1), 1000/9 (mmol/g) is the content of hydroxyl group in the water, \( W_{\text{PMDI}}, W_{\text{LCB}}, \) and \( W_{\text{water}} \) are the weights (g) of PMDI, LCB, and water, respectively (Wang et al. 2008).
Characterization of the LCB-PUF

The compressive strength of the PUF was measured using a universal stress tester (11-3; Lorentzen & Wettre, Stockholm, Sweden) at 23 °C and 50% relative humidity, with a constant crosshead speed of 5 mm/min. Prior to detecting, the foams were cut into pieces (50 × 50 × 50 mm³), and the compressive strength was determined based on the stress, which was 12% lower compared to that in the yield point (the elastic limit or the point at which a material can no longer deform elastically). The samples were coated with a thin layer of gold (JEC-3000FC; JEOL Ltd., Tokyo, Japan; 20 mA for 60 s), and the cell structure was observed using scanning electron microscopy (SEM) at 10 kV (JSM-IT300; JEOL Ltd., Tokyo, Japan). Thermogravimetric analysis (TGA) was performed using a TA Instruments (SDT-600; New Castle, PA, USA) thermogravimetric analyzer, where the samples were heated from 50 to 900 °C, at a heating rate of 20 °C/min and a nitrogen flux of 40 mL/min.

RESULTS AND DISCUSSION

Liquefaction of the CB

The fresh CB and shattered CB were dried and used for SEM detection, as shown in Fig. 1. Three types of solid particles were present in the CB, including a spherical starch granule, a fiber, and a starch-fiber floc, where the starch occupied a large proportion of the CB. After mechanical pretreatment, the shattered CB demonstrated a more uniform particle size distribution (Fig. 1b). In the mechanical pretreatment, the fiber was cut into fragments, and its particle size was similar to the starch. Moreover, the starch granules were released from the fiber-starch floc. Thus, the mechanical pretreatment promoted the reagent to penetrate into the raw material more readily, which accelerated the liquefaction of the CB and improved the liquefaction efficiency. Hence, a mechanical pretreatment is important for the liquefaction of the CB.

The changes in the residual CB and the hydroxyl numbers of the liquefied CB mixtures are shown in Fig. 2. The CB was efficiently liquefied by the polyol when the sulfuric acid was added as a catalyst. When a moderate temperature of 130 °C was used, more than 70% of the CB was liquefied within 30 min. Compared to the lignocelluloses, such as cellulose, wood powder, and lignin, the CB had a higher liquefaction rate and liquefaction yield in the same polyol system, even under a mild condition (Zhang et al. 2014). The liquefaction rate of the starch was higher than that of the lignocellulose, and the components of lignocellulose including cellulose, hemicellulose and lignin were also had different liquefaction rates (Yao et al. 1996; Zhang et al. 2014). Thus, the high liquefaction yield was mainly related to the high content of starch in the CB, as well as the size improvement (specific surface area) of the mechanical pretreatment. The reduce trend of the unliquefied residue decreased with the decreasing starch content, and the residual CB was difficult to be further liquefied when the liquefaction time was over 30 min. Thus, the liquefaction of the CB mainly contained two processes, starch liquefaction and lignocellulose liquefaction, where the lignocellulose liquefaction required more time, even under a high temperature condition. In addition, further degradation and oxidation occurred in the liquefied CB mixture, in accordance with the changes of the hydroxyl group content (Yamada and Ono 2001). At the beginning, the hydroxyl content of the mixture increased along with the liquefaction process, until it reached the maximum value, then it rapidly decreased to the end of the process, even less than the initial value. This could have been
attributed to the solvation effect between PEG#400 and glycerol (Yao et al. 1996). Furthermore, the utilization of PEG#400, glycerol, and Tween-80 decreased the re-polymerization (gelation) reaction, based on the content changes of the residue in the LCB mixture.

![SEM images of the CB (a) and shattered CB (b)](image)

**Fig. 1.** SEM images of the CB (a) and shattered CB (b)

![Graph showing the effects of temperature on the liquefaction of the CB](image)

**Fig. 2.** Effects of temperature on the liquefaction of the CB
PEG#400/glycerol/ H₂SO₄/Tween-80 = 42/14/1.7/0.16; Liquefaction reagent/CB = 2.9/1

**Morphological Characteristics of the LCB-PUF**

The liquefied CB polyol was directly used to prepare polyurethane foam via reacting with PM-200 (PMDI) in a one-pot process. The components of the reaction medium for LCB-PUF preparation are shown in Table 1 (based on the LCB polyol mixture), and the appearance of the LCB-PUF is shown in Figs. 3 and 4.

In Fig. 3, when the 4110 was substituted by the LCB with a replacement ratio of 80%, the bio-based PUF was still successfully prepared, which had a regular shape and smooth surface. The color of the LCB mixture was continuously changed during the liquefaction process, from gray to burgundy, brown, and finally to black. When the addition of H₂SO₄ was increased, or the liquefaction temperature increased, the color of the LCB
mixture darkened, correspondingly, the color of the LCB-PUF was also changed. For the self-foaming process, the density of the LCB-PUF was approximately 0.02 to 0.03 g/cm$^3$, and when water was used as a blowing agent, the density increased to 0.062 g/cm$^3$.

![Image](image1.png)

**Fig. 3.** Appearance of the LCB (replacement ratio 80%) and the LCB-PUF

**Table 1.** Composition of the Reaction Medium for the LCB-PUF

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by Weight</th>
<th>Ingredients</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCB</td>
<td>20 to 100</td>
<td>SD-60</td>
<td>1.0 to 1.5</td>
</tr>
<tr>
<td>4110</td>
<td>80 to 0</td>
<td>H$_2$O</td>
<td>0 to 2.5</td>
</tr>
<tr>
<td>Triethylene diamine</td>
<td>0.4 to 2.4</td>
<td>HCFC-141b</td>
<td>0 to 20</td>
</tr>
<tr>
<td>T-12</td>
<td>1.0 to 1.5</td>
<td>PM-200</td>
<td>60 to 150</td>
</tr>
</tbody>
</table>

![Image](image2.png)

**Fig. 4.** SEM images of the LCB-PUF liquefaction conditions ($°$C/min): a) 130/30, b) 130/60, c) 150/30, and d) 150/60

Figure 4 shows that a well-aligned cell structure and smooth surface for the LCB-PUF was obtained when the liquefied polyol mixture had a low level of residue. In Figs. 4a and 4b, a more uniform pore-wall structure and smaller pore size emerged when the liquefaction time was increased from 0.5 h to 1 h. These changes of the LCB-PUF were not only related to the viscosity of the liquefied mixture, but also influenced by the molecular weight and hydroxyl value of the LCB, where more polysaccharides with macromolecular structures were present in the mixture at the initial time of liquefaction (Yao et al. 1996). As shown in Figs. 4c and 4d (liquefied at 150 °C), the LCB-PUF contained porous particles, and its pore-wall structures were irregular compared to that of the LCB liquefied at 130 °C (Figs. 4a and 4b), where the residue size was larger, and the walls of the LCB-PUF were thicker.

**Mechanical Properties of the LCB-PUF**

The mechanical properties of the LCB-PUF were evaluated, and the effects of the isocyanate indices and the replacement ratio of the LCB on the compression properties of the LCB-PUF are shown in Fig. 5 and Table 2. All of the samples were prepared using the LCB, and the [NCO]/[OH] ratio was improved from 0.4 to 1.4 when the polyether polyol (4110) was not added into the system. It was found that the compressive strength increased along with the increased [NCO]/[OH] ratio. The ratio could have been increased through eliminating the hydroxyl groups, such as the reaction between hydroxyls and hard, segmented isocyanate groups, and the generation of the cross-linked structure. However, a high [NCO]/[OH] ratio was not beneficial for the foams. When the ratio increased to 1.4 the foams became crisp, and the amount of broken surface also increased. For the effects of the replacement ratio of the LCB, no clear yield points for the LCB-PUF were found, even the strain came up to 50%, demonstrating that the LCB-PUF had a fine semi-rigid characteristic. In addition, when the replacement ratio of the LCB was in a high level, the compression modulus of the foams obviously decreased, where a small inflection point emerged in the initial stage of the pressure curve.

![Fig. 5. Effects of the isocyanate indices (a) and the replacement ratios of the LCB (b) on the compression properties of the PUF](image-url)

In Table 2, due to the mild liquefied condition (130 °C for 30 min) of the CB and the liquefied starch, a great amount of the long and soft segments was generated and made the framework of the LCB become more flexible. This phenomenon was beneficial to improve the mechanical properties of the LCB-PUF. For instance, when more LCB polyol...
was used instead of the 4110, the MDI concentration could not be controlled to maintain the [NCO]/[OH] ratio at a constant level. Moreover, the [NCO]/[OH] ratio increased when the replacement ratio of the LCB polyol increased. Another issue was that the LCB polyol contained mixed components and incomplete liquefied fractions, such as the lignocellulose and polysaccharide. These fractions were not removed from the LCB prior to utilization, which caused the LCB polyol to have a high viscosity and heterogeneity. Correspondingly, both the cell wall and incomplete cell wall with a large size were caused by the high replacement ratio of the LCB, giving the LCB-PUF fine elasticity such as high yield stress, low compression strength, and low elastic modulus.

**Table 2. Compression Properties of the LCB-PUF**

<table>
<thead>
<tr>
<th>Replacement Ratio of the LCB (%)</th>
<th>100</th>
<th>80</th>
<th>60</th>
<th>40</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.031</td>
<td>0.027</td>
<td>0.032</td>
<td>0.036</td>
<td>0.039</td>
</tr>
<tr>
<td>Compression Strength (MPa)</td>
<td>0.057</td>
<td>0.072</td>
<td>0.091</td>
<td>0.143</td>
<td>0.171</td>
</tr>
<tr>
<td>Compression Modulus (MPa)</td>
<td>2.88</td>
<td>2.06</td>
<td>4.94</td>
<td>6.35</td>
<td>12.54</td>
</tr>
<tr>
<td>Yield Stress (MPa)</td>
<td>0.11</td>
<td>0.13</td>
<td>0.09</td>
<td>0.09</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Thermal Stability of the LCB-PUF**

The TGA of the prepared LCB-PUF was conducted under a flowing nitrogen atmosphere. The results are shown in Fig. 6, which shows that the PUF exhibited a two-stage degradation behavior. The starch and fibers present in the PUF had a visible influence on the LCB. When the replacement ratio of the LCB in the LCB-PUF was less than 60%, the temperature at both of the first and second derivative weight peaks changed minimally. However, when this ratio was above 60%, these two types of derivative weight peaks were obviously decreased, demonstrating that a high replacement ratio of the LCB had a negative influence on the thermal stability of the LCB-PUF. It also confirmed that the thermal stability of the PUF was seriously affected by chemical bonds that formed in the reaction of the polyol and MDI (Alfani et al. 1998). Thus, the LCB-PUF foams that contained more components of the liquefied CB exhibited a decreased thermal stability.

![Fig. 6. TGA of the PUF with different replacement ratios of the LCB](image-url)
CONCLUSIONS

1. Most of the liquefaction reactions of the cassava bagasse (CB) were completed in a short time (30 min), and it was mainly affected by the high starch content.

2. The residue in the liquefied CB (LCB) mainly consisted of lignocellulose and was slowly liquefied.

3. The hardness and compressive strength of the LCB-polyurethane foams (PUF) were effectively improved through increasing the isocyanate index.

4. The increase of the replacement ratio of the LCB obviously decreased the mechanical and thermal properties of the PUF.

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