Preliminary Investigation of Bio-Composites Fabricated from Liquefied Wood-Phenol-Formaldehyde Co-Condensation Resin

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Abstract
The objective of this preliminary study was to develop a wood liquefaction process as a precursor for producing liquefied products containing a large biomass content in an economically feasible manner. Compression-molded composites were made from wood fiber and a liquefied wood/phenol/formaldehyde co-condensation resin. The two experimental variables selected were 1) phenol to wood ratio (P/W) in the liquefaction reaction and 2) phenol to formaldehyde molar ratio (P/F) in the co-condensation reaction. Panels were tested in static bending for modulus of rupture and modulus of elasticity. Dimensional stability properties were also measured. It was found that P/W ratio had a significant effect on both strength and dimensional stability of the composites. P/F molar ratio and the interactions between P/W ratio and P/F molar ratio were not significant. The results of the tests suggested that 1) the optimum degree of wood liquefaction is obtained by leaving crystalline cellulose in the system to enhance the performance of molded products and 2) P/W ratio of 2/1 has potential for further development because of its favorable performance and cost factor.

Introduction
The utilization of biomass as an alternative to petroleum-based products has attracted great interest due to its bio-degradable nature and renewable properties. Biomass liquefaction is one of these novel techniques. Research has been conducted on wood liquefaction for more than 30 years and some encouraging results have been achieved. Phenol is one of the most common solvents used in wood liquefaction, and it can be applied in wood liquefaction with or without acid catalysts. The effects of several variables on wood liquefaction in the presence of phenol without a catalyst were investigated. The results showed that wood liquefaction without a catalyst needs a higher reaction temperature (250°C) to obtain the same extent of liquefaction as that of liquefaction with an acid catalyst (12-14). Wood liquefaction with an acid catalyst can be carried out under moderate temperature (120° to 180°C). Both strong acids, such as sulfuric acid and hydrochloric acid, and weak acid, such as oxalic acid, can be used as catalysts in wood liquefaction. The resulting liquefied wood using a strong acid catalyst can achieve higher combined phenol and lower residue contents than those using a weak acid catalyst (1-4,9,15-16). The liquefied wood, also called phenolated wood, can be directly developed into molding compounds or further co-condensed with formaldehyde to produce novolac-like resin. The co-condensed resin has shown improved mechanical properties over those of the phenolated wood resin and
was even slightly greater than those of the conventional novolac resin (10,11).

Most previous studies in this area used a high phenol/wood ratio to achieve a low residue content. In short, the goal was to obtain more thoroughly liquefied wood, which can be achieved by either using a high amount of solvent or a strong acid catalyst during the liquefaction reaction. However, a strong acid can corrode the reaction equipment and the high phenol to wood ratio increases the cost of the final products. Although a fairly large amount of unreacted phenol and wood residue will remain in the reaction system when a weak acid catalyst and low phenol to wood ratio is used in the liquefaction, the unreacted phenol can be converted to phenol-formaldehyde (PF) resin and the residue can be used as a filler for composite products. The objective of this research was to determine the effect of phenol to wood ratio and phenol to formaldehyde molar ratio on the mechanical and physical properties of compression molded biocomposites fabricated from wood fiber and liquefied wood-phenol-formaldehyde co-condensed resin.

**Experimental**

**Materials**

Sawdust from Chinese tallow tree (*Triadica sebifera* syn. *Sapium sebiferum*) was collected and ovendried overnight at 100°C. The dried material was then ground to pass through a 20-mesh sieve. Both the raw materials used for wood liquefaction and the wood filler were from the same wood powder. Industrial grade phenol (90% concentration) and formaldehyde (36% concentration) were used for the liquefaction. All other chemicals were of reagent grade.

**Preparation of Liquefied Wood**

Wood powder, phenol, and oxalic acid were pre-mixed until a uniform mixture was obtained. Then the mixture was transferred to a reactor equipped with a condenser and a stirring system. The refluxing reaction was conducted at 160°C for 120 minutes. Three phenol to wood ratios (P/W = 1/1, 2/1, 3/1 w/w) were selected for the liquefaction. Oxalic acid was used as a catalyst and its content was 2.5 percent of the whole reactants at all P/W ratios. Approximately 15 g of the liquefied wood was dissolved in methanol. After filtration, the non-soluble portion (i.e., residue) was ovendried and weighed. The residue content of the liquefied wood was calculated by Equation [1].

\[
\text{Residue content (\%) } = \left( \frac{W_r}{W_o} \right) \times 100 \tag{1}
\]

where:

- \(W_r\) = ovendried weight of the solid wood residue after the filtration, and
- \(W_o\) = weight of original wood particles.

After the determination of residue content, about 10 g of each residue from three P/W ratios was used to determine the acid-insoluble lignin content according to ASTM D1106-96 (5).

The crystallinity index of the cellulose in the residues and the virgin tallow wood was determined by X-ray diffraction (XRD). The Segal method was chosen to calculate the crystallinity index using Equation [2]:

\[
\text{CrI (\%)} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{2}
\]

where:

- \(\text{CrI}\) = crystallinity index in percent,
- \(I_{002}\) = intensity of the diffraction from the (002) plane at \(2\theta = 22.6^\circ\), and
- \(I_{am}\) = intensity of the background scatter measure at \(2\theta = 18.5^\circ\) (8).

**Preparation of Liquefied Wood/Phenol/Formaldehyde Co-Condensed Resin**

Liquefied wood was mixed with formaldehyde and additional oxalic acid, and then refluxed under continued stirring for 80 minutes at 105°C. Phenol to formaldehyde molar ratio (P/F) at three levels (P/F = 1/0.6, 1/0.7, and 1/0.8) was investigated. The oxalic acid was 3 percent for all P/F ratios. The solids content and acetone non-soluble part of each resin were measured.

**Preparation of Composites from Wood Fiber and Liquefied Wood/Phenol/Formaldehyde Co-Condensed Resin**

The co-condensed resin was first mixed with hexamine, calcium hydroxide, and zinc stearate according to the weight percents listed in Table 1. Sufficient acetone was then added to the mixture and stirred to thoroughly dissolve the resin. Wood filler was then added to the acetone mixture to make a homogeneous mixture. After thoroughly mixing, the acetone was removed from the mixture under reduced-pressure at 50°C. The mixture was then freeze-dried overnight to remove water and any remaining acetone. The dried material was sieved again to pass through a 20-mesh sieve and aggregated materials remaining on the 20-mesh sieve were ground into powder. The resulting material was subjected to compression molding to fabricate 5- by 5- by 1/8-inch panels using a 6-
by 6-inch single-opening laboratory hot-press. The panels were hot pressed at 185°C for 3 minutes and then cooled under the same pressure for 10 minutes. Two panels were produced for each P/W and P/F combination.

Test of Mechanical Properties

Flexural and tensile test were performed using an Instron-4465 test machine in accordance with ASTM D 1037-96 (6). Each panel was cut to yield two static-bending specimens (1/2 by 5 in.) and two dimensional stability test specimens (1/2 by 5 in.). Data for modulus of rupture (MOR) and modulus of elasticity (MOE) were automatically collected and computed by the Instron Series IX Automated Materials Tester program.

Test of Dimensional Stability

Two specimens from each panel were chosen for the 24 hour soaking and 2 hour boiling test. The thickness of the specimens before and after the tests was measured. The percent of thickness swelling was calculated by Equation [3]:

\[
TS(\%) = \left( \frac{T_1 - T_0}{T_0} \right) \times 100
\]

where:
- \( TS \) = percent of thickness swelling,
- \( T_0 \) = thickness of the specimen before the test, and
- \( T_1 \) = thickness of the specimen after the test.

Statistic Analysis

Analysis of variance (ANOVA) was used to analyze the effects of the variables of the liquefaction (P/W ratio) and resinification (P/F ratio) on the mechanical properties and dimensional stability of the molded composites.

Results

Liquefied Wood

Table 2 summarizes the residue content of the liquefied wood, acid-insoluble lignin content, and crystallinity index of the virgin tallow wood and the residues from different phenol/wood ratios (P/W).

On average, the residue content decreased as the P/W ratio increased. It is noted that the average residue contents, ranging from 65.4 percent for P/W of 3/1 to 71.8 percent for P/W of 1/1, were substantially higher than most of the residue contents obtained in previous studies reported by Alma and Yoshioka with sulfuric acid (3) or hydrochloric acid as the catalyst (4).

The acid-insoluble lignin content of the liquefaction residues decreased as the P/W ratio increased. It can be seen from Table 2 that the acid-insoluble lignin contents of the residues from three P/W ratios were lower than that of the virgin tallow wood, indicating an increasing liquefaction rate of lignin with an increase in P/W ratio. In addition, Table 2 also showed that the average crystallinity of cellulose of the residues was greater than that of virgin tallow wood. The greater crystallinity of cellulose is most likely due to a decrease of amorphous cellulose due to the liquefaction. Furthermore, it is interesting to note that the crystallinity increased consistently as the P/W ratio increased, indicating an increasing liquefaction rate of amorphous cellulose with the increasing P/W ratio.

Figure 1 shows the appearance of liquefied wood at various P/W ratios. The liquefied wood changed from a light-color dry fiber (P/W = 1/1) to a dark-color and viscous substance (P/W = 3/1). In most cases, the presence of fiber was still visible. It should be mentioned that, unlike the strong acid catalyzed system which converted the wood into a flowable viscous dark liquid, it appears that the relatively low concentration of weak acid used in this study did not catalyze the phenolysis of wood components sufficiently to be dissolved into phenol.

Liquefied Wood/Free Phenol/Formaldehyde Co-Condensed Resin

Table 3 summarizes the solids content and percent acetone-non-soluble residue of the co-condensed resins from different P/W and phenol-formaldehyde (P/F) ratios. On average, a P/F ratio of 1/0.6 resulted in consistently lower solids content as compared to that of P/F ratios of 1/0.7 and 1/0.8. As for the effect of the P/W ratio on solids content, it is noted that P/W ratios of 2/1 and 3/1 yielded higher solids content at P/F ratio of 1/0.7 and 1/0.8, while...
Table 3. ~ Major compositions of liquefied wood/phenol/formaldehyde co-condensed resin.

<table>
<thead>
<tr>
<th>P/W</th>
<th>Acetone non-soluble part</th>
<th>Solids content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/1b</td>
<td>2/1</td>
</tr>
<tr>
<td>1/0.6</td>
<td>31.90</td>
<td>18.40</td>
</tr>
<tr>
<td>1/0.7</td>
<td>32.33</td>
<td>21.15</td>
</tr>
<tr>
<td>1/0.8</td>
<td>34.49</td>
<td>18.48</td>
</tr>
</tbody>
</table>

a Phenol to formaldehyde molar ratio.
b Phenol to wood ratio.

Figure 2. ~ Liquefied wood/phenol/formaldehyde co-condensed resin. P/W of 1/1 (left), P/W of 2/1 (center), and P/W of 3/1 (right). All three resins are of P/F molar ratio of 1/0.7 and the oxalic acid content is 3% (w).

the effect of P/W ratio on solids content was rather insignificant at P/F ratio of 1/0.6.

The acetone non-soluble part decreased with increasing P/W ratio. Similar to the residue from liquefied wood, the acetone non-soluble part of the co-condensed resin mainly consisted of fibrous materials.

Three examples of resins with different P/W ratios are shown in Figure 2. It is apparent that the liquefied wood resin gradually turned into a viscous paste as the P/W ratio increased.

Mechanical Properties

Table 4 presents the values of the physical and mechanical properties of the composites from the liquefied wood co-condensed resin and wood fiber. The two-way ANOVA results listed in Table 5 show that P/W ratio had a significant effect on the flexural MOE and MOR of the molded composites. The average flexural MOE increased significantly from P/W of 1/1 to 3/1, but the MOR first increased from P/W ratio of 1/1 to 2/1 then decreased at the P/W of 3/1 (Fig. 3). The P/F molar ratio and the interactions between P/W ratio and P/F molar ratio were not significant.

Dimensional Stability

Table 6 provides the two-way ANOVA for the dimensional stability of the composites. P/W ratio had a significant effect on the thickness swelling of the specimens for both 24-hour soaking and 2-hour boiling tests. As shown in Table 6, a significant effect of P/W ratio on TS (%) was observed. The TS (%) decreased with increasing P/W ratio, indicating better dimensional stability of the composites.

Table 5. ~ Two-way ANOVA on dimensional stability of the composites by GLM procedure.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>F value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dependent variable: thickness swelling (24-hour soaking)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Factor</td>
<td>8</td>
<td>11.43</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>41.18</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>0.50</td>
<td>0.6112</td>
</tr>
<tr>
<td>P*F</td>
<td>4</td>
<td>2.01</td>
<td>0.1210</td>
</tr>
<tr>
<td>2. Dependent variable: thickness swelling (2-hour boiling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Factor</td>
<td>8</td>
<td>3.82</td>
<td>0.0040</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>9.17</td>
<td>0.0009</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>1.00</td>
<td>0.3799</td>
</tr>
<tr>
<td>P*F</td>
<td>4</td>
<td>2.56</td>
<td>0.0615</td>
</tr>
</tbody>
</table>

a Phenol to wood ratio.
b Phenol to formaldehyde molar ratio.
c Interaction of phenol to wood ratio and phenol to formaldehyde molar ratio.

Table 6. ~ Two-way ANOVA on dimensional stability of the composites by GLM procedure.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>F value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dependent variable: thickness swelling (24-hour soaking)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Factor</td>
<td>8</td>
<td>6.3</td>
<td>0.0001</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>20.3</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>1.18</td>
<td>0.3240</td>
</tr>
<tr>
<td>P*F</td>
<td>4</td>
<td>1.86</td>
<td>0.1459</td>
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<tr>
<td>2. Dependent variable: thickness swelling (2-hour boiling)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Factor</td>
<td>8</td>
<td>4.46</td>
<td>0.0016</td>
</tr>
<tr>
<td>P</td>
<td>2</td>
<td>10.27</td>
<td>0.0005</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>3.88</td>
<td>0.0331</td>
</tr>
<tr>
<td>P*F</td>
<td>4</td>
<td>1.84</td>
<td>0.1501</td>
</tr>
</tbody>
</table>

a Phenol to wood ratio.
b Phenol to formaldehyde molar ratio.
c Interaction of phenol to wood ratio and phenol to formaldehyde molar ratio.
in Figure 4, P/W ratio of 1/1 yielded substantially higher thickness swelling as compared to that of 2/1 and 3/1. This phenomenon may be due to the co-condensed resin synthesized at P/W of 1/1, which had a relatively higher non-soluble component (i.e., residue) compared to that at P/W of 2/1 and 3/1 (Table 3). Therefore, the panels with a lower P/W ratio had a higher wood filler content (including the residue) and lower resin content than those with higher P/W ratios when the same amount of these three resins was applied to the composites. Thus, these composites had greater thickness swelling.

Discussion and Conclusions

The main objective of the study was to develop a wood liquefaction process to obtain a liquefied product with maximum biomass content. Because phenol is one of the most expensive components of the molding products, it is desirable to substitute wood for phenol as much as possible in the process of wood liquefaction. Although the P/W ratio of 1/1 yielded a fairly similar strength property as compared to that of P/W ratio of 3/1, it also resulted in unacceptably high panel thickness swelling. It is generally recognized that panel dimensional stability is one of the more critical properties required for many application of molding products and also is very difficult to control. Thus, our preliminary results suggest that the P/W ratio of 1/1 is not feasible for further development even though its cost factor is the most favorable. However, P/W ratio of 2/1 yielded higher MOR, comparable thickness swelling, and only slightly lower MOE as compared to that of P/W ratio of 3/1. Therefore, P/W ratio of 2/1 will be selected for further development because of its favorable cost factor and acceptable panel properties.

One significant difference of the weak acid catalyzes decomposition of crystalline cellulose expect with a prolonged reaction time under high acid concentration and high reaction temperature. Thus, it can be postulated that the liquefaction rate of various wood components would be in a decreasing order of hemicellulose, lignin, amorphous cellulose, and finally crystalline cellulose. Therefore, for the development of molded products from liquefied wood, the optimum degree of wood liquefaction is to obtain the liquefied wood by leaving the crystalline cellulose in the system because 1) the thermal and dimensional stability of the crystalline cellulose can enhance the performance of the molded products and 2) less catalyst and milder reaction conditions can be used for wood liquefaction to achieve a substantial costs savings. The effects of hemicellulose, lignin, amorphous, and crystalline cellulose on wood liquefaction and the physical and mechanical properties of the molded liquefied wood products are in progress. It is expected that the completion of this on-going study will provide a guideline to optimize the liquefaction process to achieve economically viable molded products.

Pan, Shupe, and Hse
Literature Cited