Steam Injection-pressing Preparation and Forming Mechanism of Binderless Ramie Stem Particleboard for Modern Furniture

Yingying Guo, Zheng Xia, Jianying Xu and Xiangdong Dai

ABSTRACT

Binderless ramie stem particleboard was prepared by steam injection pressing in this paper. Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG), high performance liquid chromatography analysis (HPLC) and specific surface area (BET) were used to analyze the forming mechanism. The results show that the number of active hydroxyl in cellulose molecule was increased by the synergistic effect of the water and heat, which could form hydrogen bonds (O-H\cdots H), Van der Waals forces to enhance mechanical properties of resulting board. In addition, part of hemicellulose in ramie stem particles were hydrolyzed by the synergistic effect of the water and heat, and the hydrolysate could be subjected to polycondensation reaction to generate polycondensation furan resin which was similar to adhesives. The hydrolysate also could be subjected to polycondensation reaction with the lignin having a phenolic hydroxyl structure to generate a kind of condensation compound which was similar to phenolic resin adhesive. Moreover, the lignin in ramie stem particles were fully expanded and part of lignin was evenly distributed by the synergistic effect of the water and heat, which could improve the physical and mechanical properties of binderless particleboard to some extent.\(^1\)

INTRODUCTION

With continuous improvement of living condition, people paid more and more attention to the indoor environment pollution. Furniture material is one of the most important sources of indoor pollution, because it was usually assembled with

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wood-based panels. Conventionally, wood-based panel was manufactured by wood or non-wood plant after special machining process, in combination with various adhesive. Typical adhesive such as phenol formaldehyde (PF), urea formaldehyde (UF) is chemically synthesized with formaldehydes and other material, which will release formaldehyde free even the resins were completely cured. As an alternative, technology of self-bonding board does not need any adhesive like UF and PF. These boards were reported produce some kinds of chemicals similar with adhesive, with which the wood-based elements were bonded. It was firmly considered that bonderless boards are safe and environment-friendly for indoor application. However, wood-based panel without adhesive under ordinary hot-pressing process is time-consuming. Besides, physical and mechanical properties of these panels are relatively low, and their thickness swelling after absorbing water is inevitably high. Compare to ordinary hot-pressed binderless panels, these manufactured under steam injection pressing are of higher mechanical strength and shorter press duration. Due to reduced press cycle, it is the direction of development of wood-based panel technology in the future [1-5]. However, briquetting mechanism of that is not very clear. Therefore, it is quite necessary to carry out some research on briquetting mechanism of wood-based panel without adhesive under steam injection pressing.

Our country's forest resources are scarce, the gap between timber supply and demand is increasing. A present report surveyed the shortage of wood is about 5000-7000 million cubic meters each year in China. Meanwhile, China is a vast agricultural country, producing more than 7 million tons agricultural residues of straw every year. Boehmeria nivea, also nominated as China Grass, ranked top in the acreage and output all over the world. Every year, a large amount of boehmeria nivea was burned as fuel, with low added value and serious air pollution. The main chemical composition of boehmeria nivea is cellulose, hemicellulose, and lignin, resembling wood resource. Therefore, it is a promising raw material for the production of wood-based panel. It is also of great significance to resolve straw resource, boost income of residual farmers, save timber resource and protect environment health [6-8]. In this work, particles of boehmeria nivea were taken as raw material to produce binderless ramie stem particleboard by steam injection pressing. The major chemical constitution and mechanical properties of resulting panels was characterized for the purpose of better understanding its self-bonding mechanism.

EXPERIMENTAL SECTOPN

Materials

Boehmeria nivea was collected from Yiyang, Hunan province in China. The raw material, after depithing, was processed into particles by mechanical grinding. Particle size distribution were as follows: <0.25mm accounted for 6.4%, 0.25-0.50mm accounted for 14.4%, 0.50-1.00mm accounted for 37.3%,

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1.00-2.00mm accounted for 37.2% and size>2.0mm accounted for 4.7%. The moisture content of these particles was 25%.

**Board Production**

The dimension of the ramie stem binderless particleboard is 230*230*7mm, having a target density of 0.8/cm$^3$. The particles were hand-formed (using a forming box) into homogeneous single-layered mats. After forming, the mats were prepressed and then pressed with a sealed steam-injection press. Airproof frame was used between upper and lower press plates to prevent the releasing of hot steam. The steam pressure was 1.0MPa and maintained about 7min. Finally, ordinary hot-pressing process was used to prepare ramie stem binderless particleboard which was done like A brief description of ordinary hot-pressing was as follows: hot-pressing temperature was 190°C, pressure was 5MPa, and hot-press time was 10min.

**Test and Analysis**

Functional groups in ramie stem particles after hot water (80°C) extracting were tested and analyzed by fourier infrared spectrometer (Shimadzu Corporation, Japan). The grinded particle combined with potassium bromide was pressed as a disk for testing. The scan range was 4000-400cm$^{-1}$, resolution was 2cm$^{-1}$, and scantimes was 32.

Thermal stability was tested by Pyris6 TGA (Parkin Elmer, USA). 5mg powder sample was weighed by electronic balance with a minimum scale of 0.0001g. The test was performed at temperature range of 25-500°C, at a heating rate of 10 oC/min, and protected in the atmosphere of nitrogen with air flow of 25ml/min.

Content of free sugars, free organic acids and free furfurals in samples were measured by Waters244 high performance liquid chromatograph (Waters company, USA). The chromatographic column was Diamonsil C18 (250x4.6 mm), detector was a refractive index detector (Waters486), mobile phase was 0.05mol/L H2SO4 (V:V), temperature was 55°C, and flow rate was 0.01mL/min. The peak area were calculated by area normalization and external standard method was used to examine its content.

The Specific surface area was recorded by a specific surface area and pore size SA3100 analyzer (Beckman Coulter company, USA). Samples were put into U-tube and then dried by a constant gas (N2 and H2) flow for 30 min. After that, specific surface area was calculated by continuous flow method, in which N2 was adsorbed gas and H2 was carrier gas.

After conditioned at ambient temperature for 48-72h, major physic-mechanical properties such as modulus of rupture (MOR), internal bonding (IB), and thickness swelling (TS) of resulting panels were measured according to Chinese national standards of GB/T 4897.2-2003.
RESULT AND DISCUSSION

Analysis of Fourier Transform Infrared Spectroscopy

Infrared spectrogram of ramie stem particles after hot water extraction was shown in Figure 1. Absorption peak around 3400 cm$^{-1}$ was attributed to stretching vibration band of lignin and holocellulose hydroxyl (O-H). Absorption peak around 1624 cm$^{-1}$ was stretching vibration band of C=C in benzene ring, and absorption peak around 1055 cm$^{-1}$ was stretching vibration band of hemiacetal in ramie stem$^{[9-11]}$. As can be seen in Figure 1, stretching vibration band around 3400 cm$^{-1}$ of –OH for steam pretreated sample was significantly enhanced, indicating increased active hydroxyls due to breakdown of hemicelluloses base ring glycoside bond among cellulose and hemicellulose. The created active hydroxyls between different particles could form hydrogen bonds which help to increase mechanical strength of binderless ramie stem particleboard. Compared with raw material and ordinary hot-pressing samples, stretching vibration band of C-O-C generated by hemiacetal at 1055 cm$^{-1}$ significantly enhanced for steam pretreated samples. It is likely that the combined effect of heating and steam degrade hemicelluloses and lignin at different extents, resulting in the generation of water-soluble oligosaccharide and aldehydes. The regenerated low-molecule chemicals like aldehydes are able to create furfural homopolymer which acts as resin for particleboard.

![Figure 1. FTIR spectrums of concentrated hot water extract for different ramie stem particles.](image)
Analysis of Fourier Transform Infrared Spectroscopy

TG curves of various treated ramie stem were shown in Figure 2. As can be seen in Figure 2, processes of weight lose of three kinds of sample can be roughly divided into three stages. At the first stage, water and small amount of extractive evaporated. At the second stage, after a relatively gentle degradation process, low-molecule carbohydrates of began to pyrolyze with a reported order of hemicellulose, cellulose, and lignin. Finally, smooth curve indicated residual lignin pyrolysis at high temperature [12-13]. It was shown in Table 1, that three major degradation ranges of raw ramie stem were in 29~118°C, 119~398°C, and 399~500°C, respectively. The weight-loss ratios at three different stages were 6.16%, 61.4%, and 13.2% respectively. For steam pretreated ramie stem, the major degradation ranges located in 29~107°C, 108~372°C, and 373~500°C, respectively. Accordingly, the weight loss ratios were 5.06%, 56.7%, and 14.1% respectively.

These materials displayed similar TG curves. However, at second stage, the degradation ranges for steam pretreated ramie stem shifted to low temperature compared with raw and ordinary pressed samples. The results suggested that synergistic effect of heating and steam created more low-molecule carbohydrates from the pyrolysis of cellulose and hemicellulose.

Figure 2. Ramie Stem TG Curve.
### TABLE 1. RAMIE STEM WEIGHT LOSS RATE.

<table>
<thead>
<tr>
<th>samples</th>
<th>first stage</th>
<th>second stage</th>
<th>third stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temperature range /°C</td>
<td>weight-loss ratio /%</td>
<td>temperature range /°C</td>
</tr>
<tr>
<td>raw materials</td>
<td>29–118</td>
<td>6.16</td>
<td>119–398</td>
</tr>
<tr>
<td>material for ordinary hot-pressing</td>
<td>29–115</td>
<td>5.53</td>
<td>116–397</td>
</tr>
<tr>
<td>material for steam injection pressing</td>
<td>29–107</td>
<td>5.06</td>
<td>108–372</td>
</tr>
</tbody>
</table>

### Analysis of High Performance Liquid Chromatography (HPLC)

HPLC analysis results of free sugars, found in cold water extract of ramie stem, were shown in Table 2. As can be seen in Tab.2, free sugars in cold water extract of raw ramie stem particles was mainly oligomeric polysaccharide. While apart from oligomeric polysaccharide, monosaccharide like glucose, fructose and xylose were observed in cold water extract of ramie stem particles made by ordinary hot-pressing and steam injection pressing. Content of free sugars mentioned above in each group conformed to the following rule: materials made by steam injection pressing > materials made by ordinary hot-pressing > raw materials.

### TABLE 2. HPLC ANALYSIS RESULTS OF FREE SUGARS IN RAMIE STEM.

<table>
<thead>
<tr>
<th>samples</th>
<th>composition</th>
<th>retention time</th>
<th>peak height</th>
<th>peak area</th>
<th>Content (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw materials</td>
<td>oligomeric polysaccharide</td>
<td>4.168</td>
<td>39392.10</td>
<td>1053041.25</td>
<td>2.693</td>
</tr>
<tr>
<td>materials made by ordinary hot-pressing</td>
<td>oligomeric polysaccharide</td>
<td>4.350</td>
<td>137687.10</td>
<td>3609686.25</td>
<td>7.287</td>
</tr>
<tr>
<td></td>
<td>glucose</td>
<td>7.827</td>
<td>28.974</td>
<td>82530.40</td>
<td>0.253</td>
</tr>
<tr>
<td></td>
<td>xylose</td>
<td>8.688</td>
<td>1053.14</td>
<td>23687.83</td>
<td>0.107</td>
</tr>
<tr>
<td></td>
<td>fructose</td>
<td>9.602</td>
<td>3039.36</td>
<td>75865.02</td>
<td>0.204</td>
</tr>
<tr>
<td>materials made by steam injection pressing</td>
<td>oligomeric polysaccharide</td>
<td>4.250</td>
<td>179706.22</td>
<td>6773417.50</td>
<td>14.727</td>
</tr>
<tr>
<td></td>
<td>fructose</td>
<td>9.662</td>
<td>4342.11</td>
<td>93783.31</td>
<td>0.493</td>
</tr>
</tbody>
</table>
HPLC analysis results of acetic acid, found in cold water extract of ramie stem, were shown in Table 4. Content of acetic acid in each group conformed to the following rule: materials made by steam injection pressing > materials made by ordinary hot-pressing > raw materials. Among the main chemical compositions of ramie stem, lignin has the strongest ability to resist hydrolysis, which means lignin hardly hydrolyzed in water. Cellulose is a linear polymer composed of many glycosyl, which connected each other by glycoside bond. The glycoside bond can be broke under a certain water and heat conditions, resulted in the polymerization degree of the cellulose polymer decreased and the intermediate of polysaccharide and final product of glucose produced. Hemicellulose is a kind of heterogeneous polysaccharide consisting of two or more monosaccharide, most of which have short side chains. Monosaccharides, consisting of backbone of hemicelluloses, are mainly xylose, glucose and mannose. Monosaccharide, consisting of short side chains of hemicelluloses, are mainly xylose, glucose, galactose, arabinose, rhamnose, glucuronic acid, galacturonic acid, etc [14-15]. Hemicellulose hydrolyze easily under heat action especially interacted with heat and water, producing oligomeric polysaccharide and monosaccharide, among which some parts will remove the carboxyl. The fallen carboxyl forms the organic acid like acetic acid. Part of monosaccharide, produced by hydrolysis, turns into furfural after dehydration. Organic acid will promote the further hydrolysis of hemicellulose, realizing authigenic acid catalyzed hydrolysis of hemicellulose [16].

**TABLE 4. HPLC ANALYSIS RESULTS OF ACETIC ACID RAMIE STEM.**

<table>
<thead>
<tr>
<th>samples</th>
<th>retention time</th>
<th>peak height</th>
<th>peak area</th>
<th>content (g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw materials</td>
<td>8.355</td>
<td>48816</td>
<td>3969</td>
<td>90.83</td>
</tr>
<tr>
<td>materials made by ordinary hot-pressing</td>
<td>8.371</td>
<td>305080</td>
<td>16544</td>
<td>481.40</td>
</tr>
<tr>
<td>materials made by steam injection pressing</td>
<td>8.320</td>
<td>476430</td>
<td>34269</td>
<td>753.64</td>
</tr>
</tbody>
</table>

Free monosaccharide like oligomeric polysaccharide, free disaccharide and glucose, fructose or xylose, can be tested in cold water extract of ramie stem particles, announcing that part of hemicellulose and cellulose hydrolyzed in samples during hot-pressing. Effects of water and heat were more violent and supercritical fluid steam had high permittivity in slab, promoting a greater degree of hydrolysis of hemicellulose and cellulose. Meanwhile, hydrolysis of hemicellulose and cellulose was accelerated markedly by acetic acid. So, contents of free sugar and acetic acid were significantly higher in materials made by steam injection pressing than ordinary hot-pressing [16-17]. Furfural was produced by dehydration of pentose, the degradation product of hemicelluloses. And contents of free furfural were higher in materials made by steam injection pressing than ordinary...
hot-pressing, too. However, the differential of free furfural was not as large as that of free sugar. It was likely to be the chemical reactions between furfural produced by hydrolysis of hemicellulose and benzene ring in lignin, producing something like phenolic resin. The results showed that chemical reactions taking place in slab was more complicated; hydrolysis degree of hemicellulose and cellulose was greater; substance with a ability of adhesive was produced. The results above were consistent with the results of TG.

**Analysis of Specific Surface Area**

Pore size distribution of hot water extract residues was shown in Figure 3, and isothermal absorption curve of hot water extract residues was shown in Figure 4. As can be seen in Figure 3, there were a large amount of micropore with diameter ranging from 0.383 to 2.33nm in the three samples, and the larger diameter of micropore concentrated on the region of 0.60~1.90nm. Comparing the three kinds of samples, it can be found that micropore diameter and peak area increased especially in samples made by steam injection pressing. As can be seen in Figure 4, along with the increase of relative pressure (P/P0), adsorptive capacity of sample increased gradually. Nitrogen adsorption volume first increased slowly; then fast. Saturation adsorption did not appear when vapor pressure was near saturation (P/P0=1). It was likely that the capillary condensation appeared in samples at high relative pressure. Nitrogen adsorption volume increased after hot-pressing announcing the increase of absorbing table in samples. Besides, nitrogen adsorption volume in materials made by steam injection pressing was the largest one among the three samples announcing that this sample has the biggest specific surface area. After calculation, specific surface areas in materials made by steam injection pressing and ordinary hot-pressing were 1.704m2/g and 1.455m2/g, which increased 35.9% and 16.0% respectively than that in raw material of 1.254m2/g. The reasons were shown as follows: chemical compositions like sugar and organic acid which can be easily dissolved in hot water were produced when hemicellulose hydrolyzed during hot-pressing. Then lots of pore spaces were created after dissolution of hydrolysis products. Moreover, due to the synergistic effect during steam injection pressing, more pore spaces were created, as a result of a greater degree of hemicellulose hydrolysate and more hot water soluble chemical composition produced. The results above were consistent with the results of HPLC analysis results.
Figure 3. Pore size distribution of hot water extract residues of ramie stem particles.

Figure 4. Isothermal absorption curve of hot water extract residues of ramie stem particles.
Analysis of Specific Surface Area

Mechanical properties of national standard board, ordinary hot pressboard and steam injection particleboard were shown in Table 5. The mechanical properties of hot pressed board was better than that of standard board, and steam injection particleboard displayed best mechanical strength. MOR and IB of steam injection particleboard were 14.8MPa and 0.75Mpa, respectively, which increased 84.1% and 44.2% compared with that of hot pressed. Thickness swelling rate of steam-pretreated board after 2h water immersion was 16.0%, which decreased 60.0% compared with that of hot pressed. Significantly improved mechanical properties of steam injection particleboard were possibly ascribed to follow contributions. The increased active hydroxyls produced by synergistic effect with water and heat during steam injection pressing are good for creation of hydrogen bonds to strengthen internal bond. In addition, hydrolysis degree of hemicellulose and cellulose is greater during steam injection pressing. The hydrolysate copolymerizes with lignin to form more polycondensation furan resin and other kind of condensation compound which was similar to phenolic resin adhesive. Finally, temperature distributions in internal-mat are more uniform after fierce action of water and heat. The lignin in ramie stem particles were fully expanded, evenly distributed between ramie stem particles, which increases mechanical properties of particleboard to some extent.

<table>
<thead>
<tr>
<th>sample</th>
<th>MOR (MPa)</th>
<th>IB (MPa)</th>
<th>TS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard board</td>
<td>12.50</td>
<td>0.28</td>
<td>8.0</td>
</tr>
<tr>
<td>hot pressboard</td>
<td>8.04</td>
<td>0.52</td>
<td>40.0</td>
</tr>
<tr>
<td>steam injection particleboard</td>
<td>14.8</td>
<td>0.75</td>
<td>16.0</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1) The synergistic effect of the heating and steam resulted in increased active hydroxyls which could form hydrogen bonds and van der waals forces between ramie stem particles. The enhanced bonding force plays significant role for the increasing mechanical properties.

2) Part of hemicellulose in ramie stem particles were hydrolyzed into –furfurals, which is important chemicals for self-bonding of particleboard. The furfurals subjected to automatic oxidation and catalytic oxidation generated furoic acid which help to produce furfuryl alcohol. Regenerated polycondensation furan resin catalytically synthesized with furfuryl alcohols and organic acid. Meanwhile, furfural compounds also could be polycondensated with the lignin to generate a kind of condensation compound which was similar to phenolic resin adhesive.

3) Temperature distributions in internal-mat are more uniform with the fierce action of water and heat. The lignin in ramie stem particles were fully expanded, and evenly distributed between each of the two ramie stem particles, which increases mechanical properties of particleboard.
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