PREPARATION AND APPLICATION OF HIGH PERFORMANCE CORN STARCH GLUE IN STRAW DECORATIVE PANEL

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(Received September 2017)

Abstract. To develop a production technique for nonformaldehyde-tolerant straw veneer by using a biomass-based adhesive, this study used corn starch as the main material and combined it with polyvinyl alcohol solution, flour, and polyisocyanate prepolymer to prepare a corn starch adhesive without formaldehyde. The adhesive was applied to the straw board substrate veneer used for decorative board products, and the production process and production properties were evaluated. The results showed that the corn starch adhesive was excellent, and indexes of the product reached the performance requirements of the artificial board in GB/T 14074-2006. The surface bonding strength of the mattress board veneer decorative cover was greater than 0.40 MPa, and the physical and mechanical properties met or exceeded the national standard (GB/T 15104-2006) for a decorative veneer. Formaldehyde emission in the production process was less than 0.05 mg/L. These results have great significance in the improvement of the practicality of biomass-based adhesives in the manufacture of wood-based panels.

Keywords: Straw particleboard, decorative veneer, corn starch, nonformaldehyde adhesive, process, rice straw composite panels.

INTRODUCTION

A formaldehyde-free substrate prepared from straw and isocyanate adhesive meets the requirements of environmental development. Straw boards, which have a uniform density, smooth surface, and no obvious color difference, have been used in furniture manufacturing, flooring, sound-absorbing panels, kitchen cabinets, packaging, and interior decoration (Alyssa et al 2005). However, because of the monotonous surface color, poor decorative properties, and poor dimensional stability of rice straw boards, it is necessary to carry out surface decoration treatments,

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such as finishing or overlaying, in practical applications (Xiong et al 2016a).

At present, most of the decorative boards are finished with a wood-based panel substrate and wood veneer. Because of the influence of traditional wood-based panels and wood-based panel overlaying technology, the overlaying process of straw boards also is affected by this technological process. There are two major problems in the practical application process. One is that the veneering process is imperfect and nonstandard, often leading to dry shrinking, bending, deformation, and panel cracking on the straw board surface. The other one is that the formaldehyde resin adhesive used to attach the decorative plates continues to release formaldehyde, resulting in a straw board substrate veneer decorative plate that is, in the true sense, not environmentally safe. There are many reports of attempts to improve the quality of straw substrate veneer overlaying technology. Daniel et al (2003) reported that the species, adhesive, front and back of thin wood veneers, curing conditions, and drying time are the important factors contributing to surface cracks. When a panel attached by urea–formaldehyde glue is placed in the RH of 35% for 1 min, cracks will appear on the panel surface. Ozarska (2003) performed deep research on decorative decoration technology and published a monograph “Veneer decorative technology guide.” Previously, we reported the thorough technical specifications of a straw substrate sanding and veneering process and discussed the straw substrate veneer warping deformation phenomenon (Xiong et al 2016b). Following a literature review of this field, we found that a study of the environmental problems of veneer panels of the straw substrate has not been reported.

In the current furniture market, the adhesive used in the wood-based panel substrate veneer bonding process is mainly resin based, and a formaldehyde resin adhesive is widely used. The main reason is that urea–formaldehyde resin (UF) is easy to use, abundant in materials, low in cost, and good in bonding strength. Therefore, UF has become one of the most widely used adhesives in the wood industry (about 70% of the total mass of the synthetic resin was used) (Shi and Zhang 2009). However, the use of UF adhesive makes wood-based panels with high levels of formaldehyde emissions, environmental pollution, human health endangerment, and other shortcomings (Deng and Fu 2005). Therefore, many countries, especially in Europe, the United States, Canada, and Japan, very strictly regulate formaldehyde emissions from wood-based panels. China also has developed a mandatory national standard for formaldehyde emission. With the increased awareness of environmental protection, a formaldehyde-free wood-based panel is required, and research on formaldehyde-free straw boards is becoming more and more important.

Improvement in UF production technology, reducing the amount of formaldehyde, adding a trapping agent, and other techniques can reduce the formaldehyde emission level of wood-based panel from the initial unrestricted development to the current European formaldehyde emission standard E2, E1, and E0 levels. However, although it can reduce the formaldehyde emission of UF, modifications also affect the adhesive performance and cannot completely eliminate the release of formaldehyde (Tian 2003). With the growing awareness of environmental protection and the growing shortage of oil resources, the potential defects of and problems with synthetic polymer wood adhesives will become increasingly obvious. Therefore, the use of rich materials, renewables, and low-priced natural polymer resources, such as starch, as a main raw material to prepare a nonformaldehyde wood adhesive for the production of wood-based panels should become an inevitable trend in the development of wood-based panel industry in the future (Ye and Gao 2008). The research on the production of wood adhesives with biomass as the main material began as early as 10 yr ago (e.g Sandip et al 2003; Shi and Wei 2003). Although there have been many improvements in the bonding strength and water resistance of modified starch adhesives, many problems, such as poor stability, high production cost, and complicated production processes, exist. The main reason is that the biomass-based adhesives require a strict
gluing condition in the production process (Wang and Li 2015). It has not really been used in the actual production to get a good application till now, especially for straw board paste wood decoration technology in biomass-based adhesives (Zheng and Hao 2012). Based on these results, this study used corn starch as the main material to produce a wood adhesive and applied it to a thin wood decoration surface straw board. Through analysis of the bonding strength and peeling length of straw board paste veneer, a practical large-scale production process was demonstrated. The purpose is to improve the quality of straw board paste thin wood decorative board and the biomass-based adhesive in the field of formaldehyde-free artificial boards and provide an appropriate method for the application of thin veneer channels.

MATERIALS AND METHODS

Rice Straw Particleboard

Rice straw particleboards were purchased from Jiangsu Dingyuan Technology Development Co., Ltd. The size was 1220 mm × 2440 mm × 18 mm, density 0.75 g/cm³, MC 7.851%, thickness 18 mm, surface roughness Rₚᵥ 108 µm, Rₐ 8.65 µm, and S_m 0.16 mm.

Overlaying Material

Betula Alnoides Buch.-Ham. ex D. Don wood was used as the overlaying material. The thickness was 0.6 mm and the MC was 8-10%.

Preparation Materials of Starch Adhesive

Industrial grade corn starch was purchased from Shandong Zhucheng Xing Mao Development Co., Ltd. (Zhucheng city, Shandong Province, China).

Analytically pure HCl was purchased from Guangzhou Chemical Reagent Factory (Guangzhou city, Guangdong Province, China).

Analytically pure NaOH, K₂S₂O₈, CH₃COOH, H₂C₂O₄, and polyvinyl alcohol (PVA) were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

The flour used as filler was of industrial grade and purchased from Xi’an Guowei Starch Co., Ltd. (Xi’an city, Shaanxi Province, China); CaCO₃ was purchased from Jiangxi Haiyuan Chemical Co., Ltd. (Haiyuan city, Jiangxi Province, China); and polyisocyanate prepolymer (PMDI) enhancer was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Instruments

The following instruments were used in this study. An MC analyzer (KT-10, Italy KLORTNER); a surface roughness tester (2222 type multiparameter surface roughness tester, Harbin measuring tool factory); an extraction instrument (Sanli; Shenzhen Sanli Chemicals Co. Ltd., Shenzhen city, Guangdong Province, China); an electronic universal mechanical testing machine and auxiliary equipment (CMT6104; Shenzhen Sans Testing Machine Co., XLB, Shenzhen city, Guangdong Province, China); a hot press (Qingdao Third Rubber Machinery Factory, Qingdao city, Shandong Province, China); a precision sliding table saw (MJ6132; Ma Fujian Woodworking Machinery Factory, Fuzhou city, Fujian Province, China); a thermostating test machine (DHG-9143BS-III; made by Shanghai CIMO Instrument Co. Ltd., Shanghai, China); a custom square iron block, card head, and fixtures (square iron block size 20 mm × 20 mm × 20 mm); and a broadband sander (100 #–180 #). Stretch films and/or plastic films were used as curing treatment materials.

Pretreatment of Corn Starch

Step 1: The pH of the starch aqueous emulsion was adjusted to ≤4 with HCl solution, adding about 2% K₂S₂O₈, and reacted at 70°C for 60 min. The reactants were cooled to below 45°C and used in step 2.

Step 2: The pH of the starch solution obtained in step 1 was adjusted to pH 10 with NaOH solution, acetic acid, and esterified at room
temperature for 10-20 min. Then pH was adjusted to 9 with NaOH solution and oxalic acid added to make a cross-linking reaction at room temperature for 20-30 min. The esterification and cross-linking reactions were repeated until a stable modified starch emulsion was obtained. In general, the amounts of acetic acid and oxalic acid used in the esterification and cross-linking reaction were about 8-12% of the starch mass.

**Preparation of Corn Starch Adhesive**

Step 1: Corn starch is made from corn by soaking, separation, washing, grinding, dehydration, and other processes which make it similar to ordinary flour. Fifty parts by weight were ground with 133 parts of water to prepare the corn starch solution.

Step 2: The corn starch solution was gelled by mixing with an aqueous solution of sodium hydroxide (18 parts of sodium hydroxide dissolved in 30 parts of water) at 70°C for 30 min and mixed with 300 parts of cold water and stirred to obtain liquid A.

Step 3: One part potassium pyroantimonate was dissolved in 40 parts water in another container, stirred, and dissolved in 1000 parts of water at 35°C; then it was mixed with 65 parts of borax and 500 parts of corn starch to obtain liquid B. A mixture of A and B was stirred every 15 min in 30 min to obtain a starch binder that had excellent storage performance.

**Test of Corn Starch Adhesive**

The properties of the corn starch adhesive were measured according to GB/T 14074-2006. Through experiments with plywood veneer and straw board substrate, the tackifier, filler, and reinforcing agent were selected.

**Preparation of Thin Veneer of Straw Board**

The process of preparation of a thin veneer of straw board with corn starch adhesive is shown in Fig 1.

![Diagram](image)

**Table 1. Orthogonal test factors.**

<table>
<thead>
<tr>
<th>Level</th>
<th>A (unit pressure, MPa)</th>
<th>B (hot pressing temperature, °C)</th>
<th>C (hot pressing time, s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
<td>100</td>
<td>180</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>110</td>
<td>240</td>
</tr>
</tbody>
</table>
The press pasting process (Qian 2011; Xiong et al. 2013) includes gluing and assembly, prepressing, aging and repair, hot pressing, and sanding (Fig 1). This process was carried out in RH of 55-65% and temperature of 25-30°C. During the testing process, the pressure, hot pressing temperature, and hot pressing time were examined. The single-sided gluing amount was controlled at 80-150 g/m², pressure was 0.5-1.0 MPa, temperature was 90-110°C, hot pressing time was 120-240 s, and aging time was 3-10 min. An orthogonal test method (Cheng and Zhang 2001) was used to determine the results. An orthogonal table L₉ (3⁴) as shown in Table 1 was used, and each test was repeated three times to obtain the average value.

Surface Bonding Strength

The surface bonding strength of thin veneer straw boards was examined according to GB/T 15104-2006, GB/T 19367.1-2003, and GB/T 2828.1-2003. The testing sample size was 50 mm × 50 mm, and it was examined on a universal mechanical testing machine (Liu 2005), as shown in Fig 2.

Physical and Chemical Properties of Thin Veneer Straw Board

The thickness, width, and length of thin veneer straw boards were measured according to GB/T 19367.1-2003 and GB/T 2828.1-2003, and the water concentration, peel strength, thermal cycling, and formaldehyde emission (perforation extraction method) were examined according to GB/T 15104-2006 and GB/T 2828.1-2003.

RESULTS AND DISCUSSION

Characteristics of Corn Starch Adhesive

The characteristics of corn starch adhesive were examined according to GB/T 14074-2006, and the results are summarized in Table 2.

The results showed that the corn starch adhesive has a long shelf life (over 100 Days), and the esterification degree was 0.0166-0.030 estimated using a titration method according to GB/T 14074-2006. Although the corn starch emulsion showed good adhesion and film-forming, it needs a tackifier, fillers, and an enhancer when being used in straw board substrate veneer decorative plates.

In this study, PVA was used as the tackifier. When PVA was added to the corn starch adhesive, the results showed a significant improvement in adhesion and film-forming properties.

### Table 2. Quality index of corn starch adhesive.

<table>
<thead>
<tr>
<th>Idem</th>
<th>Quality index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exterior</td>
<td>Milky white uniform emulsion</td>
</tr>
<tr>
<td>Solid content (%)</td>
<td>≥30</td>
</tr>
<tr>
<td>Storage period (days)</td>
<td>≥100</td>
</tr>
<tr>
<td>pH</td>
<td>6–7</td>
</tr>
<tr>
<td>Esterification degree</td>
<td>0.166-0.030</td>
</tr>
</tbody>
</table>
the preformability of the emulsion obviously improved, and the optimum concentration of PVA was about 30-45% of the corn starch adhesive. Because the molecular structure of flour and corn starch is similar, flour was used as filler and the mixer was stable because of good compatibility. We also tried using light calcium carbonate as filler, but the compatibility between corn starch and calcium carbonate was poor and the mixture was unstable. Of course, light calcium carbonate as filler can result in quick thickening, but very quick thickening is not conducive to the characteristics of glue. In this study, flour was selected as filler; flour not only improves the performance of corn starch adhesive and reduces the shrinkage of corn starch after curing, but also improves the aging resistance of the product layer. The optimum concentration is about 25-30% of the total amount of corn starch and tackifier. Finally, PMDI at 8-15% of the total amount of corn starch, PVA tackifier, and flour filler was added to the mixture as an enhancer to improve the physical and mechanical properties.

### Surface Bonding Strength

The surface bonding strength of the straw adhesive on the veneer of the straw board was examined according to GB/T 15104-2006, GB/T 19367.1-2003, and GB/T 2828.1-2003, and the results are summarized in Table 3.

It can be seen from Table 3 that when corn starch adhesive is used, all surface bonding strengths were greater than 0.45 after hot pressing, which not only meets but exceeds the requirements of GB/T 15104-2006 (≥0.40 MPa).

Figure 3 shows the factors that affect surface bonding strength. It can be concluded that the optimum technological process is A3B1C2; that is, the unit pressure is 0.8 MPa, the hot pressing temperature is 90°C, and the hot pressing time is 180 s.

The analyzed results of variance of surface bonding strength are summarized in Table 4.

![Figure 3. Analysis of the influential factors of surface bonding strength.](image-url)
It can be seen that the effects of factor $A$ (unit pressure), factor $B$ (hot pressing temperature), and factor $C$ (hot pressing time) on the surface bonding strength are not very significant. Both $F$ values of factor $A$ ($= 0.936$) and $B$ ($= 0.480$) are much smaller than the critical value ($= 3.49$). However, the $F$ value of factor $C$ ($= 2.675$) is relatively large compared with factors $A$ and $B$, suggesting that the hot pressing time may strongly affect the surface bonding strength.

### Dimensional Deviation and Warping Deformation

Twenty straw board veneer decorative boards were randomly selected to test the dimensional deviation and warping deformation according to GB/T 15104-2006 measurement.

Among them, the deviations in length and width of 18 pieces were less than 2 mm, of two pieces were less than 3 mm, and all were within ±3 mm of the value specified in GB/T 15104-2006.

The thickness deviations of 17 pieces were less than ±2 mm and three pieces were less than ±3 mm, so that all were within ±3 mm specified in GB/T 15104-2006.

For warping deformation, 18 pieces were less than 0.8% and two pieces were between 0.8-1%, so that all were less than 1% that specified in GB/T 15104-2006.

### Physical and Chemical Properties

Five pieces were randomly collected from the top, middle, and bottom of 1000 pieces of straw board veneer decorative boards to test the physical and chemical properties according to GB/T 15104-2006. The results showed that 1) the average moisture concentration was 10.2%, which is stipulated in GB/T 15104-2006 to be 4-13%; 2) the dipping stripping length was 0 mm, which is stipulated in GB/T 15104-2006 to be 25 mm; 3) after the hot and cold cycle test, the surface of the samples had no cracking, bubbling, foaming, or coloring and the size was stable. Thus, it achieves the requirements for an excellent veneer decorative board adhesive according to GB/T 15104-2006. Furthermore, 4) the formaldehyde emission was less than 0.05 mg/L, and almost no free formaldehyde was released. The reason may be because of the absorption of free formaldehyde by PVA and PMDI in the corn starch adhesive. Further studies are necessary.

### Process Analysis

In the production process of straw veneer decorative boards, using corn starch adhesive and UF as binders produces different results. First, when using cold pressure to produce decorative boards, cold pressing must be performed as soon as possible after gluing, especially when the moisture concentration is lower than 10%, it is necessary to carry out cold pressing within 40 min; when the MC is higher (14-16%), it is also necessary to carry out the cold pressing within 60 min. Second, in the hot pressing process, it is necessary to control the time from applying the glue to the hot pressing. Cold pressing must be performed between 4 and 8 h. Third, hot pressing conditions need to be strictly controlled, especially the hot pressing temperature and time.
CONCLUSIONS

The corn starch adhesive developed in this study is excellent, and the indicators are in line with GB/T 14074-2006 on the performance of wood-based panel adhesive requirements. The bonding process conditions for the corn starch adhesive are similar to those of UF adhesive, so only a slight adjustment in the current production line is necessary.

The corn starch adhesive developed in this study can be used as a nonformaldehyde adhesive to apply to the straw board veneer decorative plate production, with gluing performance in line with GB/T 15104-2006 quality requirements. In the use process of renewable and cheap natural polymer materials, the corn starch adhesive can be used as a nonformaldehyde adhesive in wood-based panel production. It is a green product in the true sense.

ACKNOWLEDGMENTS

This project was partly supported by a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Postgraduate Research & Practice Innovation Program of Jiangsu Province, and Natural Science Foundation of Jiangsu Province (No. BK20150881).

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