Manufacture of Thin Rice Straw Particleboards Bonded with Various Polymeric Methane Diphenyl Diisocyanate/Urea Formaldehyde Resin Mixtures

Peng Luo,* Chuanmin Yang, Mengyao Li, and Yueqi Wang

Reducing particleboard thickness is one of the major approaches to decrease consumption volume of particleboard for furniture manufacture. This study employed an adhesive mixture of polymeric methane diphenyl diisocyanate (PMDI) and urea formaldehyde (UF) to produce single-layer medium density thin rice straw particleboard. The effects of various PMDI/UF formulations as well as board density on mechanical properties and water resistance of rice straw particleboard were studied. The results indicated that the mechanical properties and water resistance of the thin rice straw particleboard were appreciably affected by resin formulation. The panels bonded with PMDI/UF adhesive mixtures had mechanical properties and water resistance far superior to those bonded with UF. Higher PMDI content levels in resin mixtures led to improved mechanical properties and water resistance. Density influenced mechanical properties and water resistance of the thin rice straw particleboard. Increasing the density of the panel could upgrade the mechanical properties of the thin rice straw particleboard. The experimental outcomes showed that PMDI/UF resin systems had potential to substitute for pure PMDI resin in producing thin rice straw particleboard, which could effectively lower manufacturing cost and bring economic efficiencies due to reduced amount of pricey PMDI.

Keywords: Rice straw; Thin particleboard; Polymeric methane diphenyl diisocyanate (PMDI); Urea formaldehyde (UF); Resin formulations

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INTRODUCTION

China lacks forests but manufactures and consumes large amounts of wood composites every year. The scarce forest resources in China cannot meet the raw material demand of the wood composites industry. However, China generates a great quantity of agricultural residues, including rice straw, annually. Currently, only a small amount of rice straw is utilized for animal feed, organic fertilizer, pulp, and papermaking, whereas the remainder is not fully and effectively utilized (Zhang and Hu 2014). Partial or full substitution of wood by rice straw to produce particleboard may realize sustainable development of the wood composites industry as well as preserve forest resources.

However, some defects of rice straw itself pose difficulties in producing particleboards (Li et al. 2010, 2013; Zhang and Hu 2014). Less structural homogeneity, lower cellulose and lignin content, but higher hemicellulose content of rice straw compared to wood lead to a weaker strength of rice straw (Li et al. 2013). In addition, rice straw contains a high amount of ash and silica (Li et al. 2010, 2013; Zhang and Hu 2014). The silica forms a nonpolar layer at the surface of rice straw, which hampers effective
absorption of conventional UF resin and the formation of a hydrogen bond, reducing the strength of rice straw particleboard (Papadopoulos 2010; Zhang and Hu 2014). Additionally, there is an obvious smooth wax layer on the surface of rice straw, leading to a weak bond between particles (Li et al. 2010, 2013; Zhang and Hu 2014). As a result, the straw particleboards made with urea formaldehyde (UF) are weak in strength, water resistance, and dimensional stability (Grigoriou 2000; Han et al. 2001; Boquillon et al. 2004; Han et al. 2010; Li et al. 2010; Papadopoulos 2010). It was reported that polymeric diphenyl methane diisocyanate (PMDI) is effective in producing straw particleboards with high performances (Mo et al. 2003; Li et al. 2010; Zhang and Hu 2014). The PMDI, a highly reactive organic compound, is able to penetrate deeply into the wax and silicate films of straw (Grigoriou 2000). In addition, the isocyanate groups of PMDI could react with water in the straw, producing cross-linked polyureas for better mechanical bonding (Chelak and Newman 1991; Heslop 1997; Papadopoulos et al. 2002; Mo et al. 2003).

Furthermore, PMDI has some unique characteristics, such as fast curing rate, it is free from formaldehyde emission, has good weather resistance, and has a small loading quantity requirement (He and Yan 2005, 2007). However, the cost of PMDI is about 7 to 10 times higher than that of UF (Cathcart 2003; Zhang et al. 2003), resulting in much higher production cost than the UF-bonded particleboard. Besides, PMDI must be applied using certain safety precautions. Application methods with aerosol formation require the installation of effective extraction units. In case of short-term and temporary exposure, the use of personal protection equipment consisting of respiratory protection is required. Therefore, the cost and type of adhesive are two important concerns of the particleboard industry for making cost-effective products (Zhang and Hu 2014; Zheng et al. 2009). Thus, there is a significant interest to develop a new and improved resin adhesive system to produce high quality straw particleboards with lowered cost.

A study conducted by Grigoriou (2000) has shown that appropriate resin mixtures of PMDI and UF produced wheat straw-wood composites with commercially acceptable physical and mechanical properties. The UF was sprayed to the mixture of wheat straw and wood particles before spraying PMDI, with various UF to PMDI ratios. The results indicated that introducing a small quantity of PMDI to UF could increase the strength and water resistance of wheat straw-wood composites. The author attributed the improvements in performance of composite panels to the enhanced cross-linking reactions of UF assisted by the introduction of PMDI. Hse et al. (2002) and Papadopoulos (2010) also reported the fortifying effects of isocyanate resin on UF bonded particleboards. However, these studies mainly concerned particleboards of thickness of more than 12 mm. Little information is available on the fortifying effects of PMDI on UF for producing thin particleboards (less than 8 mm in thickness).

In the furniture industry, the consumption volume of particleboards is closely related to furniture manufacturing cost. Reducing the thickness of particleboards is one of the ways to lower the consumption volume of particleboards, which is a challenge in the furniture industry. Additionally, thin particleboards have the potential to replace plywood for manufacturing furniture, which may save precious wood resources.

This work employed the mixed adhesives of PMDI and UF at different PMDI to UF ratios to produce an experimental single layer medium density thin rice straw particleboard. The objectives of this study were to investigate the effects of PMDI/UF resin systems as well as board density on the mechanical properties and water resistance of the thin rice straw particleboard. In addition, PMDI and UF were used as a resin adhesive for comparison.

EXPERIMENTAL

Materials and Methods

The rice straw, with initial moisture content of approximately 11.3%, was collected from Huiguan Village, Xiaozhan Township, Jinnan District, (Tianjin, China). Commercial PMDI, type PM-200, a dark brown liquid with a solid content of 100%, was obtained from Wanhua Polyurethane Co., Ltd. (Yantai, China). Its viscosity and pH were 150 to 250 mPa.s (25 °C) and 6.2, respectively. The UF resin with a solids content of 55% was purchased from Tianjin Resin Company (Tianjin, China). Its viscosity and pH were 280 mPa.s (25 °C) and 6.6, respectively. Ammonium chloride solution with 20% solids content (Pengcai Fine Chemicals Co., Ltd., Langfang, China) was added as a curing agent to the UF resin, and the application level was 5% based on the resin solid weight. To investigate the original water resistance of rice straw, no water repellent agent was used.

After manually removing the leaves and remnant grains, the rice straw was processed into small particles through a fodder grinder (Model HLO; Zhengyuan Powder Engineering Equipment Corporation, Shandong, China). Then, the particles were screened by hand through meshes with 0.3-mm openings to remove undersized particles and dusts. The particles were oven-dried at 100°C to 4% moisture content and placed in plastic bags for further use.

Pre-weighed rice straw particles were mixed with adhesives in a blender (Model HWJ 25; Xiaoshan Commercial Equipment Corporation, Zhejiang, China). The PMDI resin was sprayed onto rice straw particles through a pneumatic atomizing nozzle. After mixing for 5 min, the UF resin was sprayed onto rice straw particles in the same way and the blend was mixed for another 5 min. The only UF- and PMDI-bonded boards were also produced for comparison. The board types made with various resin types and dosages are given in Table 1.

Table 1. Particleboards and Resins Formulations Used in the Study

<table>
<thead>
<tr>
<th>Board Type</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMDI Dosage (%)</td>
<td>0</td>
<td>2</td>
<td>2.5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>UF Dosage (%)</td>
<td>14</td>
<td>12</td>
<td>11</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

The resin dosage was percentage of resin solid weight to oven dry weight of rice straw particles.

The single layer particleboard mats were fabricated using a laboratory mold with dimensions of 500 × 500 × 150 mm³ by hand. The amount of rice straw particles and resin mixture employed was adjusted in order to make the finished particleboard have various targeted densities of 700, 750, and 800 kg/m³. Teflon films were put on top and bottom surfaces of the mat to avoid sticking of particleboard to platens. After setting aside for 10 min, the mats were prepressed under 1.5 MPa for 30 s to tighten them. Then, the mats were hot-pressed according to a three-step hot press schedule with the hot press temperature of 180 °C. For the first step, the hot press pressure and time were 3.5 MPa and 180 s, and for the second and third step, the hot press pressure and time were 2 MPa and 120 s, and 1 MPa and 60 s, respectively. A pair of thickness gauges of 6 mm were employed during hot-pressing. Three panels were made for each manufacturing condition.

After being conditioned under 20 °C and 65% relative humidity (RH) for one week, the rice straw particleboards were trimmed to a final dimension of 450 mm×450 mm×6 mm. Then, the rice straw particleboards were cut into test specimens and tested in line with the China national test standard GB/T 17657 (1999) for density, internal bonding strength.
(IB), modulus of rupture (MOR), modulus of elasticity (MOE), 24 h water absorption (WA), and 24 h thickness swelling (TS). Analysis of variance (ANOVA) and Duncan's mean separation tests were used to statistically analyze the data obtained with a SAS software (SAS, SAS Institute Inc., Version 9.1.3, Cary, NC).

RESULTS AND DISCUSSION

The test results of rice straw particleboards manufactured under different densities and PMDI/UF combinations are shown in Figs. 1 to 5. The bonding strength of adhesives containing PMDI was significantly higher than that of conventional UF. As PMDI content increased, the mechanical properties and water resistance of rice straw particleboards increased. The particleboards produced with pure PMDI yielded the best mechanical properties and water resistance while the particleboards made with UF alone performed worst. Increasing density could upgrade the mechanical properties.

![Fig. 1. IB of the different types of boards under different densities](image-url)

The IB is the most important mechanical property for particleboard. The panels bonded with adhesives containing PMDI showed IB significantly higher than those bonded with UF alone (Fig. 1). Such observation was also made by Hse et al. (2002), who investigated the effects of PMDI/UF resin systems on properties of rice husk/wood composite panels with thickness of 12.5 mm. The IB was significantly affected by the PMDI content level in the resin mixtures. This was consistent with the findings of Grigoriou (2000), who fortified UF with PMDI to make wheat straw/wood composite panels of 12 mm thickness. An important IB enhancement was observed for PMDI modified UF resin systems (Grigoriou 2000). Similar findings about fortifying effect of PMDI/UF resin systems on IB strength was also reported by Papadopoulos (2010). Papadopoulos (2010) declared that PMDI resin was able to react with both the moisture and the hydroxyl groups in the raw material to form a tough mechanical bond as well as a chemical bond, which were capable of bonding a range of agrifibers. Li et al. (2010)
investigated the effect of six different particle sizes on selected physical and mechanical properties of 4% PMDI-bonded rice straw particleboard with a thickness of 12.5 mm and density of 0.7 g/cm³. The results they obtained indicated that the IB values ranged from 0.23 to 0.47 MPa, the MOR values ranged from 8.61 to 22.19 MPa, the MOE values ranged from 1.548 to 2.911 GPa and the 24h TS values ranged from 10.98% to 22.62% (Li et al. 2010). Compared with the particleboards of the same density range made by Li et al. (2010), similar or even superior IB values of 0.29, 0.34, 0.40 MPa resulted from PMDI/UF bonded thin rice straw particleboards were observed in the present study. This was an interesting finding, which meant PMDI/UF resin systems had potential of replacing PMDI resin in medium-density thin rice straw particleboard production. As the cost of UF is much lower than that of PMDI, there could be substantial economic proceeds by employing UF as the major constituent in a PMDI/UF resin formulation. The PMDI content in the resin mixtures had no significant influence on IB at constant density. The highest IB was achieved in the boards bonded with 4% PMDI. As expected, an increase in density led to an augmentation in IB of all the particleboards produced. Similar results have been reported by Zheng et al. (2007) in the study of saline ‘Jose’ tall wheatgrass particleboard of 5.3 mm thickness bonded with PMDI. The authors demonstrated that IB strength of particleboards was significantly improved with the increase of particleboard density. High-density particleboards had lower porosity so that particles and adhesives could interact with each other more easily to form stronger crosslink in comparison to low-density particleboards (Zheng et al. 2007). This phenomenon has also been observed in the UF-bonded reed/wheat straw particleboard of 8 mm thickness treated by silane coupling agent (Han et al. 1998).

Fig. 2. MOR of the different types of boards under different densities

Figures 2 and 3 show that MOR and MOE were appreciably affected by resin formulation. At constant density, the particleboards made with adhesives containing PMDI had significantly higher MOR and MOE values than the particleboards made with UF alone, and the 4%-PMDI bonded particleboard having the highest MOR and MOE. This observation was also observed in previous studies using rice straw/wood composites.

The MOR and MOE values increased with increasing PMDI content in the resin mixtures. This observation was parallel to the studies conducted by Grigoriou (2000) and Papadopoulos et al. (2002). Li et al. (2010) researched the effect of six different particle sizes on selected physical and mechanical properties of 4% PMDI-bonded rice straw particleboard with a thickness of 12.5 mm and density of 0.7 g/cm³. They stated that the MOR values ranged from 8.61 to 22.19 MPa, the MOE values ranged from 1.548 to 2.911 GPa (Li et al. 2010). At the 0.7 g/cm³ density level, the MOR and MOE values of PMDI/UF bonded particleboards from this study were similar to the MOR and MOE values from the study by Li et al. (2010). This encouraging result indicates PMDI/UF resin systems have potential to substitute pure PMDI resin in producing thin rice straw particleboard. The PMDI content in the resin mixtures had no significant influence on MOR and MOE at constant density. As expected, the MOR and MOE increased with an increase in density. This was also observed in a previous study on the effects of silane coupling agent on reed/wheat straw particleboard of 8 mm thickness bonded with UF resin (Han et al. 1998), which demonstrated that increase of board density led to an upgrade of MOR and MOE.

Fig. 3. MOE of the different types of boards under different densities

WA and TS were appreciably influenced by resin formulation (Figs. 4 and 5). Panels bonded with PMDI had the lowest WA and TS. It was noted that the panels bonded with adhesives containing PMDI showed their WA and TS significantly lower than that of bonded with UF alone. This was expected because the PMDI had a significantly superior water resistance than UF (Mo et al. 2003; Zheng et al. 2006). This result was consistent with the study of Hse et al. (2002), who noted a positive effect of PMDI/UF on water resistance of rice hull/wood composite panels. At constant density, increasing PMDI content in the resin mixture led to reduced WA and TS, though the reduction degrees were not as prominent as IB. Previous studies found that TS was affected by bond quality (Sauter 1996) and adhesive properties (Boquillon et al. 2004). PMDI could effectively wet the surface of the straw, enhancing chemical bonding through hydrogen bonds and
polyurethane covalent bonds. In addition, the isocyanate groups of MDI could react with water in the straw, producing cross-linked polyureas for better mechanical bonding (Chelak and Newman 1991; Mo et al. 2003; Li et al. 2010). UF resin could not effectively wet and penetrate the rice straw surface due to the hydrophobic wax and inorganic silica on the outer surface of rice straw (Li et al. 2010). As a result, water was able to penetrate readily into the UF-bonded panels, as opposed to PMDI-bonded panels. Li et al. (2010) studied the effect of six different particle sizes on selected physical and mechanical properties of 4% PMDI-bonded rice straw particleboard with a thickness of 12.5 mm and density of 0.7 g/cm³. They reported that the 24h TS values ranged from 10.98% to 22.62% (Li et al. 2010). Compared with the particleboards of the same density range made by Li et al. (2010), similar TS was observed in this study. The PMDI content in the resin mixtures had no significant influence on TS at constant density. The WA and TS increased as the density increase. Such observation was also made by Cai et al. (2004), who investigated mechanical and physical performances of particleboard made from low-value eastern redcedar trees (Cai et al. 2004). It should be noted that the particleboard density was controlled by means of a fixed mold volume, so the dimension of the particleboard was constant. To produce a particleboard with a higher density, the mass of the particle and resin mixture was higher, leading to more fibers per unit volume and less void space within the particleboards than lower density particleboards, and consequently swell relatively more than lower density particleboards when soaked in water for a long time. This was further supported by Halligan (1970) and Han et al. (1998), who pointed out that high-density boards possessed more compression set than lower density ones. Following a long duration of water immersion, TS would have a tendency to increase with increasing board density because of the greater springback of compacted particles in boards of higher density (Halligan 1970; Han et al. 1998). It should be noted that no wax was used in this study. Adding wax into particleboard may effectively enhance its water resistance and dimensional stability (Lin et al. 2008; Xu et al. 2009; Li et al. 2010).

![Fig. 4. WA of the different types of boards under different densities](image-url)
CONCLUSIONS

1. The mechanical properties and water resistance of thin rice straw particleboard were appreciably affected by resin formulation. The pure polymeric methane diphenyl diisocyanate (PMDI) bonded panels had the best mechanical properties and water resistance. The panels bonded with PMDI/UF adhesive mixtures had mechanical properties and water resistance far superior to those bonded with urea formaldehyde (UF). Higher PMDI content levels in the resin mixtures led to improved mechanical properties and water resistance.

2. Density influenced the mechanical properties and water resistance of the thin rice straw particleboard. Enhancing the density of the panel could upgrade the mechanical properties of the thin rice straw particleboard.

3. PMDI/UF resin systems showed potential to substitute pure PMDI resin in producing thin rice straw particleboard, which could effectively lower manufacturing cost and bring economic efficiencies due to the reduced amount of pricey PMDI.

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