Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives

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ABSTRACT
The main goal of this work was to evaluate the technical feasibility of using rice husk (RH) as wood substitute in the production of environmentally sound medium-density particleboards using adhesives from soybean protein concentrate (SPC). Chemical modification of rice husk with sodium hydroxide and sodium hydroxide followed by hydrogen peroxide (bleaching) were undertaken to evaluate the effect of such treatments on the composition and topology of rice husk and the performance of produced panels. Both treatments were efficient in partially eliminating hemicelluloses, lignin and silica from RH, as evidenced by thermo-gravimetric analysis (TGA). Scanning electron microscopy observations suggested that alkaline treatment resulted in a more damaged RH substrate than bleaching. The dependence of mechanical properties (modulus of rupture, modulus of elasticity, and internal bond) and the physical properties (water absorption and thickness swelling) on chemical treatments performed on both, rice husk and SPC was studied. Bleached-rice husk particleboards bonded with alkaline-treated soybean protein concentrate displayed the best set of final properties. Particleboards with this formulation met the minimum requirements of internal bond, modulus of elasticity and modulus of rupture recommended by the US Standard ANSI/A208.1 specifications for M1, M5 and M2-grade medium-density particleboards, but failed to achieve the thickness swelling value recommended for general use panels. This limitation of soybean protein concentrate-bonded rice husk particleboards was counterbalanced by the advantage of being formaldehyde-free which makes them a suitable alternative for indoor applications.

1. Introduction

The use of alternative resources to substitute wood in the particleboard industry has increased in recent years mainly due to the depletion of forest resources. Potential substitutes for wood include harvesting residues, barks, annual plants, plant residues, residues of pulp plants, recycled paper, etc. (Akgül and Camlibel, 2008). Among them, agricultural residues are emerging as a source of raw materials which provide renewable and environmentally friendly alternative biomass resources for easing the high demand for woody materials (Sampathrajan et al., 1992). Besides their abundance and renewability, the utilization of agricultural residues has advantages for economy, environment, and technology (Çöpür et al., 2007). Agricultural residues, including wheat and rice straw (Mo et al., 2001; Wang and Sun, 2002; Mo et al., 2003; Bouquillon et al., 2004; Cheng et al., 2004), sugarcane bagasse (Maldas and Kota, 1991), hazelnut (Çöpür et al., 2007, 2008) and rice husks (Ajiwe et al., 1998; Gerardi et al., 1998; Lee et al., 2003; Leiva et al., 2007; Ndazi et al., 2007), sunflower stalks (Khrystova et al., 1998), coconut shells (Almeida et al., 2002) and fruit pruning (Ntalos and Grigoriou, 2002), are obtained in large quantities worldwide, and some of them have been successfully used in particleboard manufacturing. Indeed, boards based on wheat straw, sugarcane bagasse, and other lignocellulosic agro-based residues are already on the market under different trademark names such as Ecopanel System (wheat straw, rice straw, palm, bamboo, Ecopanel System Ltd.), Primeboard (wheat straw and sunflower seed hulls), and Dura-Cane (sugarcane bagasse, Acadia Board Co.), showing that industrial applications of agricultural residues could be environmentally friendly and also profitable.

Rice husks (RHs) are the hard, protective shell of the grain and are the main by-products of the rice milling process, which is available in fairly large quantities in one area. The world production of rice in 2005/2006 was approximately 413 million tons (Umaran, 2006). Particularly, Argentina contributed with about 0.28% of the world production in the same period (about 1 million tonnes in the same period). For every one million tonnes of paddy rice harvested, about 200,000 tonnes of rice husk is estimated to be burned, used as animal bedding or left in the field after harvest. Any possible usage of that will yield economic as well as environmental dividends. Indeed, the RH recycling rate into value-added...
byproducts is about 10% (Kato, 2000); in particular, it can be used as a source of high-grade amorphous silica (Vlaev et al., 2003), as a concrete additive (Rodríguez de Sensale, 2006) and as a reinforcing agent for thermoplastics and rubbers (Park et al., 2003).

RH has the same basic components as wood but in different proportions. It contains 25–35% cellulose, 8–21% hemicelluloses, 26–31% lignin, 15–17% amorphous silica and waxes, and 2–5% of other soluble substances (Gerardi et al., 1998; Mansaray and Ghaly, 1998; Stefani et al., 2005). Therefore, it would be expected that entire RH should behave similarly to wood in particleboard production. However, the high silica content could be a problem during RH-based board manufacture. Data reported in the literature indicate that silica percentage higher than 0.03% causes excessive tool wear during particleboard production (Lehmann and Geimer, 1974). The constant average dimensions of RHs save grounding operations, reducing tool wearing problems with cost benefits. However, machining the edges of the produced boards is always necessary therefore the tooling cost of this stage in board manufacturing is anticipated to be higher compared to that of the wood-based counterpart. In addition, the presence of silica and waxes at concentrations higher than those of wood may affect RH interactions with polar adhesives such as formaldehyde-based adhesives such as urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives (Gerardi et al., 1998; Park et al., 2003; Leiva et al., 2007; Ndazi et al., 2007). Different strategies have been applied to improve RH adhesion with currently used adhesives. Among them steam explosion (Gerardi et al., 1998; Ndazi et al., 2007) and alkaline treatment (Ajije et al., 1998; Ndazi et al., 2007) are the most used on RH intended to be used in panel formulations.

The immersion of lignocellulosic fibers in diluted alkaline medium facilitates the adhesive nature of the fiber surface by removing natural and artificial impurities, and causes the separation of structural linkages between lignin and carbohydrate and the disruption of lignin structure (Alvarez et al., 2003; Kumar et al., 2004; Ndazi et al., 2007; Wang et al., 2007). The combination of alkaline treatment with hydrogen peroxide, also known as bleaching, is commonly used in the paper-making industry as an environmentally friendly, easy-to-operate reagent (Salam et al., 2007; Wójciak et al., 2007). The main goal of such process is the removal of lignin left after the alkaline treatment (Wang et al., 2007). This strategy was successfully applied to modify wheat straw intended to be used in particleboards manufacture (Mo et al., 2001). Authors found that particleboards made from wheat straw treated with 1 M NaOH and 0.2% H₂O₂ solution gave tensile strength and compression strength values significantly higher than those of the un-treated counterpart and in the same range than those obtained when treating the substrate with a commercial bleaching solution (containing sodium hypochlorite).

Formaldehyde-based adhesives such as UF and PF resins dominate the current wood adhesive market. Despite the well-known advantages of such resins, formaldehyde emissions and their non-renewable nature have become a matter of increasing concern. Therefore, environmentally friendly adhesives from renewable resources and free from formaldehyde are nowadays developed to replace the UF and PF binders. Un-modified or modified soybean proteins can be used as environmentally friendly and formaldehyde-free substitutes for the traditional synthetic adhesives in particleboard manufacturing (Lambuth, 1994; Hettiarachchy et al., 1995; Mo et al., 2001, 2003; Wang and Sun, 2002; Cheng et al., 2004; Wescott and Frihart, 2004). The gluing capacity of soybean protein solution, which increases the contact area and adhesion with other substrates. The unfolding of soybean protein isolate (SPI) molecules has been promoted by different strategies, including thermal, chemical, and enzymatic treatments (Lambuth, 1994; Hettiarachchy et al., 1995; Mo et al., 2001, 2003; Wang and Sun, 2002; Cheng et al., 2004; Wescott and Frihart, 2004). However, soy protein isolate is not as economically favorable as soy protein concentrate (SPC). SPC contains both soy protein and insoluble soy carbohydrate and is obtained after water-soluble whey (soluble carbohydrate) is removed from defatted soy flour.

The main goal of the present work was to upgrade the final mechanical properties and water resistance of RH–SPC particleboards by modifying RH with NaOH and NaOH followed by hydrogen peroxide, using un-treated and alkali-treated SPC as adhesives. The effect of chemical treatments on RHs was followed by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The performance of the obtained panels was evaluated by measuring the final properties, such as modulus of elasticity (MOE), modulus of rupture (MOR), internal bond (IB), water absorption (WA) and thickness swelling (TS).

2. Experimental

2.1. Materials

RHs (Don Juan variety), was supplied by local rice milling industries of Entre Ríos (Argentina). The as-received RH, has constant average dimensions (8 ± 1 mm × 4 ± 0.5 mm × 0.3 ± 0.05 mm) which save grounding and screening operations. Soybean protein concentrate (SPC, Solcom S) containing around 65 wt% protein on dry basis and an average particle size passing through 100 mesh, was provided by Cordis SA (Villa Luzuriaga, Buenos Aires, Argentina). Sodium hydroxide was purchased from Aendra (San Fernando, Buenos Aires, Argentina) and hydrogen peroxide was from DEM (Mar del Plata, Buenos Aires, Argentina).

2.2. Methods

2.2.1. RH Chemical treatments

RH was extensively washed with distilled water in order to remove impurities (mainly dust). This operation was performed several times at room temperature and under vigorous stirring. After successive washings, RH was dried to equilibrium moisture (about 8 wt%) in an air-circulated oven at 100 ± 2 °C. This material was stored in hermetic plastic containers in order to prevent microbial attack (i.e. fungi) before using it in chemical treatments. Washed RH without any further treatment was used as control and was labeled CRH.

Some components of cellulose fibers represent a hydrophobic blockage for fiber wetting and they must be efficiently removed (Gerardi et al., 1998; Alvarez et al., 2003; Ruseckaite and Jimenez, 2003; Liu et al., 2004; Leiva et al., 2007; Ndazi et al., 2007; Wang et al., 2007). In order to improve the RH wettability, different chemical pre-treatments were applied. CRH was soaked in 1 M NaOH solution at a mass ratio 1:10, for 30 min at room temperature with occasional shaking followed by washing with distilled water for several times to leach out the absorbed alkali. The resultant RHs were subsequently oven dried as described for CRH. The alkali-treated RHs were labeled as ARH.

Oxidizing agents, such as H₂O₂ are used to chemically modify and/or partially delignify lignocellulosic fibers to improve their properties and make them suitable for textile applications (Salam et al., 2007; Wójciak et al., 2007). Polyphenolics such as lignin can form alkali resistant linkages (ether linkages) with hemicelluloses, which can be cleaved by subsequent hydrogen peroxide treatment. This process not only reduces much of the lignin content but also the stirring, which is an integral part of the process, opens the fiber structure by mechanical shear, making available free hydroxyl groups of cellulose to bind with polar compounds (i.e. water or polar adhesives). This treatment, usually called
bleaching, was successfully applied to wheat straw which, as RH, is rich in silica and waxes (Ajije et al., 1998; Gerardi et al., 1998; Mansaray and Ghaly, 1998; Park et al., 2003; Stefani et al., 2005; Ndazi et al., 2007). In the present study, bleaching was carried out at room temperature as a two-stage process. CRH was first treated with 1 M NaOH under stirring for 15 min. Afterward, the alkali-treated RH was washed with abundant distilled water until neutral pH was reached, filtered - off and subsequently soaked in a 0.02 wt% H2O2 solution under stirring for 15 min. After chemical bleaching, RH was washed with abundant distilled water, filtered and oven dried as described earlier. The bleached RH was labeled as BRH.

2.2.2. SPC modification

Un-modified soybean protein concentrate (USPC) adhesive was prepared by the dispersion of the SPC powder in distilled water at a SPC-to-water ratio 1:10 under stirring at room temperature for 2 h. An alkali-treated soybean protein concentrate (ASPc) was prepared as described elsewhere (Mo et al., 2001, 2003; Wang and Sun, 2002; Cheng et al., 2004; Leiva et al., 2007). Typically, SPC was dispersed in a 0.2% NaOH solution under the same conditions described for the USPC preparation. The resultant adhesives were then ready to be mixed with RH.

2.2.3. Particleboard formulation and processing

Particleboards were manufactured using the procedure described in our previous work (Leiva et al., 2007). Chemically treated and un-treated RHs with 8% initial moisture content were blended with the home-made SPC-based adhesives (10 wt% solids) in an orbital paddle mixer (M.B.Z., San Justo, Buenos Aires, Argentina) for 10 min at room temperature (20–22 °C). The final RH–SPC-based adhesive mixtures were oven dried at 70 °C until 40% moisture was reached in the final mixture. Moisture improves mobility of soybean protein polypeptide chains promoting the adhesion with lignocellulosic substrate in hot press processing (Li et al., 2009). The equilibrated mixtures were subsequently hot-pressed (E.M.S., Buenos Aires, Argentina) into particleboards in a 30 cm × 30 cm steel mould equipped with stops to achieve the same thickness (0.55 cm). The press time, temperature and pressure were 10 min, 140 °C and 2.9 MPa, respectively. Target bulk density for all boards was 0.80 ± 0.05 g/cm3 and accounted for about 7% of the total weight loss. All measurements were recorded against the shear rate. The viscosity values were the average of three measurements.

2.2.4. Thermo-gravimetric analysis (TGA) of rice husks

Thermo-gravimetric analysis (TGA) was used as a tool to determine the initial relative composition and the effect of chemical treatments on the composition and thermal stability of RH. Non-isothermal experiments were carried out using a thermo-balance TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland) operating from 30 °C to 800 °C at a heating rate of 10 °C/min and under nitrogen and air atmospheres (20 mL/min).

2.2.5. Scanning electron microscopy (SEM) of rice husks

The effect of chemical treatments on RH surfaces (inner and outer) was analyzed by scanning electron microscopy (SEM), using a Jeol JSM 6460-LV microscope (Eindhoven, The Netherlands) at an acceleration voltage of 15 kV. Microphotographs were taken on gold-coated surface of the specimens.

2.2.6. Adhesive viscosity

The viscosity of the SPC-based adhesives was measured with a Brookfield DV-III plate and cone viscosimeter (Middleboro, MA) at room temperature. The adhesives were prepared as above described and were transferred into the sample holder of the viscosimeter. All measurements were recorded against the shear rate. The viscosity values were the average of three measurements.

2.2.7. Particleboards evaluation

The performance of the obtained particleboards was evaluated according to the ASTM D 1037-93 standard procedure. Three-point bending was determined in an Instron 4467 universal test machine (Buckinghamshire, England). The modulus of rupture (MOR) and the modulus of elasticity (MOE) were determined on rectangular strips of 5 cm × 19 cm at a crosshead speed of 2.9 mm/min. Internal bond strength (IB) measurements were performed on 5 cm × 5 cm square probes at a crosshead speed of 1.33 mm/min. All samples were conditioned at 65% relative humidity at 20 °C and for 7 days before testing. Nine specimens were prepared for both three-point bending and IB tests and averaged for each set of the results. The moisture content (MC) was gravimetrically determined from strips previously used in flexural tests. The water absorption (WA) and thickness swelling (TS) were also measured according to the ASTM D 1037-93 standard method. Rectangular samples (6 cm × 12 cm) were soaked in water at room temperature for 2 and 24 h to evaluate the short- and long-term changes. The weight gain and thickness were measured immediately after soaking. Six specimens were used for each kind of adhesive-RH mixture.

2.2.8. Industrial standard

Modulus of elasticity (MOE), modulus of rupture (MOR), internal bond (IB) as well as thickness swelling percent (%TS) of the obtained particleboards were compared with the requirements for grades of medium-density particleboards as specified by the American National Standard Institute (ANSI/A208.1).

2.3. Statistical analysis

Data for each test were statistically analyzed. The analysis of variance (ANOVA) was used (α = 0.05) to evaluate the significance in the difference between factors and levels. Comparison of the means was done employing a Tukey test to identify which groups were significantly different from other groups (P < 0.05).

3. Results and discussion

3.1. Structural analysis

RH has the same basic components as wood but in different proportions, depending on the rice variety. Therefore, it would be expected that RH should behave similarly to wood in particleboard or composite production (Ajije et al., 1998; Gerardi et al., 1998; Mansaray and Ghaly, 1998). As it was stated before, RHs have lower cellulose and lignin content than wood, but higher amounts of silica which reduce the interactions with polar adhesives (Gerardi et al., 1998; Park et al., 2003; Leiva et al., 2007; Ndazi et al., 2007) such as soybean protein-based adhesives.

Chemical modifications were undertaken in order to upgrade RH wettability. The effectiveness of each treatment was evaluated examining their influence on RH's relative composition and topology, as well as on the performance of the obtained panels. Thermo-gravimetric analysis was used as a tool to determine the relative composition of CRH from Don Juan variety. The TG/DTG curves of CRH obtained under inert atmosphere are shown in Fig. 1. As usually occurs for other lignocellulosic compounds (García-Pérez et al., 2001; Ruseckaitė and Jimenez, 2003; Liu et al., 2004), CRH thermal decomposition seems to be a gradual process with two main steps in TG curve (Fig. 1). The initial weight loss which extended up to 130 °C and accounted for about 7% of the total weight loss was
caused by volatilization of absorbed moisture present in all samples. The second and main stage, which occurred between 250–360 °C and accounted for around 50% of the total weight loss, was associated with the degradation of main components of CRH. According to DTG curve (Fig. 1), two overlapped peaks can be easily observed. The area under each peak represents the weight loss of each component. In this work, a deconvolution method was used as a first approach for splitting the peaks and evaluating the relative contribution of each component. The first peak in DTG curve of CRH appeared as a shoulder of the main one, at a maximum degradation rate \( T_{\text{max}} \) of 301 °C and contributed with around 20% of total weight loss. This peak is likely due to depolymerization of hemicelluloses and amorphous cellulose which degrades more easily than crystalline cellulose (Mansaray and Ghaly, 1998; Stefani et al., 2005; Ndazi et al., 2007). The second and main peak \( T_{\text{max}} = 347 ^\circ \text{C} \), which contributes with about 23% to the total weight loss, was associated to the random cleavage of the glycosidic linkage of remaining cellulose (Mansaray and Ghaly, 1998; Ruseckaite and Jimenez, 2003; Stefani et al., 2005; Ndazi et al., 2007). The peak of lignin was completely overlapped by the other two because it shows a wide range of degradation temperatures (Ndazi et al., 2007). It was reported that alkaline treatments simultaneously removed by alkaline treatments, the extraction of lignin is assumed. It was reported that alkaline peroxide treatments are efficient not only in extracting hemicelluloses and lignin but also in reducing silica content. Consequently, an improvement in bonding capability of RHs through chemical interactions with polar adhesives is anticipated.

It is noteworthy that chemically treated RHs were stable up to temperature about 200 °C, which is higher than the actual temperature used in processing particleboards (ca. 140 °C). So, the thermal degradation of RHs during processing operations is expected to be minor.

Thermal degradation was also performed under oxidative atmosphere in order to evaluate the effect of chemical treatment on the silica content. Fig. 2 shows the TG/DTG curves of chemically treated and control RHs in air atmosphere and at 10 °C/min. Thermal decomposition in air displays a third stage between 366–410 °C, which was attributed to the oxidation of the degradation products of the second stage (Stefani et al., 2005). The residue at 700 °C, which accounts almost exclusively of silica, decreased from 22% for CRH to 16% for ARH and 17% for BRH. These results provide further support to the fact that NaOH and alkaline peroxide treatments are efficient not only in extracting hemicelluloses and lignin but also in reducing silica content. Consequently, an improvement in bonding capability of RHs through chemical interactions with polar adhesives is anticipated.

SEM examination of RH before and after chemical treatments gives further insight on the RH morphology and its modification during the treatments. The outer surface of CRH (Fig. 3a) was characterized by ridges meanwhile the inner one (Fig. 3b) appeared to be smoother than the outer one. At higher magnification (Fig. 3c) the CRH outer surface appeared highly undulated due to the presence of regularly spaced conical protrusions and bright spots which can be attributed to silica which is more highly concentrated 30 min of exposure to alkaline media. However, the increment in the amorphous phase might decrease thermal stability of the cellulose fraction. This was evidenced by the shifting in the initial decomposition temperatures \( T_{\text{on}} \) measured at \( m/m_0 = 0.05 \) and \( T_{\text{max}} \) of cellulose peak toward lower temperatures (Fig. 1b) compared to CRH. Chemical treatment with NaOH significantly decreased the initial and maximum degradation temperatures (about 40 °C and 35 °C lower than those observed for CRH, respectively), while the variations for alkaline peroxide were less pronounced (around 10 °C and 14 °C lower compared to those of CRH, respectively). The slightly decrease in \( T_{\text{max}} \) detected for alkaline peroxide might possibly related to secondary reactions taking place between oxidized hydroxyl groups on the glucose monomers of cellulose with un-oxidized ones from other cellulose chains (Burgess and Hanlan, 1979). The reduction of lipids and waxes treatment was assumed due to the efficiency of hydrogen peroxide in the oxidation of fatty acids (Larrea et al., 1997; Çopur et al., 2007), generating products that were not detected by the method of analysis.
Fig. 3. (a) Outer and (b) inner surface of control rice husk (1000×); (c) outer surface of control rice husk at higher magnification (1000×); (d and e) outer and inner rice husk surface after 30 min soaking in NaOH (1000×); (f and g) outer and inner surface of bleached rice husk.
in regions corresponding to dome-shaped protrusions and adjoining sloping areas (Park et al., 2003). The topological differences between inner and outer surface of RH should be taken into account during particleboard manufacture since both surfaces will be randomly exposed for binding SPC adhesives.

The morphological characteristics of the RHs were altered by chemical treatments. Treatment with NaOH induced the cracking of the conical protrusions of the outer surface (Fig. 3d), and increased the roughness of the inner surface (Fig. 3e). This could be a consequence of the preferential elimination of the cementing materials of the interfibrillar region (mainly hemicelluloses and lignin) supporting TGA results. These observations suggest the weakening of RH structure, which may have a key influence in the performance of the produced boards.

The outer surface of bleached RH showed the conical protrusions broken at the top and there was little brightness in this region which was attributed to the lost of silica (Fig. 3f). The inner surface also showed topological changes including higher roughness and cracks in the direction of the major axis of RH (Fig. 3g).

The results of TGA and SEM put forward that chemical treatments change the RH morphology (inner and outer surface), eliminate hemicelluloses and lignin components, reduce silica content and probably decrease the crystallinity of cellulose fraction. This possibly will favor chemical interactions between the more exposed hydroxyl groups of RHs and the polar groups of soy proteins and mechanical bonding because the protein-based adhesives could penetrate more easily into RH microstructure (Mo et al., 2001). However, the partial elimination of hemicelluloses and lignin may lead to an increase in substrate brittleness, associated to the increased rigidity of the treated fibers.

3.2. Viscosity of SPC adhesives

The glueing ability of soybean proteins depends on their capacity to disperse and unfold in solution. The unfolded protein molecules increase their contact area and adhesion onto surfaces and become entangled with one another during the curing process, which in turn increases their bonding strength (Lambuth, 1994; Hettiarachchy et al., 1995; Wescott and Frihart, 2004). Alkaline treatment is the most simple and widely used method to increase the bonding strength. In our previous work we reported that alkaline-treated SPC was more efficient as binder for RH-medium-density particleboards (Leiva et al., 2007). Consequently, similar treatment was performed on SPC adhesives.

Table 1

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Rice husk treatment</th>
<th>CRH</th>
<th>ARH</th>
<th>BRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>USPC</td>
<td>8.3 ± 1.3a</td>
<td>13.4 ± 1.9b</td>
<td>17.9 ± 3.2c</td>
<td></td>
</tr>
<tr>
<td>ASPC</td>
<td>11.2 ± 1.1d</td>
<td>15.4 ± 3.2b</td>
<td>18.4 ± 2.1c</td>
<td></td>
</tr>
<tr>
<td>ANS/A208.1</td>
<td>Grade a</td>
<td>M1</td>
<td>MS</td>
<td>M2</td>
</tr>
<tr>
<td>MOR (MPa)</td>
<td>11.0</td>
<td>12.5</td>
<td>14.5</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

Table 2

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Rice husk treatment</th>
<th>CRH</th>
<th>ARH</th>
<th>BRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>USPC</td>
<td>1875 ± 189a</td>
<td>2472 ± 290c</td>
<td>2717 ± 358de</td>
<td></td>
</tr>
<tr>
<td>ASPC</td>
<td>2307 ± 300b</td>
<td>2665 ± 405bce</td>
<td>2844 ± 420df</td>
<td></td>
</tr>
<tr>
<td>ANS/A208.1</td>
<td>Grade a</td>
<td>M1</td>
<td>MS</td>
<td>M2</td>
</tr>
<tr>
<td>MOE (MPa)</td>
<td>1725</td>
<td>1900</td>
<td>2225</td>
<td>2750</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

Table 3

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Rice husk treatment</th>
<th>CRH</th>
<th>ARH</th>
<th>BRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>USPC</td>
<td>0.23 ± 0.05a</td>
<td>0.27 ± 0.08ac</td>
<td>0.35 ± 0.13ad</td>
<td></td>
</tr>
<tr>
<td>ASPC</td>
<td>0.43 ± 0.15b</td>
<td>0.37 ± 0.12bc</td>
<td>0.45 ± 0.15bd</td>
<td></td>
</tr>
<tr>
<td>ANS/A208.1</td>
<td>Grade a</td>
<td>M1</td>
<td>MS</td>
<td>M2</td>
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<tr>
<td>IB (MPa)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.45</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

3.3. Physical and mechanical properties of particleboards

The effect of RH chemical treatments on mechanical properties will be the result of the competition between the increased adhesion due to the more exposed polar groups onto RH’s surface and the damage (defibrillation, cracks, etc.) caused by the chemical agents used. The average values of modulus of rupture, modulus of elasticity and internal bond (MOR, MOE, and IB, respectively) of boards produced with CRH, ARH and BRH and bonded with USPC and ASPC, are given in Tables 1–3, respectively. Average MOR and MOE values showed that chemical treatments on RH induced better performance on the obtained panels (P < 0.05), while chemical treatment on SPC seemed to have minor influence on this property. The average MOR and MOE values increased up to 18.4 ± 2.1 MPa and 2844 ± 420 MPa, respectively, for BRH–ASPC-bonded boards. In contrast, chemical treatment on SPC only induce significant changes on MOR and MOE values of boards produced with CRH (P < 0.05). It is believed that the changes produced in RH surface by alkaline peroxide treatment favors the adhesion by mechanical anchorage, with minor reduction in RH stiffness. The values of MOR and MOE for ARH-based boards were between of those determined for panels based on CRH and BRH, whatever the adhesive. This could be attributed to the higher physical and chemical deterioration of RH provoked by soaking in NaOH during 30 min, as demonstrated by TGA and SEM. This reduction in the intrinsic resistance of RH might be the main cause responsible for this behavior.

On the other hand, IB proved to be more sensitive to the chemical treatments on the adhesive. Table 3 summarizes the average IB values for the different panels produced. It is noteworthy that alkali-treated SPC produced an increment in the average IB values whatever the substrate. These findings are mainly attributed to the augmented glueing ability of ASPC. Alkali can break internal hydrogen bonds in the coiled protein molecule; which in turn...
unfolds and exposes many polar groups (hydroxyl and carboxyl side-chain groups), able to bond with exposed hydroxyl groups from the lignocellulosic substrate. In addition, the unfolded protein has increased contact area, which can also contribute to the increasing bonding ability.

According to the tests results, ASPC–BRH particleboards had the minimum requirements of MOE (2844 ± 420 MPa), MOR (18.4 ± 2.1 MPa) and IB (0.45 ± 0.15 MPa) to satisfy the US Standard ANSI/A208.1 requirements for M1, MS and M2-grade medium-density particleboards, but fail to meet M3 grade because the IB values are inferior to that required (0.55 MPa). On the other hand ASPC–CRH panels met the minimum mechanical property values specified in the standard for M1-grade panels whereas ASPC–ARH specimens agreed well with standard values for M2-grade panels. However, in order to evaluate the potential applications of SPC–RH particleboards they must also meet the minimum thickness swelling percent (%TS) required by the standard.

Tables 4 and 5 show the effect of the chemical treatments on RH and SPC on the average water absorption percent (%WA) after 2 and 24 h of immersion. WA was affected by the adhesive nature and the interactions between the substrate and adhesive. USPC-bonded panels exhibited the highest average WA values at 2 and 24 h. SPC contains both soy protein and soy carbohydrate. The presence of carbohydrates in SPC [ca. 15% of cellulose (Leiva et al., 2007)] favors water uptake because of their hydrophilic nature. Once water penetrates, it may diffuse into RH through amorphous regions of cellulose, which is considered the main thing responsible for WA. Similar findings were reported for particleboards based wheat straw/soy flour (Cheng et al., 2004) and panels made from CRH and USPC (Leiva et al., 2007). The higher WA after 24 h for chemically treated RHs, might be caused by the elimination of hydrophobic substances (i.e. waxes and fats) which are still present in CRH besides the reduction in cellulose crystallinity, which promoted to the water penetration and retention (Leiva et al., 2007). On the other hand, ASPC-bonded panels experienced an improvement in water resistance in comparison with those based on USPC adhesive for panels prepared with CRH or BRH (P < 0.05). This may be attributed to the enhanced bonding capacity of SPC by alkaline treatment. Besides the presence of non-polar groups (Wescott and Frihart, 2004), the more exposed polar groups on ASPC may interact through hydrogen bonds with hydroxyl groups of cellulose from both ASPC and RH (treated or un-treated), reducing the water binding ability of ASPC–RH boards. The most water resistant ASPC-bonded panels were those based on CRH and BRH, in agreement with the stronger bonding strength exhibited for these samples (Table 3). On the other side, ASPC–ARH-based boards displayed the lowest water resistance (Tables 4 and 5), probably due to the increment in amorphous fraction in cellulose after soaking RH in NaOH during 30 min.

Thickness swelling percent (%TS) results at 2 and 24 h are represented in Tables 6 and 7. TS could be affected by several factors such as insufficient resin content and distribution, poor compatibility between substrate and adhesive, and adhesive properties (Wang and Sun, 2002). As a general trend, ASPC-bonded panels showed the lowest mean TS values; meanwhile, USPC exhibited higher ones whatever the soaking time, for boards produced with CRH and BRH (P < 0.05). As expected, these findings are in accordance to the trend observed in WA results and evidence that TS depends on the bond quality and adhesive type. Because the bonding strength resulting from ARH with ASPC adhesive was not as strong as that determined for CRH or BRH larger amount of water was able to penetrate the weakly bonded particleboard structure, resulting in greater swelling. ASPC–CRH and ASPC–BRH particleboards had lower TS values than those reported by Mo et al. (2001) for panels made of wheat straw and soy protein isolate as adhesive. Taking into account that SPC is more economical than soy protein concentrate.

<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%WA) at 2 h.</td>
</tr>
<tr>
<td>Adhesive type</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>USPC</td>
</tr>
<tr>
<td>ASPC</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water absorption (%WA) at 24 h.</td>
</tr>
<tr>
<td>Adhesive type</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>USPC</td>
</tr>
<tr>
<td>ASPC</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

Table 6

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Rice Husk treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRH</td>
<td>ARH</td>
</tr>
<tr>
<td>USPC</td>
<td>31.53 ± 3.80a</td>
</tr>
<tr>
<td>ASPC</td>
<td>22.47 ± 1.80b</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

Table 7

<table>
<thead>
<tr>
<th>Adhesive type</th>
<th>Rice Husk treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRH</td>
<td>ARH</td>
</tr>
<tr>
<td>USPC</td>
<td>43.58 ± 3.56a</td>
</tr>
<tr>
<td>ASPC</td>
<td>28.57 ± 1.70b</td>
</tr>
</tbody>
</table>

Means followed by the same letter are not significantly different (P > 0.05).

4. Conclusions

The results of this study indicate that the SPC-based adhesives and waste RHs are suitable materials to produce particleboards. RH chemical modifications were undertaken in order to upgrade the adhesion with polar adhesives such as those derived from soy protein concentrate.
The final properties of SPC-bonded particleboards were upgraded by alkaline treatment of SPC and bleaching of RHs. Bleaching enhanced the adhesion of RHs with polar adhesives such as those derived from SPC due to the removal hemicelluloses and lignin, the reduction in silica content and the decrease in crystallinity of the cellulose fraction. This favored chemical interactions through hydrogen bonds, between the more exposed hydroxyl groups of cellulose from RHs, and polar groups from the unfolded proteins of alkali-treated SPC. In addition, chemical treatment produced morphological changes in RHs (inner and outer surfaces) which promoted adhesion through mechanical interlocking leading to a higher adhesive strength.

In terms of mechanical properties, ASP–BRH particleboards met the minimum standard requirements MOE 2844 ± 420 MPa, MOR 18.4 ± 2.1 MPa and IB 0.45 ± 0.15 MPa recommended by the US Standard ANSI/A208.1 specifications for M1, MS and M2-grade medium-density particleboards, but failed in meeting the thickness-swelling requirements for general uses. This shortcoming is counterbalanced by the advantage of the adhesive of being formaldehyde-free and the fact of using entire RHs for particleboard manufacture which saves milling and screening operations, which would have cost benefits. The ASPC–BRH particleboards were found to be an environmentally sound option for applications for which the requirements for water resistance are not stringent.

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References

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