Medium-Density Particleboards from Rice Husks and Soybean Protein Concentrate

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ABSTRACT: Rice husks are a valuable agricultural residue produced worldwide with potential applications as a wood substitute in particleboard manufacturing. In this work, the feasibility of producing medium-density particleboards based on waste rice husks bonded with environmentally friendly adhesives from soybean protein concentrate was analyzed. The mechanical properties, internal bond strength, and water resistance of the obtained panels bonded with the homemade soybean protein concentrate adhesives were compared to those of boards glued with commercial adhesives such as phenol–formaldehyde and urea–formaldehyde resins. An alkaline treatment improved the gluing ability of the soybean protein concentrate. The mechanical properties of the alkali-treated soybean protein concentrate were comparable to those determined for panels with urea–formaldehyde. The lower water resistance of the alkali-treated soybean protein concentrate particleboards, compared with that of the formaldehyde-based resins, was counterbalanced by the advantage of being more environmentally sound, which makes them suitable for applications for which the requirements for water resistance are not stringent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1301–1306, 2007

Key words: adhesives; mechanical properties; renewable resources

INTRODUCTION

The increasing demand for raw wood materials in particleboard manufacturing and the need to preserve natural resources have encouraged research into alternative lignocellulosic materials. In this sense, agricultural residues are emerging as an economically promising and environmentally friendly source of raw materials able to substitute for wood from natural and plantation forests. Agricultural residues, including wheat and rice straw, sugarcane bagasse, husks, shells, seed hulls, and fruit pruning, are obtained in large quantities world wide, and some of them have been successfully used in particleboard manufacturing.[1–11] Indeed, boards based on wheat straw,[1–4] sugarcane bagasse,[5] and other lignocellulosic agrobased residues are already on the market under different trademark names such as WheatBoard (wheat straw, Daproma Co.), Primeboard (wheat straw and sunflower seed hulls), and DuraCane (sugarcane bagasse, Acadia Board Co.), showing that industrial applications could be profitable. Rice husks (RHs) are a byproduct of the rice milling process, which is available in fairly large quantities in one area. The world production of rice is approximately 500 million tons per year, containing approximately 50–100 million tons of RHs, 90% of them generated in developing countries.[12] At the present, RHs are mainly disposed off or used as bedding material for animals, and industrial applications are still limited. Indeed, the RH recycling rate into value-added byproducts is about 10%;[13] in particular, they produce carbon-free ash as a source of high-grade amorphous silica,[14] as a concrete additive,[15] and as a reinforcing agent for thermoplastics and rubbers.[16,17] Nowadays, the interest in using the entire RH to produce valuable products is growing. An attractive but less explored application is as a wood substitute in particleboard manufacturing.[6–8]

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.[6] Therefore, it would be expected that RH should behave similarly to wood in particleboard production. However, the presence of abundant silica and waxes at high concentrations, mainly in the outer layers, affects RH interactions with polar adhesives such as phenol–formaldehyde (PF) and urea–formaldehyde (UF) resins.[6,16] Different strat-

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egies have been proposed to improve RH adhesion properties. Gerardi et al.[6] used steam explosion to improve the bondability of RH with UF resins. They found that the increase in the severity conditions of the process led to panels with good tensile strength and water resistance. Low-cost ceiling boards based on alkali-treated RH, sawdust, and a commercial UF adhesive were reported by Ajiwe et al.[7] The obtained boards' properties were superior to those of commercial standards in terms of moisture sorption and tensile strength, and the production cost compared favorably to that of commercial products. Stefani et al.[8] studied the effects of the pressing conditions and adhesive content on the mechanical properties of low-density particleboards based on untreated RH. The modulus of rupture (MOR) and modulus of elasticity (MOE) values were in the same range as those obtained for wood-shaving particleboards bonded with the same adhesive.

Despite the well-known advantages of UF resins as wood adhesives, formaldehyde emissions have become a matter of increasing concern.[18] Unmodified or modified soybean proteins can be used as environmentally friendly and formaldehyde-free substitutes for the traditional synthetic adhesives in particleboard manufacturing.[19] The gluing capacity of soybean protein is based on its dispersing and unfolding ability in solution, which increases the contact area and adhesion with other substrates. The unfolding of soybean protein molecules has been promoted by different strategies, including thermal, chemical, and enzymatic treatments.[1–4,19–24]

The objective of this work was to prepare and characterize medium-density particleboards with RH as a low-cost lignocellulosic substrate and formaldehyde-free adhesives based on soybean protein concentrate (SPC). The performance of the obtained panels was evaluated by a comparison of the final properties with those of panels bonded with commercial adhesives.

EXPERIMENTAL

Materials

RHs (Don Juan variety) were kindly supplied by rice milling industries of Entre Ríos (Argentina). The as-received RHs had constant average dimensions (8 ± 1 mm × 4 ± 0.5 mm × 0.3 ± 0.05 mm), which saved grounding and screening operations. RHs were extensively washed with distilled water and dried at 100 ± 2°C until they reached a 6% moisture content. SPC (Solcom S) containing around 65 wt % protein on a dry basis and an average particle size passing through 100 mesh was provided by Cordis SA (Villa Luzuriaga, Buenos Aires, Argentina). PF resin (51% solids) and UF resin (65% solids) were kindly supplied by Atanor (Munro, Buenos Aires, Argentina) and Jucarbe (Villa Zagala, Buenos Aires, Argentina), respectively. The UF resin was prepared by the addition of 1 wt % NH_4Cl (based on the solid resin weight) to the prepolymer to obtain the desired viscosity and curing time.

Modification of SPC

A unmodified soybean protein concentrate (USPC) adhesive was prepared by the dispersion of the SPC powder in distilled water at a 1 : 10 ratio under stirring at room temperature for 2 h. An alkali-treated soybean protein concentrate (ASPC) was prepared as described elsewhere.[1–4] Basically, 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. The viscosity was measured with a Brookfield DV-III plate and cone viscosimeter (Middleboro, MA) at room temperature. The adhesives were prepared as described and were transferred into the sample holder of the viscosimeter. All measurements were recorded against the shear rate.

RH board preparation

RHs with 6% initial moisture were mixed with commercial PF and UF adhesives and homemade SPC-based adhesives in an orbital paddle mixer (M.B.Z., San Justo, Buenos Aires, Argentina) for 10 min. The final solid contents in the PF–RH and UF–RH mixtures were 10 and 15 wt %, respectively, and no further drying was required before pressing. Mixtures of RHs with SPC-based adhesives were oven-dried at 70°C until 40% moisture and 10 wt % solids were reached in the final mixture.

The different adhesive–RH mixtures were transferred to a 30 cm × 30 cm steel mold equipped with stops to achieve a constant gap (0.55 cm). The target bulk density for all boards was 0.80 ±0.05 g/cm^3. The resinated mixtures were compressed into particleboards in a hot press (E.M.S., Buenos Aires, Argentina) for 20 min and 2.9 MPa at 150°C for UF- and PF-bonded particleboards and at 140°C for USPC- and ASPC-bonded particleboards.

Three replicates for each kind of adhesive-bonded particleboard were produced. The obtained boards were trimmed to avoid edge effects.

RH board evaluation

Particleboards were evaluated according to the ASTM D 1037-93 standard procedure. The mechanical tests were performed in an Instron 4467 universal test machine (Buckinghamshire, England). The particleboards were cut into 5 cm × 19 cm rectangular strips for three-point-bending evaluation. MOR and MOE were determined from tests carried out at a cross-

TABLE I
Standard ANSI A 208.1-1999 Requirements for Medium-Density Particleboards (640–800 kg/m^3)

Property	Grade M1	Grade MS	Grade M2	Grade M3
MOR (MPa)	11.0	12.5	14.5	16.5
MOE (GPa)	1.725	1.900	2.225	2.750
IB (MPa)	0.40	0.40	0.45	0.55

head speed of 2.88 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. The moisture content and density were 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 determine 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. The average values were reported as percentages of the values before soaking.

Industrial standard

Mechanical properties (MOE, MOR, and IB) were compared with the requirements for grades of medium-density particleboards as specified by the American National Standard Institute (ANSI; A208.1; Table I).

RESULTS AND DISCUSSION

The gluing 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, this increases their bonding strength.[20] An alkali treatment is the most simple and widely used method to increase the bonding strength. Hettiarachchy et al.[21] used an alkali-modification method (pH 10 and 50°C) and obtained adhesives with enhanced bonding capacity. Wescott and Frihart[22] prepared soybean-flour-based adhesives with improved properties by treating the flour with an 8–12% NaOH solution at 70°C, and this was followed by the addition of formaldehyde to stabilize the denatured protein solution and to activate the protein for a further reaction with the phenol. Strandboards produced with the obtained soybean-flour/PF adhesive showed strength and water-resistance values similar to those obtained with PF adhesives. In this work, SPC was treated with a 0.2% NaOH solution for 2 h at 25°C.[1–4] Room temperature was selected to control protein hydrolysis during the alkaline treatment. A low level of protein hydrolysis may produce peptide chains with a suitable molecular weight distribution, which may contribute to an enhanced protein bonding capacity.[1] The control adhesive (USPC) was prepared under similar conditions by the dispersion of SPC powder in distilled water. Figure 1 shows the Brookfield viscosity for the homemade adhesives. The initial viscosities (shear rate = 2.75 s^{-1} at 25°C) were 1664 MPa s for ASPC and 2843 MPa s for USPC. On the other hand, the initial viscosities of the commercial adhesives were 611 MPa s for PF and 950 MPa s for UF, which are in the usual range for particleboard manufacturing.[25,26] The higher initial viscosity values of soybean adhesives versus those of the synthetic adhesives is not a drawback for their use in particleboard preparation. Indeed, SPC dispersions exhibit shear thinning, so the higher apparent viscosity may decrease under shear conditions such as mixing operations.[22]

The mechanical properties (MOE, MOR, and IB) of the RH boards bonded with different adhesives are summarized in Figures 2–4. The results show that PF-bonded particleboards have higher MOE, MOR, and IB values than UF-bonded boards. This difference may be ascribed to the inherent nature of the synthetic adhesives and their interactions with the substrate. RH contains significant amounts of silica and waxes, which reduce its interactions through secondary forces (e.g., hydrogen bonds) with the polar resins. PF and UF resins possess hydrogen-

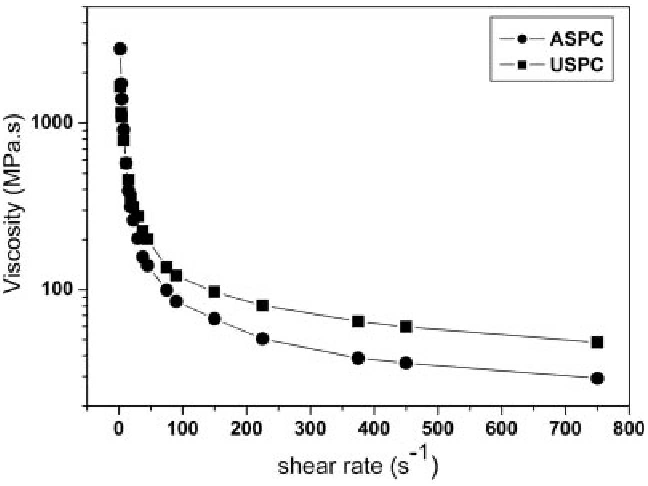

Figure 1 Brookfield viscosity values as a function of the shear rate for SPC suspensions (1 : 10 ratio).

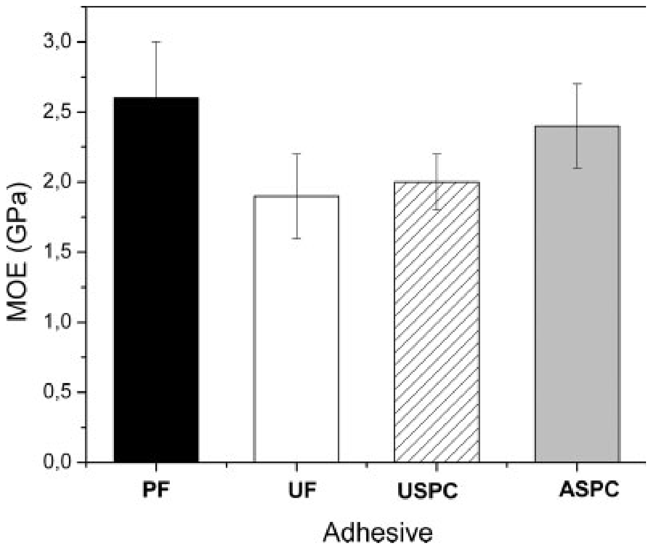

Figure 2 MOE of RH particleboards bonded with commercial and homemade SPC adhesives.

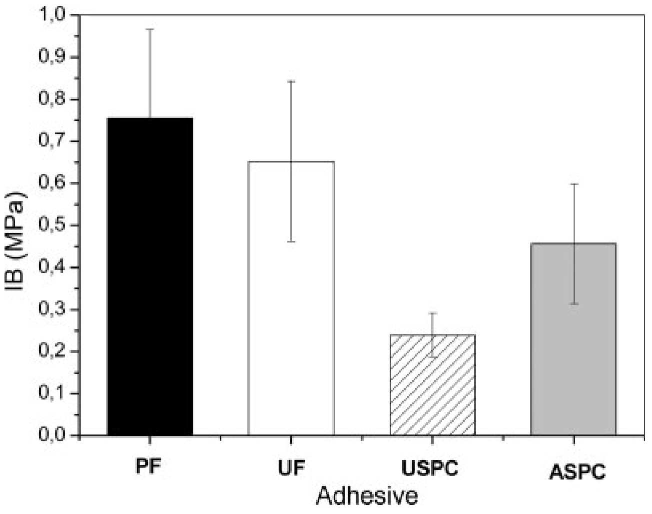

Figure 4 IB of RH particleboards bonded with commercial and homemade SPC adhesives.

bonding functionalities able to interact with hydroxyl groups of lignocellulosic substrates. Additionally, they may also diffuse into the RH microstructure during pressing operations as they do with other cellulosic substrates.[27,28] However, alkaline resole may interact with cellulosic substrates more easily than other adhesives because the presence of alkali causes the partial conversion of cellulose I to cellulose II. This fact is accompanied by an increment in the amorphous phase that may enhance the flow of the resole into the RH microstructure and favor the PF–RH interactions.[29] If one takes into account the slow curing rate of PF resins,[28] significant amounts of alkali resole may penetrate the RH microstructure. Therefore, adhesion may be achieved by the formation of hydrogen bonds with different components of RH and also through mechanical interlocking leading to a higher adhesive strength.

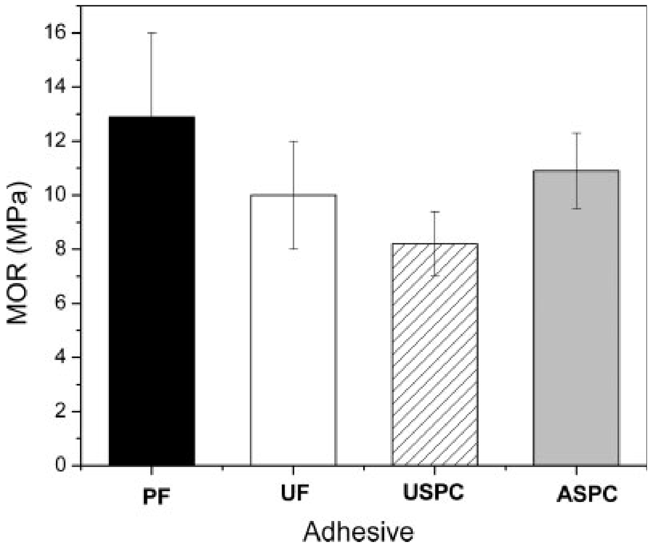

Figure 3 MOR of RH particleboards bonded with commercial and homemade SPC adhesives.

Particleboards bonded with ASPC showed improved properties in comparison with those produced with USPC as a bonding agent (Figs. 2–4). These findings are mainly attributed to the increased gluing 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 good bondability.[1,20,21] The maximum mechanical properties for the ASPC-bonded boards were 2.4 GPa for MOE, 11 MPa for MOR, and 0.45 MPa for IB, which match the ANSI requirements for M1-grade boards but fail to meet the MS grade because the MOR values are inferior to the standard requirements (see Table I).

Figure 5 shows the effect of the adhesive type on WA after 2 and 24 h of immersion. WA was affected by the adhesive nature and the interactions between the substrate and adhesive. PF-bonded boards showed the lowest WA. This finding is attributed to the greater attraction of cellulose for PF oligomers rather than water molecules, and this implies that PF oligomers are likely to displace water to adhere to the cellulosic material surface.[30] If water resistance is important for particleboard applications, PF appears to be the preferred adhesive despite its higher cost. On the contrary, the USPC-bonded panels exhibited the highest WA. The presence of carbohydrates in SPC (ca. 15% of cellulose) 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 results were reported by Cheng et al.[3] for boards based on wheat-straw/soy-flour particleboards. However, ASPC-bonded panels suffered an improvement in water resistance in comparison with the control adhesive. Besides the presence of nonpolar groups,[22] exposed polar groups on ASPC may interact through hydrogen bonds with hydroxyl groups of cellulose from both ASPC and RH, reducing the water binding ability of ASPC–RH boards.[3] TS results are shown in Figure 6. PF-bonded panels showed higher lower TS values; meanwhile, USPC exhibited higher ones. This is evidence that TS depends on the bond quality. Because the bonding strength resulting from the USPC adhesive was not as strong as that of PF, a larger amount of water was able to penetrate the weakly bonded particleboard structure, resulting in greater swelling. The alkaline treatment of SPC reduced TS, which reached values slightly higher than those obtained for UF-bonded boards. As mentioned previously, strong interactions between cellulose and ASPC reduce the water intake and thus reduce the swelling. The ASPC–RH particleboards showed lower WA values than those reported by Mo et al.[4] for panels made of wheat straw and soybean protein isolate (SPI). Taking into account that SPC is less expensive than SPI and that RHs do not require grounding and screening operations before use, we believe that ASPC-bonded RH boards may be an interesting alternative for indoor applications.

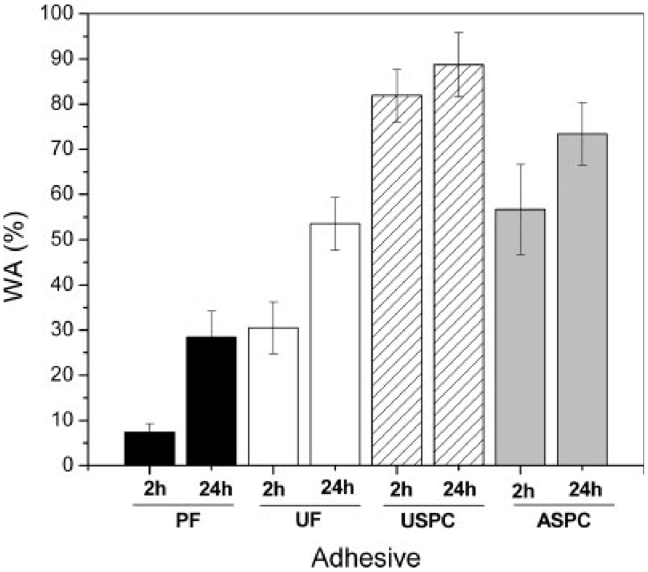

Figure 5 WA of boards bonded with different adhesives.

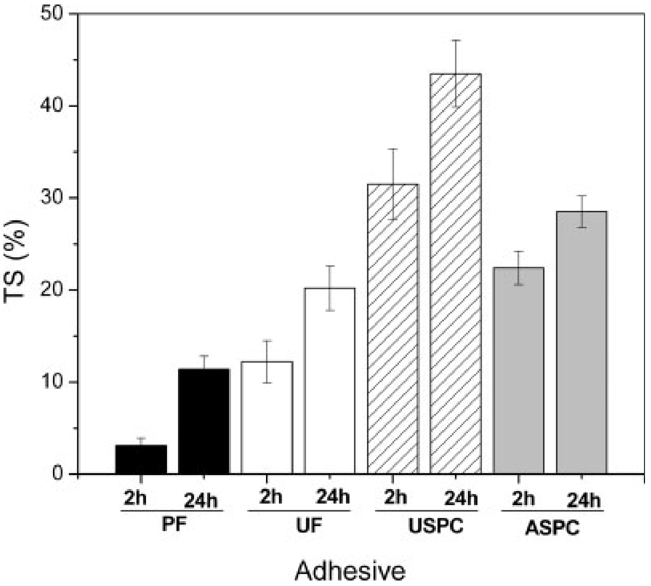

Figure 6 TS of RH particleboards after soaking in water for 2 and 24 h.

CONCLUSIONS

SPC-based adhesives and waste RHs can be successfully used as raw materials for making medium-density particleboards with appropriate mechanical performance. The final properties of USPC-bonded particleboards were upgraded by an alkaline treatment of SPC. The resultant ASPC-bonded boards showed comparable MOR, MOE, and IB values but lower water resistance than UF ones. This shortcoming was counterbalanced by the advantage of the materials being formaldehyde-free. In addition, ASPC-bonded panels met relevant international standard specifications (grade M1), and this makes them an environmentally sound alternative for indoor applications.

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