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

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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, MS 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 Çamlibel, 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 Kokta, 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 (Khristova et al., 1998), coconut shells (Almeida et al., 2002) and fruit pruning (Ntalos and Grigoriou, 2002), are obtained in large quantities world wide, 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

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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 (Rodriguez 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 (Ajiwe 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% H_2O_2 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 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 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 $\times$ 4 ± 0.5 mm $\times$ 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 Anedra (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 H_2O_2 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