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Cornstarch and tannin in phenol–formaldehyde resins for plywood production

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ABSTRACT

The aim of this work is to demonstrate the performances of cornstarch–quebracho tannin-based resins designed as adhesive in the plywood production. In this way, the cornstarch and quebracho tannin was introduced in the classic adhesive formulation in order to supply a part of phenol–formaldehyde (PF). The physical properties (rheological characterization, thermogravimetric analysis and solid phase ^{13}C NMR analysis) of the formulated resins were measured. In order to evaluate the mechanical performances of optimal cornstarch–quebracho tannin-based resins, plywood panels were produced and mechanical properties were investigated. These mechanical properties included tensile strength, wood failure and 3-point bending strength. The performance of these panels is comparable to those of plywood panels commercial PF made.

The results showed that plywood panels bonded with cornstarch–quebracho tannin–PF resins (15:5:80, w/w/w) exhibited better mechanical properties than plywood panels commercial PF made. The introduction of small proportions of cornstarch and quebracho tannin in PF resins contributes to the improvement of the boiling water performance of these adhesives. The formaldehyde emission levels obtained from panels bonded with cornstarch–quebracho tannin–PF were lower to those obtained from panels bonded with control PF. Solid state CPMAS NMR spectra indicates that no reaction at all between PF resins and cornstarch and quebracho tannin. Even when reaction does evidently not occur, the addition of cornstarch and quebracho tannin improves markedly the water resistance of PF resins.

1. Introduction

Phenol–formaldehyde adhesives are used to glue the veneer plies of exterior-grade plywood panels, the flakes of oriented strandboard (OSB) panels and particleboards panels. PF resins provide high strength and are extremely resistant to moisture, which prevents delamination and gives excellent temperature stability and low initial viscosity (Pizzi, 1993). This is in part due to the more flexible nature of phenolic resins (Pizzi, 1983). However, PF resins can be very expensive products as regards to the phenol price. Therefore, investigations aimed at using natural and economical products as substitutes for PF resins. These materials contain lignin from kraft lignin (Olivares et al., 1988, 1995), black liquor (El-saied et al., 1984), lignosulfonate (Olivares et al., 1995; Barry et al., 1993; Janiga, 1987), or organosolved lignin (Cook and Hess, 1991; Senyo et al., 1996). Also, studies have been made with tannin extracted from the bark of wattle (Marcos et al., 1995; Stefani et al., 2008; Pizzi and Scharfetter, 1978; Vazquez et al., 2000) and starch (Farag, 1995; Yoshida et al., 2005; Turunen et al., 2003; Basta et al., 2006) in co-condensed resins with phenol and formaldehyde.

Starch, obtained from renewable resources, has many advantages, such as low cost, abundant supply, and environmental amity (Imam et al., 1999). Starch has been used as wood adhesive in interior applications (Imam et al., 1999). More recently, we described starch based adhesive formulations for exterior-grade plywood fortified with other polymer systems such as PF and urea formaldehyde (UF).

Recently, there have been growing interests on tannin-based resins. Tannins are naturally occurring phenolic compounds, which have been a subject of extensive research leading to development of a wide range of industrial applications (Pizzi, 1993). Tannins represent the best substitute for phenol in resin preparation. Tannin is the renewable resource which is most widely used in adhesive production. Wattle bark tannins (*Acacia mearnsii*) adhesives have been used without fortification to bond hardwood species in Brazil (Coppens et al., 1980; Santana and Sobral Filho, 1983) and China (Zhao et al., 1994), most tannin-based adhesive formulations for exterior-grade plywood are fortified with other polymer systems. Common fortifying agents are commercial UF (Pizzi, 1977; Bisanda et al., 2003); commercial PF (Scharfetter, 1975; Vazquez et al., 2003); pre-polymers of PF, phenol–resorcinol–formaldehyde. Or

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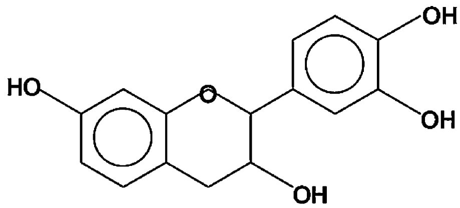

Fig. 1. The chemical structure of quebracho tannin (*Schinopsis balansae*) flavonoids.

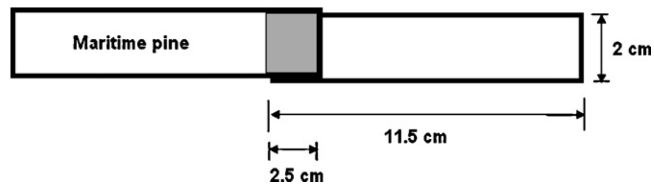

Fig. 2. Schematic representation of a lap joint sample preparation using cornstarch–tannin crosslinked adhesives (125 °C, 6 min and 0.45 MPa).

resorcino-formaldehyde (Saayman and Oatley, 1976; Pizzi, 1983); and diisocyanates (Dix and Marutzky, 1989). Wattle bark tannins have higher reactivity with formaldehyde than phenol (Bisanda et al., 2003; Joseph et al., 1996). In addition, tannin–PF adhesives can reduce the tendency of resin to migrate to the interior of high-moisture veneers due to the broader molecular weight distribution of tannin-based adhesives (Steiner et al., 1993).

In this study, a part of the PF resin was substituted by cornstarch and quebracho bark tannin. The effects of the substitution level in the PF resin on the physical properties (rheological and thermogravimetric analysis) of adhesives and mechanical properties (modulus of rupture "MOR", modulus of elasticity "MOE", tensile strength and wood failure) of plywood manufactured using cornstarch–tannin–phenol formaldehyde adhesives were investigated.

2. Experimental methods

Unmodified commercial grade cornstarch (extra pure) was obtained from ACROS ORGANICS; the moisture content was in the range of 10–12%. The whole bark of quebracho (*Schinopsis balansae*) was collected from plantations in Tanzania. Quebracho is a condensed tannin that has a polymeric structure containing the flavanoid units. Fig. 1 shows the chemical structure of quebracho tannin. Quebracho bark tannin (Fintan 737) was obtained after commercial extraction and was purchased from SILVATEAM. Commercial resol-type liquid PF resin (code P6A1679, P/F = 0.45, which is a plywood binder resin) was supplied by Smurfit Kappa Rol Pin.

2.1. Preparation of resols and adhesives

A phenol formaldehyde resol with a solids content of 46% and a viscosity of about 450 cp was prepared using a 2.2:1 formaldehyde:phenol ratio and 7.3% (w/w) of NaOH. The resols were prepared in a two litres glass reactor with mechanic stirring and temperature control. The necessary amount of the reactive according to the established formulation was fed into the reactor and, when the operating temperature was reached (90 °C), the extension of reaction was monitored, measuring resol viscosity at 25 °C.

The adhesives were prepared by copolymerisation at room temperature of cornstarch and quebracho bark tannins in variable quantities with the previously prepared resols.

2.2. Bond strength of resins

The bonding ability of the resins was examined in a lap joint test using an Instron testometric M500-50 AT testing machine at a crosshead speed of 1 mm/min. Lap bond strength measured the degree of adhesion to a substrate and the rigidity of the bond. Maritime pine (*Pinus pinaster*) veneer with thickness of 3 mm was cut to rectangular specimens 2.5 cm × 11.5 cm, according to British Standard 1204, 1965, part 2, for synthetic resins adhesives. Resin was applied to an area of 2.5 cm × 2.5 cm on one side of one end section of the two pieces (Fig. 2). The spread rate of the adhesive was 120–150 g/m^2 on a dry weight basis (Pizzi, 1977; Moubarik et al., in press). Two adhesives-coated veneer boards were lapped together with the grain parallel to each other and then pressed at 0.45 MPa. The press temperature and press time were fixed at 125 °C and 6 min, respectively. After bonding, the assemblies were conditioned in a Vötsch climate room (25 °C and 65% humidity) for 24 h. Bonding quality was evaluated from the percentage of wood failure at the bonding area and the bond strength of each specimen. Ten samples were tested of each formulation, with the average value being recorded.

2.3. Plywood preparation and testing

5 ply laboratory plywood panels of dimension 200 mm × 200 mm × 10 mm were prepared from 2 mm thick maritime pine veneers of moisture content of 4% at a glue mix spread of 225 g/m^2 single glueline. Plywood bonded with cornstarch–quebracho tannin–FP resin has assembled and hot pressed under 12 bar pressure at 125 °C, for 6 min. The fixed bonding conditions of 160 °C pressing temperature and 12 bar were selected to reproduce the industrial conditions used to bond plywood panels. The longer pressing time of 6 min was used to assure full reaction.

Mechanical properties commonly taken into consideration in the general usage areas of plywood panels were investigated. Tensile strength, bending strength and modulus of elasticity values of plywood panels were determined according to EN 314 (1993) and EN 310 (1993), respectively. Ten specimens were used for each test method, and the results obtained are shown in the tables.

2.4. Rheological characterization

The adhesives were tested with a rotary rheometer (ARES) with parallel plate's geometry; the plate diameter used was 25 mm and the gap between the plates was 1.5 mm. The experiments were carried out in an environment with controlled temperature. Silicone oil was used to prevent water evaporation. Three replicates were used for each adhesive.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the thermal stability and degradation of optimal adhesive. TGA was done using a TGA Q50 thermogravimetric apparatus. Ten milligrams of each cured sample was placed on a balance located in the furnace and heat was applied over the temperature range of room temperature to 600 °C at a heating rate of 5 °C/min in air. The derivatives of the weight loss vs. temperature thermograms were obtained to better show the different decomposition processes. Three replicates were used for each adhesive.

2.6. Formaldehyde emission by desiccator method

The formaldehyde emissions from the plywood were determined according to the European Norm (ISO/CD 12460-4) using a