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Exterior grade plywood adhesives based on pine bark polyphenols and hexamine

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ABSTRACT

The aim of this work was to formulate environmental friendly adhesives for plywood production. This adhesive is based on polyphenol extracts from Pinus radiata D. Don bark, the most important by-product from the Chilean forest industry. We focused on a bio-based formulation free of formaldehyde, phenol, and isocyanates. Hexamethylenetetramine was used as hardener. The influence of pH on gel time, rheological behaviour, and pot life was evaluated. The curing process was evaluated by differential scanning calorimetry, Fourier transform infrared spectroscopy, and automatic bonding evaluation system (ABES). For the first time, exterior grade plywood (EN 314) was manufactured with pine bark extracts obtained at pilot scale. Two alternatives for adhesive application were studied: (1) wood veneers activation using a diluted solution of the bio-adhesive, and (2) pine bark extract application as dry powder on the wood veneers. Both alternatives were not reported before and demonstrated an increase in the final plywood quality, as measured by the internal bond strength (IB). On basis of this research, pine bark from Chilean forest industry is an interesting polyphenolic source for the development of adhesives free of formaldehyde and phenol.

1. Introduction

Nowadays, wood panels are primarily manufactured with thermosetting synthetic resins, most of them based on formaldehyde. However, environmental and health considerations are leading to increasingly severe standards regarding the maximum formaldehyde emission from wood boards. In addition, the increasingly high cost of synthetic resins based on petrochemicals has intensified the search for alternative resins based on natural materials for the formulation of wood adhesives (Norström et al., 2018; He, 2017; Hemmilä et al., 2017).

The use of natural extracts with high content of polyphenols combined with alternative hardeners such as hexamethylenetetramine is a convenient alternative for reducing the use of formaldehyde (Böhm et al., 2016; Santos et al., 2017), aiding the design of wood panels with low emission (Vázquez et al., 2012; Santos et al., 2017).

Polyphenols were industrially extracted from pine bark (Pinus radiate D. Don) in Chile and New Zealand during the 1990s. However, production has since ended. Such natural extracts were mostly used in adhesive formulations for particleboards and fiberboards (Zhang et al., 2017; Niro et al., 2016; Ghahri and Pizzi, 2018) as a partial component of phenol-formaldehyde resins (Li et al., 2018; Feng et al., 2016), or were combined with p-MDI (4,4′-methylene diphenyl diisocyanate) (Valenzuela et al., 2012). The use of isocyanates in adhesive formulations offer several advantages. However, isocyanate-based adhesives show high toxicity (Carré et al., 2016).

The application of radiata pine bark extracts in plywood adhesives have been studied previously (Zhou and Pizzi, 2014; Ghahri et al., 2018; Rhazi et al., 2017). However, good results were obtained only when pine bark extract was added in a 20–35% proportion to either phenol formaldehyde, urea formaldehyde resin, or to pMDI.

The greatest drawbacks that inhibit the use of polyphenols in wood adhesives are their high viscosities and the short pot life, particularly in pine bark extract (Vázquez et al., 2005). In addition, the current industry standards for adhesive formulations require low viscosity (< 2000 mPa s), adequate pot life (minimum 5 h), and short gel time based on compatibility with new technologies used in the wood board industry. In fact, these tasks are mainly focused on minimizing adhesive cost and increasing board production. Any biobased formulation must

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show the same performance compared to conventional phenol-formaldehyde resins.

In previous work, the extraction of polyphenols from radiata pine bark were studied at bench and pilot scales. The results revealed large variability in material properties when the process was carried out at a pilot plant scale (Bocalandro et al., 2012). However, polyphenol extracted from P. radiata bark remains a valuable source of natural compounds for developing novel valorization strategies.

In this study, a polyphenol extract was obtained on the pilot-plant scale by using an abundant forestry commercial feedstock with the goal of replacing conventional chemicals. No previous selection of the raw bark was performed. The aforementioned by-product is composed of pine bark (inner and outer), as well as a variable proportion of pine wood. In addition, differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR-ATR) were used to study the chemical cure. Automated bonding evaluation system (ABES) was used to analyze the mechanical cure. In order to overcome the high viscosity and short pot life constraints of the pine bark extract, a new and easy methodology for activation of the wood surface was performed. Some chemical pre-treatments with chemical reagents are widely applied to wood surfaces in order to improve their bonding ability and wettability, as well as to reactivate wood surfaces for glue–wood bonds (Aydin, 2004; Fang et al., 2014). In the present study, the activation consists of pre-treatment of plywood veneers with the same polyphenolic extract (as a solution or as a powder) used in resin formulation. That pre-treatment facilitates an increase in the polyphenolic content by more than 20–35%. Finally, plywood was manufactured, and the board material properties were evaluated according to international standards.

2. Materials and methods

2.1. Materials

Pinus radiata bark (mixture of bark and wood) was supplied by Cerro Colorado sawmill (Accsa, Los Ángeles, Biobío Chile). The industrial by-product was milled in a shredder-cutting mill and sieved (particle size < 1 cm). The 1,3,5,7-Tetraazatricyclo[3.3.1.13,7]decane, hexamethylenetetramine (HEX) was reagent grade supplied from Sigma Co® with purity higher than 99.4%.

2.2. Pine bark extraction

Polyphenol extraction was carried out at UDT (Technological Development Unit, Biobío, Chile) by a continuous pilot-plant process (100 kg/h of pine bark based on dry weight). A methanol aqueous solution (75%, v/v) was used as a solvent (65 °C).

After the polyphenol extract was obtained, the extract was evaporated in vacuum (absolute pressure: 0.05 bar) in order to remove methanol, thus obtaining water-soluble and water-insoluble polyphenol fractions.

The water-soluble fraction was used to formulate adhesives. Polyphenols in aqueous solution were concentrated by evaporation, either under vacuum in a rotavapor (Buchi, Germany), or were dried in a spray-dryer (BH, Germany) to use as pine bark extract powder.

2.3. Gel time estimation

In order to study the influence of the HEX concentration (5–10% of the dry extract weight) and its pH (6–10) on the adhesive gel time, aqueous solutions of pine bark polyphenol extract at 30% (solid content by weight) were prepared. The pH was modified with a sodium hydroxide aqueous solution. Five grams of the solution were introduced into a test tube. The test tube was placed in a boiling water bath, and a defined amount of hardener was added. A wire spring was manually moved upwards and downwards until the mixture gelled (Pizzi, 1994). The gel time was monitored with a stopwatch. Analyses were performed in triplicate and the results were averaged.

2.4. Rheological and pot life behavior

The pot life of the pine bark extracts and the resulting formulations were evaluated. The temporal rheological behavior of the extracts and adhesives was analyzed by assuming the rheological parameters obeyed a power law (equation N°1).

$$\sigma = K\gamma^{n} \tag{1}$$

The consistency coefficient K (Pa s^n) is the measured shear stress (σ) at an applied shear rate (γ) of 1.0 s^{-1}. The dimensionless exponent n is the flow behavior index and reflects the correspondence to Newtonian flow. The rheological behavior was measured at 25 °C and 35 °C with a Fungilab Smart L viscometer at different times (60, 120, and 300 min).

First, the influence of pH on the rheological behavior and the pot life of a 30% (wt/v) aqueous solution of pine bark polyphenols extracts (PB) was measured. Second, the dependence of the rheological behavior and the pot life on solids content (solids content by weight up to 40%), pH (7 and 8), and temperature (25 °C to 35 °C) was also studied.

HEX (powder) was used as a hardener during adhesive preparation. HEX was dissolved in a sodium hydroxide solution for a period of 10 min. Then, the polyphenol based solution was added and mixed for at least 20. The effect of hardener concentration (5–10%) and pH (7–8) on the rheological behavior and pot life was also analyzed.

2.5. Differential scanning calorimetry (DSC) experiments

DSC analysis was performed on a NETZSCH DSC instrument (204 F1 Phoenix, Selb, Germany). Samples (7 ± 3 mg) were sealed in high pressure steel pans. The temperature range was scanned from 25 °C to 250 °C with a 10 °C min^{-1} heating rate. Temperature and enthalpy calibrations were performed using indium pills calibration standards (purity > 99.999%).

2.6. Automated bonding evaluation system (ABES) assay

An ABES instrument (Adhesive Evaluation Systems, Corvallis, Oregon, USA) was used to evaluate the maximum strength of the wood-adhesive-wood system at defined temperature and time conditions (Wescott et al., 2007).

The wood veneer samples (Fagus sylvatica L., thickness 0.7 mm) were stored in a conditioned chamber for one week at 20 °C and 53% relative humidity prior to testing. Probes were cut into 117 mm × 20 mm strips using a pneumatically-driven sample cutting device for ABES sample preparation (supplied by Adhesive Evaluation Systems, Corvallis, Oregon, USA).

Two peeled wood veneer strips were glued along the fiber direction with a 100 mm^2 overlap using 20 µg of adhesive. Analyses were conducted at 120, 160, and 190 °C and over 30, 60, 90, and 120 s time frames. Measurements were repeated five times for each data point.

2.7. Fourier transform infrared spectroscopy (FTIR) assay

FTIR spectra were recorded on a Bruker Alpha T FTIR spectrophotometer equipped with a diamond-attenuated total reflectance (ATR). As many as 32 scans were collected over the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. All spectra were recorded and processed with OPUS 7.0 software.

2.8. Adhesive preparation

Adhesives for plywood manufacturing were prepared as follows: