



Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Esterified organosolv lignin as hydrophobic agent for use on wood products

Oihana Gordobil, René Herrera, Rodrigo Llano-Ponte, Jalel Labidi*

Chemical and Environmental Engineering Department, University of the Basque Country UPV/EHU, Plaza Europa, 1, 20018, Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:

Received 27 December 2015
Received in revised form
22 September 2016
Accepted 23 October 2016
Available online xxx

Keywords:

Esterified lignin
Coating
Impregnation
Artificial aging
Contact angle
Color

ABSTRACT

Lignin from Spruce and Eucalyptus wood was isolated by organosolv process, and subsequently was chemically modified using a long aliphatic chain (12C) of dodecanoyl chloride as reagent, to obtain a hydrophobic lignin derivative to be used as protective agent on wood products. Each esterified lignin was applied on wood by two different methods. In the first method, the lignin was applied as coating using for that a press moulding (current industrial processing technology) at two different conditions. The other method consisted in impregnation using acetone as solvent and immersing the samples during different periods of time. The chemical modification of lignins was confirmed by FTIR, GPC and DSC resulting in an increase of its molecular weight and great reduction of glass transition temperature, allowing to process lignin by press moulding besides improving the solubility in acetone. The wood hydrophobicity (WCA $\approx 140^\circ$), oleophobicity (OCA $\approx 120^\circ$) and stability against water and oil dramatically increase after treatments observed by dynamic contact angle analysis. Furthermore, the efficiency of treatments over time was confirmed by accelerated aging test. Aesthetical assessments, by meaning of color analysis (CIEL*a*b* system) showed significant differences between application methods, being more pronounced in case of coating treatments. Additionally, after aging test the color was quite stable.

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1. Introduction

Wood is an incredibly essential raw material that has been used extensively throughout human history and is employed in a great variety of applications such as building materials or indoor-outdoor products [1]. Although wood is a versatile material some of its intrinsic properties represent disadvantages in some applications. Its hydrophilic nature, instability against moisture and degradation due to microorganism or ultraviolet radiation are the main drawbacks that require improvements [1,2]. On these grounds, wood treatments are required to deal with its natural features and enhance its durability in order to increase the service life of wood products [3].

Achieving wood protection from external factors to prevent its deterioration involves different protective methods such as chemical modifications of wood [4–8], thermal treatments [9,10] and the use of additives or chemicals as coatings or penetrating finishes [11–14]. However, the use of toxic products [8] as wood preservative represents diverse risks to humans and other life forms which

should be avoided and that involves the desire to develop new biobased products for wood preservation.

Lignin, one of the most available natural polymers on the earth, presents significant potential as raw material to be used as hydrophobic agent for wood protection. Depending on the origin, growing conditions and the used isolation process, the chemical structures of lignins have distinctive characteristics [15,16]. Lignin backbone is based on three phenylpropane units (*p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S)) which are bound to each other via ether and C–C linkages and are substituted with numerous functional groups like methoxyl groups, phenolic and aliphatic hydroxyl groups principally [17].

However, to increase its hydrophobicity and solubility in organic solvents [18], chemical modification of its functional groups is often carried out. Esterification is one of the easiest reactions to perform considering the reaction parameters and used reactants [17]. Moreover, when lignin is modified by esterification, hydroxyl groups are replaced by ester substituent [19] and thus, reduce the number of hydrogen bonding and generate an increased free volume in the molecule, providing mobility of the chains [20] reducing the glass transition point of lignin and increasing its thermoplasticity [6,21,22]. These gained thermal properties are highly desirable for current industrial processing technology like press moulding.

* Corresponding author.

E-mail address: jalel.labidi@ehu.es (J. Labidi).

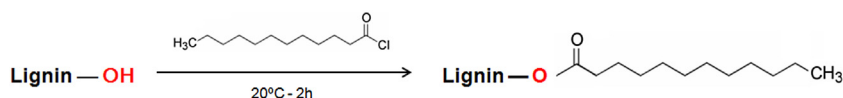


Fig. 1. General schemes of esterified lignins synthesis.

On the other hand, the introduction of vegetable oils composed by different fatty acids has a long tradition in the coatings industry for wood protection [6,23]. Therefore, the synthesis of lignin derivatives using a long aliphatic chain as reactive (with 12 carbons) could be a good choice to develop a hydrophobic natural product with a possible protective action on timber, besides providing a new added value for lignin.

In general, long aliphatic alkyl-lignin derivatives or esterified lignin, consist of two domains, lignin can be considered as polyaromatic domain, and the introduced aliphatic chain could be polyaliphatic domain linked by ester bonds. In nature already exists a macromolecule with similar structure called suberin which is present in most of plants and acts as a barrier between the plants and the environment [23].

The aim of this study was to synthesize long aliphatic alkyl-lignin derivatives from hardwood and softwood organosolv lignins and investigate their possible use in wood treatments as protective agent as well as the influence of lignin derivatives on water and oil affinity, their resistance to artificial aging and appearance on wood veneers. Esterified lignins were applied on the veneers by two different methods. First method was a coating by press moulding at two different conditions; the second one was impregnation using acetone as solvent and immersing the samples at different periods of time.

2. Experimental methods

2.1. Materials

For lignin extraction two different raw materials were used; Spruce and Eucalyptus wood, provided by KTH University in Sweden. Ethanol absolute (99.9%), *N,N*-Dimethylformamide (99%), pyridine (99%), dodecanoyl chloride (98%) and hydrochloric acid (37%) were used as supplied by Panreac and Sigma Aldrich. Veneers were obtained from Poplar and Beech wood.

2.2. Lignin isolation

Organosolv extraction process was performed for both raw materials with small differences between them. The extractions were carried out in a 4 L pressure (20 bar) stainless steel batch reactor with constant stirring (EL0723 Iberfluid) with electronic control unit for pressure and temperature control. Spruce lignin (OS) was extracted with a mixture of ethanol-water (50/50 w/w), H_2SO_4 was used as catalyst (1.2% w/w), and the treatment was carried out at 180 °C for 60 min. The solid to liquid ratio was 1:7 (w/w) [24]; dissolved lignin was isolated by precipitation with four volumes of cold water. For Eucalyptus lignin extraction (OE) a mixture of ethanol water (60/40 w/w) without catalyst was used, the treatment was carried out at 180 °C for 90 min. Solid to liquid ratio was 1:10 (w/w) [25]. Dissolved eucalyptus lignin was isolated by precipitation from the obtained liquor with two portions of acidified water (pH=2). Both lignins were recovered by filtration, washed until neutral pH and then dried at 50 °C.

2.3. Lignin esterification

Esterification procedure was performed with 0.5 g of lignin dissolved into 15 mL of DMF in a two-necked flask with a magnetic

stirrer, pyridine (2.75 mL) was used as a catalyst and dodecanoyl chloride was added (0.9 mL), the reaction was conducted at 20 °C for 2 h. After that, the solution was poured into 650 mL of 2% ice-cold hydrochloric acid. The precipitate was filtered and washed with excess distilled water and ethanol. The samples were then dried in vacuum at 35 °C overnight. Fig. 1 shows the general schemes of esterified lignins synthesis. The obtained modified lignins were called OS_{12C} and OE_{12C} for Spruce and Eucalyptus lignins respectively.

2.4. Wood veneers treatments

Samples prepared for finishing with lignin derivative products were sanded using silicon carbide (SiC) sandpaper with 280-grit (Beech) and 180-grit (poplar). These wood veneers samples were treated with esterified lignins using two different methods; first method was coating by press moulding at two different conditions (90 °C/100 bar and 100 °C/200 bar). Final experimental design was set at 2 min and a dosage of 0.002 g of product per cm². The treatment time assigned was the most suitable time where the product was coated to the substrate without visual defects as well as the quantity of product. The second method was impregnation by immersion of veneers at room temperature in a prepared solution of acetone and esterified lignins (0.5 wt%) at different times (2, 4, 8, 12, 24, 48 and 72 h). Prior to immersion wood veneers were dried at 105 °C in an oven during 2 days and then samples were put under vacuum for 1 h.

2.5. Characterization of lignin ester derivatives

2.5.1. FTIR

The FT-IR analysis of unmodified and esterified lignins was performed on a PerkinElmer Spectrum Two FT-IR Spectrometer equipped with a Universal Attenuated Total Reflectance accessory with internal reflection diamond crystal lens. A total of 8 scans were accumulated in transmission mode with a resolution of 4 cm⁻¹. The spectrum was obtained from a range of 4000–700 cm⁻¹.

2.5.2. GPC

Size exclusion chromatography analysis was used to evaluate the average molecular weight (M_w) and polydispersity (M_w/M_n) of the obtained lignin samples. *N,N*-Dimethylformamide (ethylDMF) eluent was used as GPC mobile phase, at a flow rate of 0.7 mL/min and 35 °C, using a Jasco Inc. chromatograph provided with an LC-NetII/ACD interface, a column oven CO-2065Plus and a RI-2031Plus Intelligent Refractive Index Detector. A guard column and two columns PolarGel-M (Varian Inc.) were employed. Calibration was made using polystyrene standards provided by Fluka, ranging from 250 to 70,000.

2.5.3. DSC

The glass transition temperature of unmodified and esterified lignins was determined by METTLER TOLEDO DSC 822 differential scanning calorimetry. Samples about 5–10 mg were tested under nitrogen atmosphere at a heating rate of 10 °C/min. The isolated and were heated from 25 °C to 200 °C. However, chemical modified lignins were analyzed from –60 °C to 200 °C.

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