



Solvent-free catalyst-free microwave-assisted acylation of lignin



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ARTICLE INFO

Article history:

Received 6 August 2014

Received in revised form 21 October 2014

Accepted 27 October 2014

Available online 13 November 2014

Keywords:

Lignin esterification

Acetylation

Maleation

Solvent-free

Catalyst-free

Microwave-assisted

ABSTRACT

Valorization of lignin into biomaterials requires its good compatibility with the polymeric matrix it is incorporated into. Softwood Kraft lignin was esterified with various anhydrides (acetic, propionic, butyric, methacrylic, maleic) using a solvent-free, catalyst-free, microwave-assisted method. The esterification was fast and efficient (degrees of substitution >90% after 10 min). The reaction was worked up using water or ethanol as purification agent. Esterified lignins were characterized by FT-IR, GPC, quantitative ^{31}P NMR and TGA/DSC. NMR analyses indicated that non-cyclic anhydrides reacted with both aliphatic and phenolic OH groups, while maleic anhydride reacted exclusively with aliphatic OH groups. All acylated lignins except the maleated one showed higher thermal stability than the unmodified lignin. Lignins acylated with non-cyclic anhydrides can be applied as green fillers in apolar polyolefins while maleated lignin can serve as metal adsorbent or macroreagent for the synthesis of polyesters or polyamides. We showed in this study that lignin can be modified in a fast and easy way.

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1. Introduction

With the current rapid depletion of non-renewable fossil fuel based resources, there is a strong interest worldwide in using renewable biomass to replace petroleum-based chemicals in products manufacturing. In this context, lignin which exhibits a great variety of functional groups including aliphatic hydroxyl groups, phenolic groups, and carboxylic groups, is an attractive feedstock for the preparation of polymers (Lora and Glasser, 2002; Lora, 2008; Gandini and Belgacem, 2008; Stewart, 2008; Satheesh Kumar et al., 2009; Doherty et al., 2011; Ragauskas et al., 2014). Lignin can, for instance, be used as green filler in thermoplastics and thermosetting polymers (Feldman, 2002; Thielemans et al., 2002; Košičová et al., 2006; Gandini and Belgacem, 2008; Doherty et al., 2011; Schorr et al., 2014; Takur et al., 2014) or as macromonomer in polyurethanes (Hatakeyama, 2002; Gandini and Belgacem, 2008), polyesters (Gandini and Belgacem, 2008), and phenolic and epoxy resins (Gandini and Belgacem, 2008; Stewart, 2008; Doherty et al., 2011).

In order for a lignin to be successfully introduced into an industrial polymer, it must have the desirable structural characteristics and levels of purity. A first approach to enhance the suitability of lignin for specific polymer applications is to select the right biomass source along with the right isolation process (Gandini and

Belgacem, 2008; Monteil-Rivera et al., 2013). A second approach consists in modifying lignin functional groups to make them more reactive or more compatible with the bulk matrix (Gandini and Belgacem, 2008); however, to be viable, the second approach must involve minimal amounts of reagents and energy and be environmentally friendly. The use of toxic, non recyclable, or expensive solvents to modify reactive nuclei of lignin is not acceptable for industrial applications.

The numerous hydroxyl groups on the lignin molecule are local centers of high polarity which hamper the incorporation of lignins into apolar polymers like polyolefins. Chemical modification of hydroxyl groups through esterification, and in particular through acetylation, has been used for decades to modify the solubility of lignin in organic solvents and to increase the polymer-lignin compatibility (Lewis et al., 1943; Glasser and Jain, 1993; Meister, 2000; Thielemans and Wool, 2005). Lignin has been esterified by reaction with various carboxylic acids, acid halides, or anhydrides. Amongst these reactions, acetylation with acetic anhydride has been by far the most widely applied (Lundquist, 1992; Glasser and Jain, 1993). Acetylation of lignin with acetic anhydride can occur at room temperature provided that a catalyst, e.g. zinc chloride, dimethylformamide, trifluoroacetic acid, boron trifluoride, sodium acetate, 1-methyl imidazole, or the widely used pyridine (Glasser and Jain, 1993; Thielemans and Wool, 2005; Fox and McDonald, 2010) is present in the reaction medium, or without catalyst provided that the medium is energy activated (Rowell et al., 1994; Cachet et al., 2014). Esterification of lignin with larger chain derivatives has received little attention, and the few reported reactions

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were conducted in the presence of a catalyst and under heating conditions (Lewis et al., 1943, Ralph and Lu, 1998; Thielemans and Wool, 2005; Fox and McDonald, 2010).

Recently we and others demonstrated that microwave irradiation could be efficiently used to extract lignin from various biomasses (Sun et al., 2009; Monteil-Rivera et al., 2013), liquefy lignin into phenolic biooil or phenols (Bu et al., 2011; Sequeiros et al., 2013; Toledano et al., 2014), or chemically modify lignin (Ouyang et al., 2011). On the other hand, microwave irradiation was used to acetylate phenolic monomers (Deka et al., 2001), cellulosic residue (Li et al., 2009, Yang et al., 2010) or wood lumbers (Neogi et al., 2007) but never lignin. In this study we used microwave irradiation to esterify the OH groups of a Kraft lignin without solvent and without catalyst. The purpose of this study was to (1) develop a new simple green protocol for the acetylation of lignin and to (2) validate the applicability of this protocol to other anhydrides, including one (maleic anhydride) which is solid at ambient temperature.

2. Experimental

2.1. Materials

Lignin used in this study was a Kraft lignin from mixed softwoods (Indulin AT) supplied by MeadWestvaco (Charleston, SC). Basic chemical properties of Indulin AT are provided in Table S1. Anhydrides were obtained from Sigma-Aldrich (Oakville, ON). Deionized water was obtained with a Milli-Q Advantage A10 system (Millipore, Mississauga, ON). Tetrahydrofuran (THF, HPLC grade) and methanol (reagent grade) were from Fisher Scientific (Ottawa, ON); anhydrous ethanol was from Commercial Alcohols (Brampton, ON). Anhydrous pyridine (99.8%), deuterated chloroform, *N*-hydroxynaphthalimide, chromium(III)acetylacetonate, and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) were from Sigma Aldrich (Oakville, ON). Lignin and all other chemicals were used without further purification.

2.2. Conventional acetylation of lignin

Lignin was acetylated according to the conventional method that uses pyridine as catalyst (Lundquist, 1992). Briefly, lignin (500 mg) was reacted with 10 mL of anhydrous pyridine/acetic anhydride (1:1, v/v) at room temperature for 24 h or 72 h in a glass flask and the acetylated lignin was isolated after adding and evaporating ethanol five times.

2.3. Microwave-assisted acylation of lignin

Acylation of lignin was conducted by reacting lignin with the desired anhydride without solvent and without catalyst using a MARSXpress™ (CEM Corporation, Matthews, NC) microwave system. Lignin (1.0 g) was introduced in a 30-mL Teflon pressure sealed tube, together with 10 g of anhydride. The tube equipped with a thermocouple was screw capped and microwave-heated. Various conditions were applied. The temperature program consisted of a heating step using a fixed power (200 or 400 W) followed by a plateau step (0 to 30 min) during which a fraction of the fixed power was applied to maintain temperature at the target value (80 to 150 °C). When the reaction was finished, the sealed vessel was allowed to cool down to room temperature (~ 1 h). The reaction mixture was then poured into water (50 mL) unless otherwise mentioned and stirred until lignin was precipitated. The solid residue was filtered and washed with water (or solvent used for the precipitation) to remove the unreacted anhydride, the coproduced carboxylic acid and other eventual byproducts. Sample was dried in an oven at 60 °C for 24 h. The reaction yield was determined by

measuring the degree of substitution (DS) using quantitative ³¹P NMR as described below.

2.4. Acetylation of lignin using conventional heating

For comparison, acetylation of lignin was also conducted using a high pressure-high temperature 300-mL Parr (Moline, IL) reactor equipped with a magnetic drive, a ceramic heater assembly, and a cooling loop. Lignin (10 g) was introduced in the reactor with 100 g of acetic anhydride. Reactor was closed, stirred at 150 rpm, and heated to 130 °C (duration of heating = 10 min). Temperature was maintained at 130 °C for 30 min and reactor was cooled down to room temperature. The reaction mixture was then poured into water (500 mL) and stirred for 2 h. The solid residue was filtered, washed with water, dried at 60 °C for 24 h, and analyzed similarly to acylated samples obtained using microwave.

2.5. Structural characterization of acylated lignins

Fourier transform infrared (FT-IR) spectra of raw and acylated lignin were obtained using a Tensor 27 (Bruker, Germany) spectrometer in the Attenuated Total Reflectance (ATR) analysis mode. Spectra were collected from 500 to 4000 cm⁻¹ (64 scans; resolution of 4 cm⁻¹) after positioning the pure powder directly on the diamond crystal plate, and a six-point baseline correction was applied on each spectrum.

Molecular weight distributions of the acylated lignins were determined by gel permeation chromatography (GPC) using THF as mobile phase, a multi-detection system from Viscotek (Houston, TX) and a universal calibration that used UV (Viscotek UV 2600 model; 280 nm) and viscosity (Viscotek TDA 305 model) measurements, as previously reported (Monteil-Rivera et al., 2012).

Functional OH groups of the original and modified lignins were quantified by ³¹P NMR after phosphorylation with TMDP using *N*-hydroxynaphthalimide as internal standard (Granata and Argyropoulos, 1995) and acquisition conditions reported elsewhere (Monteil-Rivera et al., 2012). All chemical shifts are reported relative to the signal of the product of water with TMDP (132.2 ppm). The content of hydroxyl groups was obtained by integration of the following spectral regions: aliphatic OH (149.1–144.6 ppm), condensed phenolic OH (144.6–141.2 ppm), guaiacyl phenolic OH (140.5–138.5 ppm), *p*-hydroxyphenyl phenolic OH (138.5–137.4 ppm), COOH (136.0–134.0 ppm).

The degree of substitution (DS) of acylated lignins was calculated according to Equation (1), using the NMR quantitative data obtained with TMDP and a correction factor that took into account the increase of mass in the acylated lignin:

$$DS = \frac{[C(OH)_i - C(OH)_f]}{[C(OH)_i + C(OH)_f \times \Delta m_{\max}]} \quad (1)$$

where C(OH)_i (mmol g⁻¹) is the initial concentration of hydroxyl units in the unmodified lignin, C(OH)_f (mmol g⁻¹) is the concentration of hydroxyl units, as measured by ³¹P NMR, in the modified lignins, and Δ_{m_{max}} is the increase of weight (g) per g of lignin for 100% conversion. The initial content of OH units (phenolic + aliphatic) in Indulin AT, C(OH)_i, was measured by ³¹P NMR and found equal to 5.93 mmol g⁻¹.

Thermogravimetric analysis (TGA) of the acylated lignins (10 mg) was performed using a NETZSCH STA 449 F1 instrument operating from 25 °C to 800 °C at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere (20 mL min⁻¹). The decomposition temperature (*T_d*) was determined as the temperature at which a 5% weight loss was measured. Differential scanning calorimetry (DSC) analysis was conducted using a NETZSCH STA 449 F1 instrument under a nitrogen atmosphere (20 mL min⁻¹). Samples (10 mg) were first

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