Reactive and Functional Polymers 123 (2018) 20–25

Contents lists available at ScienceDirect

Reactive and Functional Polymers

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

Laccase modified lignosulfonates as novel binder in pigment based paper coating formulations

Andreas Ortner[a], Karin Hofer[b], Wolfgang Bauer[c], Gibson S. Nyanhongo[a,*], Georg M. Guebitz[a]

[a] Institute of Environmental Biotechnology, University of Natural Resources and Life Sciences Vienna, Konrad Lorenz Strasse 20, Tulln 3430, Austria
[b] Sappi Papier Holding GmbH, Brucker Strasse 21, Gratkorn 8101, Austria
[c] Graz University of Technology, Institute of Paper, Pulp and Fibre Technology, Inffeldgasse 23, Graz 8010, Austria

ARTICLE INFO

Keywords:
Laccase
Paper coating
Lignosulfonate
Polymerization
Binders

ABSTRACT

The exploitation of renewable and cheaper paper coating formulations especially for graphic paper products is gaining increasing importance due to concerns regarding the use of fossil based raw materials. For this reason, a novel process for enzymatic modification of lignosulfonates to substitute fossil based styrene-butadiene (SB) latex as binders in conventional paper coating formulations was developed. Laccase polymerization of ultrafiltrated lignosulfonates (LS) resulted in an increase of the molecular weight from an average of 26 kDa to 170 kDa as compared to non-ultrafiltrated LS which increased from 5.7 kDa to 76 kDa. When used in coating formulations, laccase polymerized LS resulted in coated paper with improved printing properties (reduced picking compared to non polymerized LS) provided that the LS was ultrafiltrated before polymerization. Abo Akademi gravimetric water retention properties of the paper coatings were comparable (395 g m^{-2}) to those obtained with reference latex (350 g m^{-2}). Similarly, cross sectional fluorescence microscopy images showed that ultrafiltration prior to laccase polymerization reduced penetration of the polymerized lignosulfonates into the base paper to 33% and additionally reduced polymerization time from 6 h to 2 h. These results demonstrate the possibility of substituting fossil based styrene-butadiene (SB) latex binders with on-site produced lignosulfonates which have traditionally been considered so far mainly as a by-product used for energy production in the pulp and paper industry.

1. Introduction

Paper is a porous fibre network often coated with various materials to enhance surface smoothness, optical properties, print performances as well for adding desired functionalities [1,2]. A coating formulation typically consists of mineral pigments, latex binders, polymeric thickeners and other additives (e.g. dispersants, biocides, pH controllers, dyes and foam controllers) in lower quantities [2,3]. Considering an amount up to 50 kg of latex used per ton of e.g. coated printing papers, a single paper mill may use several of ten thousand tons of these oil based chemicals annually. As alternative sustainable raw materials, biopolymers like starch, proteins and lignocellulose based materials are gaining in importance in paper coating applications [4,5]. Lignin, a major component of wood (up to 32%) liberated during the pulping process with currently only 2% being exploited commercially [6], could be a possible biomaterial for application in paper coating formulations. Indeed lignins have been shown to impart interesting properties for coatings which could make them suitable to replace oil-based styrene-butadiene (SB) or styrene-acrylate latex as a binder in paper coating formulations [7–9]. However, over the years it has become clear that successful application of lignin requires pretreatments to decrease its heterogeneity, increase its entropy, poldispersity and miscibility properties [10–15], properties which are limiting its widespread industrial application. Among the processes, enzymes - especially laccases are gaining increasing importance. Laccases (benzenediol: oxygen oxidoreductases, EC.1.10.3.2) are multicopper enzymes, catalyzing the oxidation of various phenolic molecules to phenoxy radicals while reducing molecular oxygen to water [16]. Laccases are widely distributed in plants and fungi; they play an important role in the biosynthesis of lignin as well as in its degradation. Laccases are used to improve lignin properties for various applications [15] while often expensive and/or toxic electron mediators are used to broaden the range of substrates that can indirectly be oxidized by laccase [17]. We recently developed a novel laccase lignin polymerization method which employs external oxygen and resulted in extensive polymerized lignosulfonates (LS) with potential for applications as coating materials [18,19]. Through these studies it became clear that oxygen was limiting in previous laccase mediated polymerization studies thereby discrediting the need to use

* Corresponding author.
E-mail address: gnyanhongo@boku.ac.at (G.S. Nyanhongo).

https://doi.org/10.1016/j.reactfunctpolym.2017.12.005
Received 6 October 2017; Received in revised form 5 December 2017; Accepted 8 December 2017
Available online 09 December 2017
1381-5148/

laccase mediators (small molecules which when oxidized by laccase form reactive species supposedly with high redox potential to effectively oxidize technical lignins) which have erroneously been popularized as the only way to achieve extensive polymerization of technical lignins. This process is set to make the synthesis of lignin based materials cheaper, easier and more efficient. In this study we apply and optimize the developed laccase lignin treatment method and investigate the potential of the modified LS to replace oil-based styrene-butadiene (SB) latex as a binder in paper coating formulations.

2. Material and methods

All used chemicals were of analytical grade, purchased from Sigma-Aldrich (Steinheim, Germany), Merck (Darmstadt, Germany) or VWR (Vienna, Austria). Laccase from *Myceliophthora thermophila* was obtained from Novozymes. Styrene-butadiene latex (SBL) and thickener were provided by BASF (Ludwigshafen, Germany), polyvinylalcohol (PVOH) (Mowiol 4–98) from Kuraray Europe GmbH (Hattersheim am Main, Germany), and calcium carbonate from Omya (Oftringen, Switzerland). Industrial Mg-sulfite spent liquor containing lignosulfonates from an acid magnesium bisulfite process from the intermediate evaporation stage (approx. 30% solids) and precoated base paper was kindly provided by SAPPI Gratkorn, Austria.

2.1. Ultrafiltration of lignosulfonates

A Memcell unit supplied by Osmo Membrane Systems GmbH (Korntal-Muenchingen, Germany) was used to ultrafiltrate sulfite spent liquor. The sulfite spent liquor having a solids content of 30% was always pre-filtered with a 5 µm paper filter to remove solid particles and fibrous material. In the ultrafiltration trials a second prefiltering step using the Memcell device was performed using a 2 µm membrane. Salts, sugars and smaller lignin fractions were subsequently removed using a 150 kDa membrane by repeatedly adding water until the permeate was colorless. Thereafter, the retentate retained on the 150 kDa ultrafiltration membrane (R150), which had a solids content of around 10–12%, was brought to 30% solids using a rotary evaporator and was used for the experiments.

2.2. Laccase activity assay

Laccase activity was measured spectrophotometrically according to the procedure described by Nugroho Prasetyo et al. [20], while monitoring the oxidation of 2,2′-Azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) to its cation radical at 420 nm using a plate reader (Tecan, Infinite M200, Switzerland). The activity was expressed in katal (defined as the amount of enzyme necessary to convert 1 mol substrate per second). *Myceliophthora thermophila* laccase (MTL) activity was measured in 100 mM TRIS HCl buffer at pH 7. Unless otherwise indicated, all experiments were carried out in triplicates.

2.3. Enzymatic polymerization of lignosulfonates

The recently developed laccase mediated lignosulfonate polymerization process based on continuous oxygen supply avoiding the use of expensive mediators [18,19] was used. The pH of all lignosulfonates were first adjusted to pH 7 using NaOH prior to the enzymatic treatment. During incubation of lignosulfonate with the laccase, oxygen consumption was monitored using a FireSting-O_2 device from *PyroScience* GmbH (Aachen, Germany). The sensor was placed in a 100 ml glass bottle containing 60 ml of the 30% TDS lignin sample and then supplied with pure oxygen (100% saturation) before introducing 233 nkatal ml^{-1} laccase to start the reaction. Samples were withdrawn after 6 h and the change in molecular weight was measured by using SEC.

2.4. Size exclusion chromatography (SEC) analysis of lignosulfonates

The molecular weights of treated and untreated lignins were determined by using size exclusion chromatography (SEC) equipped with degasser, binary pump, auto sampler, a DAD (Diode Array Detector) and a RI (Refractive Index) -detector system (Agilent Technologies 1260 Infinity). A guard column (Waters Ultrahydrogel, 200 Å, 6 × 40 mm, maximum pressure 3.93 MPa) was placed before the two separating columns (Waters Ultrahydrogel 500, 500 Å, 7.8 × 300 mm, 3.93 MPa and Waters Ultrahydrogel 250, 250 Å, 7.8 × 300 mm, 1.96 MPa) connected in series. Samples were run using an isocratic gradient with a 0.1 M $NaNO_3$ solution as mobile phase for 120 min. The lignins were diluted with the mobile phase to a concentration of 1 mg ml^{-1} before loading 100 µl onto the column. The Agilent GPC/SEC Software (Version 1.2) was used for analysis of chromatograms. The standards used for size exclusion chromatography (SEC) were polystyrene sulfonate sodium salts with molecular weights ranging from 208 g/mol–1,188,400 g/mol.

2.5. Preparation of the paper coating formulation and paper coating

Coating formulations (topcoat for a triple coated WFC paper) were prepared as summarized in Table 1 with always 1000 g (dry substance) calcium carbonate. Latex was substituted partially by untreated and enzymatically modified lignosulfonate, which either was a spent liquor just purified from larger particles and fibers by a 5 µm paper filter or was ultrafiltrated as specified above. Latex was subtituted by Lignosufonate in the ratio of 1:2, therfore the latex amount could be reduced by 25% (see Table 1).

Coating was performed on a laboratory reel-to-reel coater using a stiff blade at a speed of 15 m/min. The base paper was a pre-and middle-coated wood free base paper provided by Sappi Gratkorn. Target coat weight was 8 g/m^2 per side.

2.6. Coating and coated paper testing

Water retention of the coating was quantified by measuring the Abo Akademi Gravimetric Water Retention Value (AA-GWR) as per TAPPI standard (T-701). Furthermore, pH, low shear (Brookfield) and mid shear viscosity (Paar Physica) was controlled. Optical properties were measured using a Technidyne Color Touch 2 according to ISO 2470–2. Printability parameters (passes-to-fail, set-off, droplet test (ink repellence) were determined using a Prüfbau device and picking resistance using an IGT device.

Penetration of lignosulfonate based binder into the base paper was measured in the coating, applied directly on an uncoated base paper using a method developed by Hofer et al. [21], which makes use of the autofluorescence of lignosulfonates by evaluation of cross sectional images of the produced paper sheets using standard visible (VIS) and

Table 1
Composition of coating formulations expressed as % w/w (dry substance) related to calcium carbonate. All formulations contained 1000 g (dry substance) calcium carbonate.

Ingredients	Coating formulations		
	Untreated lignosulfonate	Laccase polymerized lignosulfonates	Reference
Calcium carbonate	100	100	100
Untreated lignosulfonates	4		
Laccase polymerized lignosulfonates		4	
SB-Latex	6	6	8
PVOH	0.8	0.8	0.8
Thickener	0.25	0.25	0.25
Target solids content	60	60	60