ENZYMATICALLY MODIFIED LIGNOSULFONATES AS COATING BINDERS

UPORABNOST ENCIMATSKO MODIFICIRANIH LIGNOSULFONATOV KOT VEZIVA V PREMAZIH

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ABSTRACT

The exploitation of renewable and cheaper paper coating formulations especially for graphic paper products is gaining importance due to concerns regarding the use of fossil-based raw materials. For this reason, a new process for enzymatic modification of lignosulfonates to substitute fossil-based styrene-butadiene (SB) latex as a binder in conventional paper coating formulations was developed. Laccase polymerization of lignosulfonates resulted in the increase of molecular weight. When used in coating formulations, laccase polymerized lignosulfonate resulted in coated paper with good printing properties (reduced picking) provided that the lignosulfonate was ultrafiltrated before polymerization. Similarly, cross-sectional fluorescence microscopy images showed that ultrafiltration and laccase polymerization reduced the penetration of the polymerized lignosulfonates into the base paper by 33 % in view of coating formulation. These results demonstrate the possibility of substituting fossil-based styrene-butadiene (SB) latex binders with on-site produced lignosulfonates which have traditionally been considered mainly as a by-product used for energy production in the pulp and paper industry.

Key words: laccase, paper coating, lignosulfonate, polymerization, binders

IZVLEČEK

Izkoriščanje obnovljivih in cenejših vrst papirnih premazov predvsem za grafične papirje ima vse večji pomen predvsem zaradi vedno večjih pomislekov pri uporabi fosilnih surovin. Iz tega razloga je bil razvit novejši postopek za encimatsko modifikacijo lignosulfonatov, kot zamenjava za veziva na osnovi stiren butadienskega lateksa (SB), ki se običajno uporabljajo kot vezivo v premazih za premazovanje papirja. Polimerizacija lignosulfonatov z lakazo vpliva na povečanje molekulske mase. Pri uporabi v sestavi premaza za premazovanje papirja vpliva na premazan papir z izboljšanimi tiskovnimi lastnostmi (zmanjša se cepljenje papirja) pod pogojem, da je bil lignosulfonat pred polimerizacijo ultrafiltriran. Tudi prečni posnetki fluorescenčne mikroskopije kažejo, da ultrafiltracija in polimerizacija lakaze za 33 % zmanjša penetracijo polimeriziranih lignosulfonatov v osnovni papir glede na sestavo premaza. Rezultati prikazujejo možnosti zamenjave klasičnega lateks veziva na osnovi stiren-butadiena (SB) z lokalno proizvedenimi lignosulfonati, ki se tradicionalno pridobivajo kot stranski produkt v proizvodnji celuloze in se običajno uporabljajo za proizvodnjo energije v industriji celuloze in papirja.

Ključne besede: lakaza, premazovanje papirja, lignosulfonati, polimerizacija, veziva

1 INTRODUCTION

Pigment coatings are applied to optimize the surface and printing properties of coated papers (Huang and Lepoutre, 1998). A coating color consists of several components having different functions. To bind the pigments and to fix the coating layer to the base paper, today mainly petroleum-based latex binders are used. There are efforts to increasingly substitute these petroleum-based products with renewable binders (Flory et al., 2013; Gosselink et al., 2010). Biopolymers like starch, proteins and lignocellulosic materials are gaining in importance in paper coating applications (Imam et al, 2013). Technical lignins, such as lignosulfonates or kraft lignins, are an abundant source of biopolymers which today are mainly used for energy production. Material applications of technical lignins for special products range only between 1 and 2% (Gosselink et al., 2004), which is mainly due to the heterogeneity of technical lignins. Still more and more applications of technical lignins as building blocks for polymers, resins or adhesives have been developed recently (Stewart, 2008).

The aim of this work was to test the feasibility of the development of a renewable binder based on the lignosulfonates contained in the spent liquor from an industrial source (Mg-sulfite pulp mill) in order to substitute partially petroleum-based SB-latices in pigment coating applications. The potential of enzymatic polymerization of lignosulfonates to enhance the binding properties via the modification of the molecular structure was also studied.

2 MATERIALS 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 (Bagsvard, Denmark).

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).

Ultrafiltration of lignosulfonate

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 first pre-filtered with a 5µm paper filter to remove solid particles and fibrous material. Another prefiltering step using the Memcell device was performed using a 2µm membrane. Salts, sugars and smaller lignin fractions were subsequently removed using a 150kDa membrane by repeatedly adding water until the permeate was colorless. Afterwards, 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.

Enzymatic lignin polymerization

A recently described laccase mediated lignosulfonate modification process based on oxygen supplementation was used, which avoids the use of expensive mediators (Ortner et al., 2015; Huber et al., 2016). Enzymatic polymerization of 30% TDS lignosulfonate with the Myceliophthora thermophila laccase (MTL) (introducing 233 nkatal ml^{-1} laccase) was carried out at pH 7 in the presence of external oxygen supply (monitored using a FireSting-O_2 device from PyroScience GmbH (Aachen, Germany)).

Size exclusion chromatography (SEC)

The molecular weights of treated and untreated lignosulfonate samples were determined using size exclusion chromatography (SEC) equipped with a degasser, a binary pump, an 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 x 40 mm, maximum pressure 3.93 MPa) was placed before the two separating columns (Waters Ultrahydrogel 500, 500 Å, 7.8 x 300 mm, 3.93 MPa and Waters Ultrahydrogel 250, 250 Å, 7.8 x 300 mm, 1.96 MPa) connected in a series. 0.1 M $NaNO^3$ solution was used as the mobile phase and the runtime was 120 minutes. The lignosulfonates were diluted with the mobile phase to a concentration of 1 mg*mL-1 before loading 100µl onto the column. Chromatograms were analyzed with the Agilent GPC/SEC Software (Version 1.2). The standards used for size exclusion chromatography (SEC) were Polystyrene Sulfonate Sodium Salts with molecular weights ranging from 208 g/mol to 1,188,400 g/mol.

Coating color preparation and laboratory coating process

Coating formulations (precoat for a double coated WFC paper) were prepared using calcium carbonate HC60 from Omya (Oftringen, Switzerland), SB-latex from BASF (Ludwigshafen, Germany), PVOH (Mowiol 4-98) from Kuraray Europe GmbH (Hattersheim am Main, Germany) and CMC (Finnfix 30) from CP Kelco (Cumberland, USA). Latex was partially substituted by untreated and enzymatically modified lignosulfonate in a ratio of 1:2, i.e. latex amount was reduced by 2%, and 4% of the ultrafiltrated lignosulfonate was added, either with or without enzymatic polymerization. Coating was performed on a film press using profiled rod with 30µm depth of profile at a lab coater speed of 15 m/min. The base paper was an uncoated wood-free base paper. The target coat weight was 10g/m² per side.

Coating and paper testing

Water retention of the coating colors was quantified by measuring the Abo Akademi Gravimetric Water Retention Value (AA-GWR). Furthermore, pH and low shear (Brookfield) viscosity were controlled. Grammage was determined according to EN ISO 536. Optical properties (R457 +/+UV) were measured using Technidyne Color Touch 2 (DIN 6174/ TAPPI T452). Printability parameters (passes-to-fail, set-off, droplet test (ink repellence)) were determined using a Prüfbau device and picking resistance using an IGT device.

3 RESULTS AND DISCUSSION

Preliminary trials with lignosulfonates containing spent liquor

First coating trials using lignosulfonate containing spent liquor directly from the pulping process at 30% TDS, only filtered through a 5µm paper filter to remove solid particles and fibrous material, showed dusting immediately after coating drying of the reel-to-reel coater, indicating a very low binding force of the lignosulfonates. Extremely poor IGT picking tests verified this observation. For lignosulfonate containing samples, no values could be determined, because the first signs of picking were evident below 2 cm under the lowest loading.

As the water retention value (AA-GWR) of 975 g/m² (see also Figure 3, left bar) of this coating was very poor, binder penetration into the base paper was measured for this coating applied directly on an uncoated base paper using a method developed by Hofer et al. (2015), which makes use of the autofluorescence of lignosulfonates. In the BF and GFP images on the left side of Figure 1, a cross-section of a coated paper with untreated lignosulfonate containing spent liquor (no ultrafiltration, no enzymatic polymerization) is illustrated. The BF (visual light) image shows the coating layer appearing darker, whereas the GFP image (UV light) shows the green fluorescing lignosulfonate; the white lines in the GFP image indicate the segmented coating layer from the BF image. The lack of lignosulfonate binder in the coating layer is obvious; the lignosulfonate is penetrating deeper into the base paper and the depletion of the lignosulfonate binder in the coating layer is clearly visible. Almost all of the binder penetrated into the porous system of the base paper and the binding force of the coating layer is too low.

To overcome this excessive penetration of lignosulfonates contained in the spent liquor into the base paper by an increase in molecular weight, enzymatic polymeriza-

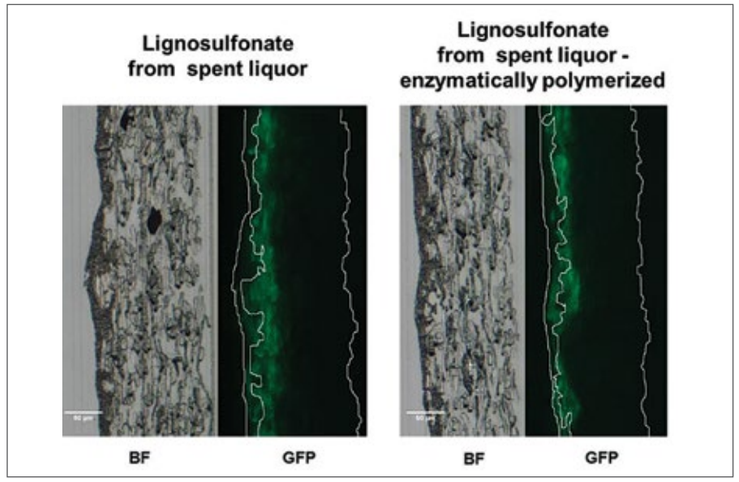


Figure 1: Penetration of lignosulfonates from spent liquor into the base paper. Brigthfield (BF) and green fluorescent (GFP) images of blank lignosulfonate (untreated lignosulfonate from spent liquor) (left) compared to BF and GFP image of enzymatically polymerized lignosulfonate from spent liquor (right)
Slika 1: Penetracija lignosulfonata iz odpadne lužnice v osnovni papir. Primerjava BF (brigthfield) in GPF (green fluorescent) posnetkov neobdelanega (levo) in encimatsko polimeriziranega lignosulfonata iz odpadne lužnice (desno)

Table 1: Precoat formulations [% dry substance]
Preglednica 1: Sestava predpremaza [% suhe snovi]

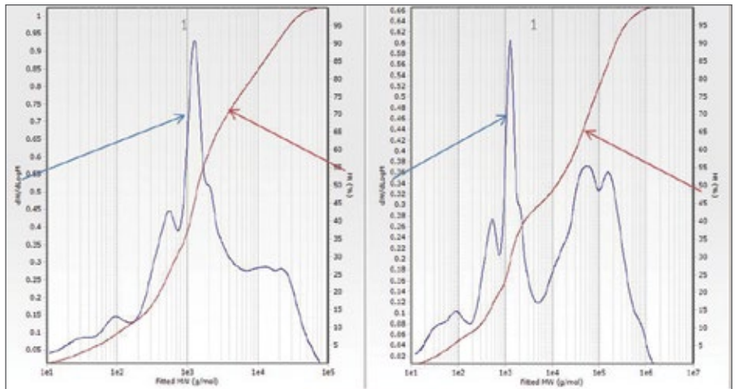
	Modified* lignosulfonate	Untreated** lignosulfonate	Reference
Calcium carbonate (HC60)	100	100	100
Modified lignosulfonate*	4		
Untreated lignosulfonate**		4	
SB-Latex	6	6	8
PVOH	0.5	0.5	0.5
CMC	0.5	0.5	0.5
Target solids content	60	60	60

* enzymatically polymerized, ultrafiltrated
** no enzymatic polymerization, ultrafiltrated

tion of the lignosulfonates with a laccase mediated modification process based on oxygen supplementation (Ortner et al., 2015; Huber et al., 2016) was tried. First trials with industrial spent liquor containing lignosulfonates originating directly from the intermediate evaporation stage, only filtered through a 5 µm paper filter, showed a significant increase in the average molecular weight after six hours of enzymatic polymerization (Figure 2).

The penetration of lignosulfonates into the base paper could be reduced dramatically by enzymatic polymerization (see GFP image on the right side of Figure 1). Three-dimensional evaluation of 100 cross-sections similar to/like the ones depicted in Figure 1 (image length > 5mm) resulted in the penetration depth illustrated in Figure 3. Due to enzymatic polymerization, the penetration depth was decreased by around *10µm*. *The penetration depth for the SB-latex* reference was not determined because SB-latex needs to be stained by a fluorescent dye and the results are not directly comparable to the lignosulfonate coatings.

The observations regarding penetration depth were confirmed by measuring a more than 50% higher water retention (low AA-GWR) for the enzymatically polymerized lignosulfonates compared to untreated samples. As can be seen in Figure 3, the modified lignosulfonates were in the same AA-GWR range as the reference.



	Mn	Mw	Mz	PD
Blank	277	5714 Da	23445	20.63
Enzymatically polymerized	423	76453 Da	370387	180.7

Figure 2: Molecular weight distribution (SEC) of enzymatically polymerized lignosulfonate from spent liquor with 30% TDS (right) compared to blank lignosulfonate (untreated lignosulfonate) at 30 % TDS (left, no enzyme treatment) and their average molecular weights (table below figure)
Slika 2: Porazdelitev molske mase (SEC) encimatsko polimeriziranega lignosulfonata iz odpadne lužnice s 30 % suhe snovi (TDS) (desno) v primerjavi z neobdelanim lignosulfonatom s 30 % suhe snovi (levo, brez encimatske obdelave) in njihova povprečna molska masa (preglednica pod sliko)

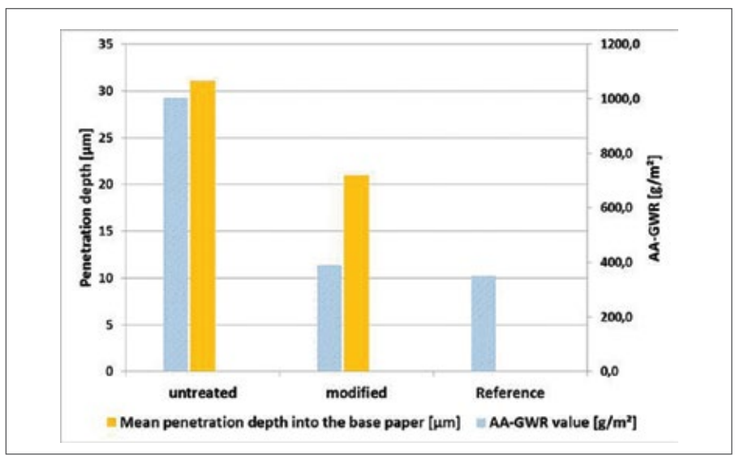


Figure 3: Penetration depth of lignosulfonates into the base paper (measured according to Hofer et al. (2015)) and AA-GWR water retention of coatings containing lignosulfonates from spent liquor compared to the reference
Slika 3: Globina penetracije lignosulfonata v osnovni papir (merite izvedene v Hofer et al., 2015) in retencija vode (AA-GWR) v premazu, ki vsebuje lignosulfonate, v primerjavi z referenčnimi vrednostmi

Although binder penetration was significantly reduced using enzymatically polymerized lignosulfonates from the spent liquor, the binding force was still insufficient, which we attributed to a large amount of impurities contained in the industrial lignosulfonates, as e.g. salts, sugars or extractive. Therefore, ultrafiltration was applied in all further trials to eliminate the impurities, which were assumed not to contribute to the binding function on the one hand and to hinder the lignosulfonate binder to form a continuous film on the other.

Trials using ultrafiltrated lignosulfonate

Using such ultrafiltrated lignosulfonate samples, the incubation time in enzyme polymerization could be reduced from six to two hours to reach a similar molecular weight increase compared to non-ultrafiltrated samples.

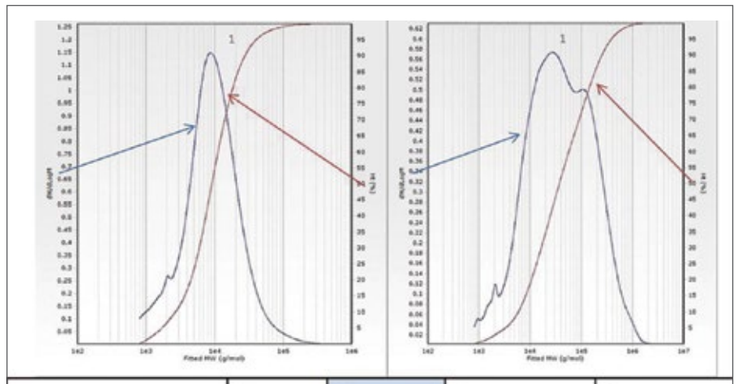
Thus a sufficiently reproducible high degree of polymerization was achieved after merely two hours of incubation at an oxygen supply rate of 15cm³, leading to an increase of the average molecular weight from 14092 to 97574 Da (see Figure 4). It should be noted that ultrafiltration alone leads to a higher molecular weight of the lignosulfonates (compare blank in Figure 4 to blank in Figure 2).

Lignosulfonates as binders in precoat application

Ultrafiltrated and enzymatically polymerized lignosulfonates were tested in the application in a precoat (for recipes see Table 2) to hide the brown color of lignosulfonates under a white top-coating layer. Precoats were applied with a film press in single sheet mode, which also allows better adjustment of the coat weight. The results of the IGT pick test of the precoated samples are listed in Table 2. Untreated (ultrafiltrated, no enzyme treatment) lignosulfonate showed a slightly lower picking resistance than modified (ultrafiltrated, enzymatically polymerized) lignosulfonates, and both showed clearly lower values than the reference.

The three precoated papers were topcoated using a standard topcoat. In Table 3, the Prüfbau printing results for the topcoated papers are shown. The offset suitability of all three samples is comparable, with a slight advantage for the reference in passes-to-fail wet. Ink setting of the modified lignosulfonate containing precoat is comparable to the reference, while untreated lignosulfonate containing precoat shows slower ink setting. The droplet test as a measure for water repellence shows significantly higher values for the lignosulfonate containing samples compared to the reference.

The brightness level of the double coated samples is listed in Table 3. Brightness measured with and without UV is significantly lower compared to the reference.



	Mn	Mw	Mz	PD
Blank	5853	14092 Da	40793	2.408
Enzymatically polymerized	13493	97574 Da	365735	7.231

Figure 4: Molecular weight distribution (SEC) of enzymatically polymerized lignosulfonate (ultrafiltrated 2µm > x > 150kDa) with 30% TDS (right) compared to blank lignosulfonate (untreated ultrafiltrated lignosulfonate) at 30% TDS (left, no enzyme treatment,) and their average molecular weights (table below figures).
Slika 4: Porazdelitev molekularne mase (SEC) encimatsko polimeriziranih lignosulfonatov suhe snovi (levo, brez encimatske obdelave) in povprečna molska masa (preglednica pod sliko).

Table 2: Coat weight and IGT picking of precoatings
Preglednica 2: Nanos premaza in IGT suho cepljenje predpremaza

	Modified Lignosulfonate in PC	Untreated Lignosulfonate in PC	Reference
Precoat weight [g/m²]	10.4	9.9	9.6
IGT pick test [cm/s]	118	109	141

Table 2: Coat weight and IGT picking of precoatings
Preglednica 2: Nanos premaza in IGT suho cepljenje predpremaza

	Modified lignosulfonate in PC	Untreated lignosulfonate in PC	Reference
Offset suitability dry [passes to fail]	3	3	3
Offset suitability wet [passes to fail]	2	2	2,5
Ink setting after 30 s	0.38	0.48	0.36
Droplet test [%]	81.3	84.3	62.9
R457 +UV	83.23	81.7	92.38
R457 -UV	79.34	78.02	85.56

4 SUMMARY AND OUTLOOK

Ultrafiltrated and enzymatically polymerized lignosulfonates were applied as partial replacement of SB-latex in woodfree coated paper coating formulations. Lower penetration depth of lignosulfonate-based binder into the base paper was achieved by ultrafiltration and enzymatic polymerization of the spent liquor containing lignosulfonates. This also led to a significant improvement in water retention of the coating formulations containing lignosulfonates. The coated papers containing a lignosulfonate-based binder showed promising results regarding offset printability, which justifies further research.

As expected, brightness values are significantly below the reference and need to be improved. Therefore, trials to bleach the lignosulfonates are currently in progress with promising first results.

Enzymatically polymerized lignosulfonates might also be interesting in size press applications for packaging papers, where brightness is not an issue. First results in such applications have shown promising results.

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5 REFERENCES

Flory, A.R., Vicuna Requesens, D., Devaiah, S.P., Teoh, K.T., Mansfield, S.D., Hood, E.E. (2013). Development of a green binder system for paper products. BMC Biotechnology, 13 (28)

Gosselink, R.J.A., de Jong, E., Guran, B., Abächerli, A., (2004). Co-ordination network for lignin—standardisation, production and applications adapted to market requirements (EUROLIGNIN). Ind. Crops Prod, 20, 121–129.

Gosselink, R.J.A., Van Dam, J.E.G., De Jong, E., Scott, E.L., Sanders, J.P.M., Gellerstedt, G. (2010). Fractionation, analysis, and PCA modelling of properties of four technical lignins for prediction of their application potential in binders. Holzforschung, 64(2), 193-200.

Hofer, K., Seidl, B., Ortner, A., Nyanhongo, G.S., Winter, H., Kozich, M., Gübitz, G., Bauer, W. (2016). Serial Sectioning of Coated Paper as a Novel Method to analyze Binder Penetration, Paper Technology, 57 (1), 39 – 41.

Huber, D., Ortner, A., Daxbacher, A., Nyanhongo, G.S., Bauer, W. Guebitz, G. (2016). Influence of Oxygen and Mediators on Laccase-Catalyzed Polymerization of Lignosulfonate. ACS Sustainable Chemistry & Engineering 4 (10), 5303-5310

Imam, S.H., Bilbao-Sainz, C., Chiou, B-S., Glenn, G.M., Orts, W.J. (2013). Biobased adhesives, gums, emulsions, and binders: currrent trends and future prospects. Journal of Adhesion Science and Technology, 27(18-19), 1972 – 1997.

Nugroho Prasetyo, E., Kudanga, T., Steiner, W., Murkovic, M., Nyanhongo, G., Guebitz, G. (2009). Antioxidant activity assay based on laccase-generated radicals. Analytical and Bioanalytical Chemistry, 393(2), 679-687.

Ortner, A., Huber, D., Haske-Cornelius, O., Weber, H., Hofer, K., Bauer, W., Nyanhongo, G., Guebitz, G. (2015). Laccase mediated oxidation of industrial lignins: Is oxygen limiting? Process Biochem., 50(8).

Stewart, D. (2008). Lignin as a base material for materials applications: Chemistry, application and economics. Industrial Crops and Products, 27(2), 202 – 207.

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