

WOBAMA – WOOD BASED MATERIALS AND FUELS

MONICA EK, CHRISTINE CHIRAT,^{*} LINDA FOGELSTRÖM, TOMMY IVERSEN,^{**} DONGFANG LI,
EVA MALMSTRÖM, EMELIE NORSTRÖM, HERBERT SIXTA,^{***}
LIDIA TESTOVA,^{***} TERHI TOIVARI^{***} and DARIUSZ WAWRO^{****}

*Department of Fibre and Polymer Technology, KTH Royal Institute of Technology,
Teknikringen 56-58, 10044 Stockholm, Sweden*

^{}Grenoble INP-Pagora, Laboratory of Pulp and Paper Science and Graphic Arts, 461 rue de la Papeterie –
CS 10065, 38402 Saint-Martin d'Hères Cedex, France*

*^{**}Innventia AB, Drottning Kristinas väg 61, 11486 Stockholm, Sweden*

*^{***}Department of Forest Products Technology, Aalto University, P.O. Box 16300, Vuorimiehentie 1, 00076
Espoo, Finland*

*^{****}IBWCh Institute of Biopolymer and Chemical Fibres, ul. M. Skłodowskiej-Curie 19/27,
90570 Łódź, Poland*

✉ *Corresponding author: Monica Ek, monicaek@kth.se*

WOBAMA – Wood Based Materials and Fuels is a biorefinery oriented scientific research project supported by Wood Wisdom-Net Research Programme and ERA-NET Bioenergy. In this project, the wood based raw materials were converted to a range of value added products through unconventional techniques. So far, many demonstrators have been prepared, such as the dissolving pulps with high cellulose content, the regenerated cellulose films with high tenacity, the hydrophobic materials based on cellulose and birch bark suberin, as well as the adhesives based on polysaccharides.

Keywords: biorefinery, dissolving pulp, regenerated cellulose, hydrophobic material, adhesive

INTRODUCTION

WOBAMA – Wood Based Materials and Fuels is a biorefinery oriented scientific research project, financed by Wood Wisdom-Net Research Program and ERA-NET Bioenergy. The aim of WOBAMA is to converse wood based raw materials to a range of value added products, both

materials and fuels, using different conversion technologies, within the biorefinery concept.

Hitherto, this project has resulted in a series of demonstrators that were prepared through the newly developed processes in different work packages.

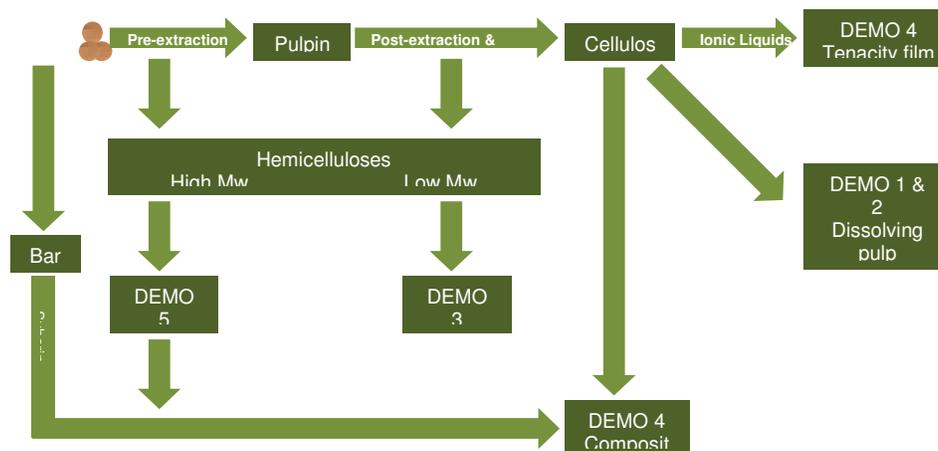


Figure 1: The WOBAMA project workflow

The entire workflow of WOBAMA is shown in Figure 1.

HIGH-PURITY CELLULOSE PULP MANUFACTURED BY HYDROTHERMOLYSIS FOLLOWED BY ALKALINE DELIGNIFICATION

Approximately half of the dissolving wood pulp is currently manufactured by the prehydrolysis-kraft (PHK) process. However, conventional application of aqueous-phase prehydrolysis, as opposed to its steam equivalent, has been limited due to the formation of sticky lignin precipitates. On the other hand, steam prehydrolysis does not allow the recovery of the hemicellulose-rich dissolved organic fraction. Here, a prehydrolysis by consecutive recirculation and percolation modes is seen as a process combining the advantages of both modes. The aim is to develop a novel method that would remove most of the pine wood hemicelluloses during the prehydrolysis in order to produce high purity dissolving pulp.

The prehydrolysis experiments are performed in a reactor that allows the modification of the liquid feed. First, a prehydrolysis in recirculation (batch) mode is performed at elevated temperature until side reactions start to take place. Second, subsequent percolation mode with a continuous fresh water feed is applied in order to maximize the removal of hemicelluloses while avoiding carbohydrate degradation and lignin recondensation. The reference prehydrolysis is performed by water recirculation only. Remaining hemicelluloses and lignin are removed during the following pulp production steps, kraft cook, oxygen delignification, and bleaching.

The effects of the prehydrolysis on wood composition were evaluated. The treatment with circulation mode only and the treatment with consecutive circulation and percolation of water have been studied at 170 and 200 °C. The results show that batch prehydrolyses of 10 min at 200°C and of 90 min at 170 °C result in similar removal of hemicelluloses; 52.0 and 50.5% of initial hemicelluloses, respectively, while cellulose is not notably affected.

Experiments with prehydrolysis treatment followed by a kraft cook were then carried out. The aim was to adjust the process conditions so that pulp with Kappa number around 20 and a high purity in cellulose would be produced. Prehydrolysis with consecutive circulation and percolation of water has been performed under

170 and 200 °C with different treatment times and liquid-to-wood ratios. The chosen prehydrolysis conditions for reference experiments (batch mode) were 90 min at 170°C, with liquid-to-wood ratio of 7.2:1. Kraft cooks have been performed at 160°C with effective alkali of 22%, sulfidity of 40% and liquor-to-wood ratio of 4:1. The main results of these experiments are summarized in Table 1.

The results show that with the studied method it is possible to produce pulp with Kappa number of about 20 and cellulose purity up to 95%. After kraft cooking, kappa number varies between 13 and 46 and the amount of cellulose in the samples between 92.0 and 95.3%. However, the pulp viscosities gained after the recirculation/percolation experiments are not on the requisite level of around 800 ml/g. The viscosities vary between 450 and 730 mL/g, while the viscosity of the reference sample is higher, 790 mL/g. The next steps of the study will focus on minimizing the viscosity loss after recirculation/percolation hydrolysis and kraft cook, especially with higher prehydrolysis temperatures. The experiments are continued with lower prehydrolysis intensity by shortening the treatment time. When the viscosities are adjusted to an acceptable level, the bleaching and acetylation experiments can be performed.

HIGH-PURITY CELLULOSE PULPS BY POST-EXTRACTION IN CAUSTIC-BORATE SOLUTION

Sodium borate ($\text{Na}_2\text{B}_4\text{O}_7$) has a potential of improving glucomannan (GGM) extraction from softwood pulps.¹ In the present study, pulps with the hemicelluloses content of 1% xylan and under 2% GGM were obtained after post-extraction (CCE+B) of bleached commercial pine kraft pulp under optimised conditions (NaOH 12 wt%, $\text{Na}_2\text{B}_4\text{O}_7$ 3 wt%, consistency 5% for 1 h at 30 °C). However, under highly alkaline extraction conditions the major concern for the acetate grade pulp production is the formation of cellulose II. Under the present conditions, 70% of cellulose I in the pulp was converted to cellulose II.

Enzymatic treatment prior to the CCE+B extraction was suggested as a potential measure to reduce the alkalinity of the extraction stage necessary to achieve similar final content of residual hemicelluloses. Xylanase treatment (X) was performed with the enzyme load of 2000 AXU/g pulp in the buffer solution of 11 mM NaH_2PO_4 + 9 mM Na_2HPO_4 at 70 °C and

consistency of 3% for 120 min. The implementation of enzymatic treatment before CCE+B enhanced extraction efficiency and the caustic concentration could be reduced to 10 wt% (Table 2). However, the further reduction of caustic concentration to 8 wt% resulted in a pulp with the residual content of xylan and GGM of 1.2 and 3.3%, respectively, which cannot comply with the typical acetate grade specification.

The pulp obtained after xylanase and CCE+B extraction at the caustic concentration of 10 wt% demonstrated promising performance in laboratory acetylation trials, but the content of cellulose II remained high (Table 2). Further attempts to improve the purity and reactivity of the pulps will continue by applying combined enzymatic treatment of xylanase and mannanase.

Table 1
Circulation or circulation/percolation prehydrolysis followed by a kraft cook

Sample	Reference	1	2	3
Prehydrolysis	Circulation	Consecutive circulation and percolation		
Temperature (°C)	170	170	200	200
Time (min)	90	60 and 30	10 and 5	15 and 15
Liquid:wood	7.2:1	7.2:1 and 45:1	7.2:1 and 8:1	7.2:1 and 22:1
Prehydrolysis yield (%)	81.7	77.9	74.1	69.3
Kraft cook	160 °C, EA 22%, sulfidity 40%, liquor:wood 4:1			
H-factor	1600	1800	1600	1550
Kraft yield (%)	42.4	44.6	42.1	43.2
Total yield (% on wood)	34.6	34.7	31.2	30.0
Kappa number	16	13	25	46
Viscosity (mL/g)	790	730	620	450
Cellulose (% of sample)	93.8	93.7	95.3	92.0
Glucomannan (% of sample)	1.0	1.6	0.0	0.3
Xylan (% of sample)	2.5	2.8	1.4	1.0
Lignin (% of sample)	2.7	1.8	3.3	6.7

Table 2
Properties of the acetate-grade pulp produced from commercial paper-grade bleached pine kraft pulp in comparison with two commercial sulphite acetate grade pulps (pine and spruce)

	Pulp			Acetate dope		
	Xylan (%)	GGM (%)	Cellulose II (%)	Molar mass (kg/mol)	Yellowness	Transmittance (%)
Pine	0.8	0.7	0	595	0.11	85
Spruce	1.8	1	0	475	0.14	81
X-CCE+B	0.6	1.9	63	540	0.27	65

EXTRACTION OF HEMICELLULOSES AND IMPACT ON SUBSEQUENT BLEACHING

Predrolysed kraft (PHK) cooking is one way to produce cellulose for viscose or textile applications. Several mills are converting, or have in project to convert, their kraft process into PHK. Little has been published on the bleaching ability of PHK pulps, and this study aims at comparing the oxygen bleaching ability of PHK and kraft pulps of softwood species.

Prehydrolysed softwood kraft pulps of high (50-55 and 70-78) and classical kappa numbers

(20-25) were prepared. Producing PHK of high kappa could be a way to improve the viscosity of the pulp, which can be interesting for high grade cellulose usages.

Single oxygen stages were applied with caustic soda charges varying from 2 to 4% on pulp. PHK pulps were delignified much more extensively than the corresponding control kraft pulps: a PHK pulp of kappa 25.6 could be delignified down to 3.5 kappa in a single O stage using 4% caustic soda. The final viscosity was 520 cm³/g. About the same delignification efficiency was obtained with the high kappa PHK

pulp; the 55.5 kappa number PHK pulp could be delignified down to 9.2 in a single O stage (83.4% delignification) with 4% caustic soda compared to 25.3 (50.3%) for the control kraft pulp (starting kappa number 50.9). The viscosity of this PHK O pulp was 650 cm³/g.

Table 3 gives the results for the 70-78 kappa number pulps. The 78.1 kappa number PHK pulp could be delignified down to 9.4 in two oxygen stages, to be compared to 23.5 for the control kraft pulp. With three oxygen stages the kappa number was 6.0 for the PHK OOO pulp. This very good reactivity of PHK pulps to oxygen delignification would thus enable to stop the cooking at higher kappa numbers, to save yield and viscosity.

In a previous study by Chirat *et al.*,² the lignins of the kraft and PHK unbleached pulps were analysed, and it was found that neither the molecular weight distribution of lignin, nor the number of free phenolic groups was significantly modified. A modification in the lignin-carbohydrates (LCC) linkages could be an explanation for the easiest oxygen delignification of the PHK pulps compared to the kraft ones. This point is currently studied in our research group at Grenoble INP-Pagora.

Direct P and Z stages were also applied to PHK and kraft pulps to see if the easiest oxygen delignification was verified with the other oxidants, and this was confirmed. The result also favours a modification in the amount of LCC bonds.

The sugar content of the different pulps was analysed after total hydrolysis of carbohydrates.

The xylose and mannose contents in the control 50.9 kappa number pulp were of 7.2% and 7.9%, respectively, whereas they were 2.0% and 1.4%, respectively, in the 55.5 kappa number PHK pulp. The 21.5 PHK pulp had slightly lower xylose and mannose contents (1.7 and 1.0). Hemicelluloses content is rather low and would be suitable at least for viscose applications.

CELLULOSE FUNCTIONALIZATION FOR HIGH-TENSILE STRENGTH FILMS

In recent years, research attempts have been made to harness ionic liquids (ILs) as cellulose solvents and to elaborate conditions to cast films from IL-cellulose solutions. It has been anticipated that ILs as cellulose solvents would offer the chance for an environment-friendly, safe-to-humans and low energy-consuming process. Good transparency and high tensile strength is expected from cellulose films cast from IL solutions.

The hydrothermal treatment enables a controlled reduction of the polymerization degree and improves cellulose properties: increases solubility in alkali, decreases polydispersity, and removes traces of lignin.³⁻⁵ The purpose of this work was to elaborate conditions to form cellulose films with the tenacity as high as 100 MPa from IL solutions.

PHK dissolving pulp after hydrothermal treatment was used to prepare the solution, characterized by a polymerization degree DP of 290-440 and low polydispersity. HT cellulose was used for IL solutions with a concentration of 10-16%.

Table 3
Two stage oxygen delignification of 70-78 kappa number kraft and PHK pulps

Pulping	Kraft	PHK
T (°C)	160	
NaOH/Na ₂ S/AQ	16.1/6.9	
Kappa number	70.3	78.1
Viscosity (mL/g)	1176	837
Oxygen bleaching (100 °C, 1 h, 5 bars O ₂ , 0.3% MgSO ₄ , 7H ₂ O)		
1 st stage oxygen delignification		
4% NaOH, kappa	31.0	17.8
4% NaOH, viscosity (mL/g)	908	673
2 nd stage oxygen delignification		
1.5% NaOH, kappa	23.5	9.4
1.5% NaOH, viscosity (mL/g)	894	616

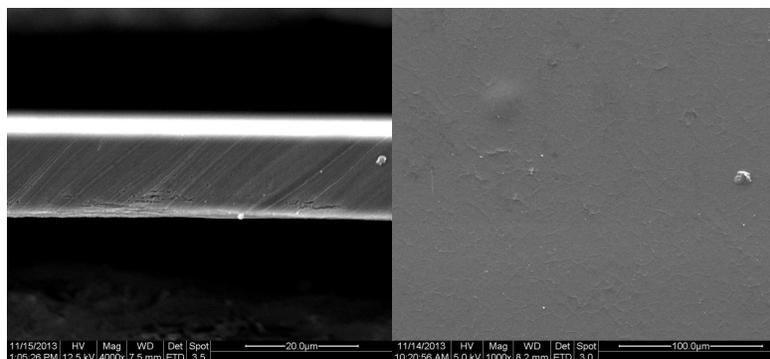


Figure 2: SEM images of cellulose films made from 16.0 wt% HT cellulose/IL solution (left: cross section;right: surface)

Table 4
Mechanical properties of cellulose films made from HT cellulose/IL solution

Type of solvent	DP of HT cellulose	Cellulose concentration in solutions (wt%)	Thickness (mm)	Tensile strength (MPa)	Elongation at maximum stress (%)
[EMIM]OAc [BMIM]OAc	255-440	10-16	0.024-0.060	90-126	25-60

The solutions were poured onto a heated glass surface and distributed by means of a collector device with a slot and then put into a regeneration bath consisting of ethanol/water (80/20 v/v). The films were then placed into a washing bath at a temperature of 20-90 °C. The films were kept for 24 h in distilled water at ambient temperature before being dried at 50 °C.

The cellulose films cast from the 16.0 wt% solution (Figure 2) were slightly stronger (tensile strength of 126 MPa) than the films from the 12.0 wt% solutions (tensile strength of 115 MPa) prepared under the same conditions (Table 4). This confirms the impact of the cellulose concentration on the films' mechanical properties. All films showed tensile strength values in the vicinity of 100 MPa, which is close to commercial cellophane. The elongation at the maximum stress of these films was 25-60%. The use of the HT treated wood cellulose having a DP of 325 did not cause a considerable drop of the tensile strength, in comparison with the films made from higher DP.

The change of the solvent to [BMIM][OAc] did not cause any change in the film morphology. The structure is comparable with that of the former film, and is also of high quality. The film surface is more even, which can be seen at higher magnification. The films were characterized by high transparency.

PREPARATION OF HYDROPHOBIC POLYESTER-CELLULOSE MATERIALS

Cellulose as the most naturally abundant polymer is widely used to prepare low density, low cost, and environmentally friendly materials with versatile functionalities. However, the hydrophilicity of cellulose is a crucial obstacle for some applications. Therefore, the interest in the hydrophobization of cellulose has driven increased attention. Generally, such a goal could be achieved by introducing hydrophobic structures onto the surface of cellulose fibers. However, in many processes, expensive, toxic, and petro-based chemicals are used.

Natural products, which are hydrophobic and renewable, such as suberin found in birch outer bark, could be "greener" alternatives. Suberin as a polymer consists of many monomers, and *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid (or epoxy acid) is the most abundant among them, amounting to approximately 100 g per kg of dried birch outer bark.⁶⁻⁸ The epoxy, hydroxyl, and carboxyl functional groups of the epoxy acid make it an interesting structure for polymerization and crosslinking.

In this study, the epoxy acid was isolated from birch outer bark, and polymerized through enzymatic catalysis, in order to keep the epoxy groups intact. The epoxy-activated polyester

wascured on the cellulose surface by dicarboxylic acids through compression molding. The prepared materials were hydrophobic, shown by the contact angle measurement. The possibility to use the side-stream products from forest industries for preparing functionalized materials was demonstrated. This is in line with the biorefinery concept.⁹

POLYSACCHARIDES FOR ADHESIVES

Wood adhesives are mainly prepared from petroleum-derived chemicals, which is a non-renewable and limited resource. Some wood adhesives also contain substances such as formaldehyde, which are harmful for the environment and human health. Therefore, research is being conducted to find bio-based alternatives to the fossil-based adhesives. In the pulp industry, large volumes of wood hemicelluloses are lost during the process to extract the cellulose. There is an urge to find new applications for all wood components from the

pulp industry; the biorefinery concept is of great interest, where all wood components are utilized. Within this work, hemicelluloses are studied for the potential of using them as binders in wood adhesives. It is important that the hemicelluloses adhesive should have the same properties as the commercial wood adhesives of today and should not cost more to enable the transition. A wood adhesive has to possess properties such as bond strength, water resistance and heat resistance. Several bio-based polymers have been suggested as binders for adhesive applications, such as protein, tannin, lignin and polysaccharides.¹⁰ However, the bio-based alternative often had insufficient properties, especially regarding water resistance, or was too expensive to be profitable in adhesive applications. Other alternatives must therefore be tested, for example hemicelluloses. It has been shown that it is difficult to get hold of wood hemicelluloses in larger amounts. Therefore, gums have been evaluated in a previous study in our group.¹¹

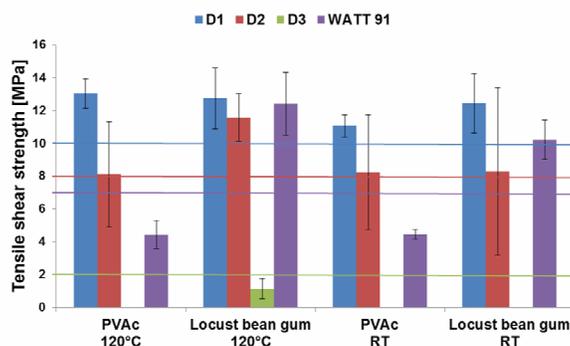


Figure 3: Tensile shear strengths of wood specimens bonded with PVAc and locust bean gum pressed at room temperature or 120 °C. The straight lines show the limits to pass as a D1, D2, D3 or WATT 91 wood adhesive

Table 5
Conditioning methods and tensile shear strength limits to pass the criteria of D1, D2, D3 and WATT 91 adhesives

Conditioning method	Tensile shear strength [MPa]	Durability classes
7 days in standard atmosphere	≥10	D1
7 days in standard atmosphere, 3 h in water at 20±5 °C, 7 days in standard atmosphere	≥8	D2
7 days in standard atmosphere, 4 days in water at 20 ± 5 °C	≥2	D3
7 days in standard atmosphere, 1 h in oven at 80 °C	≥7	WATT 91

Gums are polysaccharides with higher molecular weight compared to wood hemicelluloses and can be obtained for example from different plants. It was demonstrated that it is possible to disperse gums in water to give

dispersions with a proper viscosity, which can easily be applied on wood surfaces. A commercial polyvinyl acetate (PVAc) D2 wood adhesive, used for indoor applications, was chosen as a benchmark. By bonding wood panels together and

pressing them either at room temperature or 120 °C, wood specimens were prepared. The wood specimens were conditioned using different methods (Table 5) according to European Standards EN204 and EN14257.^{12,13} The tensile shear strength of each specimen was thereafter measured and the adhesives could be divided into different durability classes if they passed certain criteria (Table 5). Locust bean gum show remarkable results regarding bond strength, water resistance and heat resistance (Figure 3). It was possible to use the locust bean gum adhesive both at room temperature and at elevated temperatures, and in comparison with the PVAc wood adhesive, similar and even superior results were obtained. Locust bean gum shows surprisingly good results and can compete with the commercial PVAc wood adhesive.

ACKNOWLEDGEMENTS: We would like to express great thanks to Wood Wisdom-Net Research Programme and ERA-NET Bioenergy, Formas, Akzo Nobel, Andritz, Metsä Fibre, Organo Click, Solvay Rhodia, SP Processum and StoraEnso, for the financial support.

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