

Lignin-Containing PMDI-Binder for Wood Particle Board Production

Ivan Sumerskii¹, Pia Solt^{2,3}, Hendrikus W. G. van Herwijnen^{2,3}, Irina Sulaeva¹, Ters Thomas⁴, Thomas Rosenau¹, Antje Potthast¹

¹ Institute of Chemistry of Renewable Resources, Department of Chemistry, University of Natural Resources and Life Sciences (BOKU), Konrad-Lorenz-Strasse 24, A-3430 Tulln an der Donau, Austria.

E-mail: ivan.sumerskii@boku.ac.at

² Wood K plus - Competence Center of Wood Composites and Wood Chemistry, Kompetenzzentrum Holz GmbH, Altenberger Str. 69, A-4040, Linz, Austria

³ University of Natural Resources and Life Sciences, Vienna, Department of Material Science and Process Engineering, Institute of Wood Technology and Renewable Materials, Konrad-Lorenz-Strasse 20, 3430 Tulln an der Donau, Austria

⁴ Fritz Egger GmbH & Co. OG, Tiroler Str. 16, 3105, Unterradlberg, Austria

Abstract

Comprehensive testing of various routes of lignin pretreatments and the final adhesive preparation and performance allowed a better understanding of kraft lignin properties and margins within which this lignin can be utilized in the application with pMDI.

The prospects and properties of adhesive formulations prepared, such as homogeneity, viscosity, stability and mechanical properties are discussed in detail.

Introduction

Application of technical lignins, such as kraft, ligno-sulfonates, organosolv and other biorefinery lignins, in various adhesive systems to bind different wood composites has so far been among the most promising lignin utilization scenarios and at the same time one of the hardest challenges [1]–[3].

The pulp and paper industry is still the largest biorefinery branch and generates with the kraft process around 80% of the lignin theoretically available for material use. Prior to further application, lignin has to be isolated from the black liquor, which is produced as one of the intermediate product streams. Generally, the black liquor is burned to recover the cooking chemicals and to generate energy for the process. The recovery may be a bottleneck in the entire process, hindering further expansion of the pulp production. Hence, an increase in the capacity of the recovery

boilers incinerating black liquor can resolve such limitations to a certain extent. Another workaround, namely the isolation of kraft lignin from the black liquor, can significantly decrease the load on the recovery boiler, allowing to proportionally increase the production and potentially reach higher profit by implementing isolated lignin as a high value-added raw material in various applications. The latter, of course, depends on whether the isolated lignin can be sold, and this implies that there is a certain market for applications. High-tonnage scale and economically feasible kraft lignin isolation technology has lately become industrially available [4]. The range of companies, such as Valmet, Stora Enso (Lineo®), Domtar (BioChoice™), UPM (BioPiva™) or Suzano to name a few, offering lignin produced with LignoBoost™, LignoForce™ or SLRP™ technology at a ton scale is constantly expanding.

The application of lignin in different adhesive formulations allows achieving certain advantages, such as improving the thermal properties, modulus of elasticity and water resistance, as well as to achieve good bonding strength [5]. Lignin-containing materials would offer a higher portion of renewable materials in existing applications, although a full substitution of all adhesive components is currently not conceivable on industrial scale.

Usually, positive aspects often come at the expense of some negative side effects. For lignin in adhesives this is a curing rate reduction, an increase in viscosity of the adhesive, and a limited lignin solubility, to name but a few [6].

The physicochemical properties and reactivity of technical lignins is highly dependent on the source of the lignin, the process of its extraction from lignocellulosic biomass, i.e. pulping conditions, as well as further isolation and purification protocols. There is one particular reason why an effective utilization of technical lignins in industrial applications is still scarce [7], [8]. The rather broad molecular weight distribution, and the accompanying high dispersity of lignins with regard to functional group profiles are among the fundamental parameters which influence the lignins' behavior and final product performance [9].

Lignin depolymerization was proposed to improve lignin reactivity [8]. However, modern understanding of lignin applications, based on aspects of economical sustainability and viability, rather prefers maintaining the macromolecular nature of lignin. As an alternative to depolymerization methods, lignin fractionation by means of different approaches has been investigated [8], [9]. As already mentioned above, an essential parameter of lignin is its composition and content of functional groups. Because of a relatively high content of hydroxy ($-OH$) and carboxy ($-COOH$) groups, lignin usually has a higher affinity towards polar matrices (solvents or other polymers) and, therefore, usually possesses a limited compatibility with non-polar matrices, which generally lead to poor mechanical properties of the final composite and requires significant adjustment of process parameters, such as temperature, reaction time and others [10]. At the same time, the $-OH$ and $-COOH$ groups can readily be used as starting points for chemical modifications, such as: alkylation, esterification, acetylation etc., towards decreasing the lignin's hydrophilic character and, therefore, improving its incorporation into the required matrix [8]. However,

one should be aware, that masking those functional groups will inevitably also lead to the decrease of lignin reactivity in polymerization reactions, e.g., with diisocyanates.

To improve lignin reactivity, many other structure modification strategies, targeting different functions in aromatic or aliphatic moieties, have been proposed [6], [7]. Chemical modifications, such as: demethylation, methylation, phenolation and others, allowing generation of additional $-OH$ groups and/or unoccupied positions in aromatic rings, have been confirmed to have a positive impact on the lignin's reactivity with diisocyanates [7].

Undoubtedly, any additional lignin pretreatment predictably leads to the increase of process complexity and increase in costs. In order to improve the economic competitiveness and rationality of lignin modification in an effective utilization an integrated or concerted process is proposed. The simultaneous generation of vanillin and oxidized and degraded kraft lignin is an example of such an approach, which can further be applied in combination with polyurethane manufacture [11].

In general, the elaborated knowledge on lignin structure and reactivity, wide variety of approaches for its modification, new methods for fast and precise lignin characterization as well as testing of lignin-based composite materials, provide strong flexibility in future development of lignin utilization strategies [12].

Beside lignin properties and reactivity, the utilization of a proper crosslinking agent comprises another key factor influencing successful applications of lignin within adhesive formulations [7]. One of the most common crosslinkers is polymeric 4,4'-diphenylmethane diisocyanate (pMDI), which is already widely applied as a sole adhesive in wood panel industry in production of oriented strand board (OSB), and seldom in medium-density fiberboard (MDF) and highly specialized particle boards [5], [12]. pMDI represents a fast-curing, formaldehyde-free adhesive, providing quite high mechanical bonding at relatively low charge, and a high resistance against water [12]. The direct reaction of pMDI's isocyanate groups and lignin hydroxy groups, leading to the formation of urethane bonds, has been found to proceed comparatively slow. It is considered that pMDI applied as an adhesive also reacts with water constituent, present as a moisture in wood, being one of the most crucial parameters [13]–[15].

The selection of an appropriate lignin type is the key for lignin implementation into materials or substitution of oil-based chemicals. Unlike lignosulfonates, which global production and market availability are comparably limited, kraft lignin is currently the only type of technical lignin potentially available in large quantities. Its relative simplicity of isolation, possible high purity, decently strong interest of pulp and paper companies in lignin stream separation and utilization as well as a rather high abundance of kraft mills made this lignin type a good candidate for the present investigation. Though phenol in phenol-formaldehyde adhesives can be successfully substituted - at least partially - by kraft lignins, the corresponding binders still suffer from toxicity concerns. The alternative adhesive approach is cross-linking of the wood particles by polymeric diisocyanates (polymeric diphenylmethane diisocyanate – pMDI) [16]. The chemical, although toxic as the starting compound, forms unproblematic polymers. Although the overall amount of pMDI used relative to the wood particles ranges around 2%, it is still desirable to partially exchange pMDI with lignin [16].

The aim of this research was to elaborate a binder formulation, comprised predominantly of polymeric diphenylmethane diisocyanate (pMDI) and technical lignin, with a superior performance compared to current adhesives and to achieve an economically attractive decrease in the pMDI consumption in wood particle board production.

Experimental

Materials and chemicals

Indulin AT (MeadWestvaco, USA) lignin, as one commercially available kraft lignin, was selected as a reference lignin in this project, serving as a standard, well-characterized kraft lignin.[14]. In addition, a range of kraft lignins of various European mills have been applied as well (Lignin-A, B and low molecular weight (LMW) Lignin-A, B).

A solvent-free polymeric diphenylmethane diisocyanate (pMDI; ONGRONAT WO 2750) with average functionality of 2.7 and an NCO content of 30.0 – 32.0 wt% from BorsodChem Zrt. (Kazincbarcika, Hungary) was used. The viscosity of 220 ± 5 mPa·s was determined with a cone plate rheometer at 20 °C with a shear rate of 100 s^{-1} .

Propylene carbonate (PC), glycerol 1,2-carbonate (GC), polyethylene glycol 200 (PEG), poly(ethylene glycol) diglycidyl ether (PEGDGE), acetyl triethyl

citrate and other chemicals were of p.a. quality and were purchased from Sigma-Aldrich.

Analysis methods

Phosphorus-31 NMR experiments and sample preparation were done according to [17], [18]. The samples were dried in a vacuum oven prior to dissolution in the standard mixture of chloroform-*d* / pyridine-*d*₅ followed by derivatization step with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The NMR experiments were performed on a Bruker Avance II 400 (at 162 MHz for ³¹P) equipped with a 5 mm cryoprobe (Prodigy) with z-gradients at room temperature (standard Bruker pulse programs; Bruker, Rheinstetten, Germany). Data were collected with 64 k data points and apodized with an exponential window function ($lb = 5$) before Fourier transformation. A 0.6 s acquisition time and a relaxation delay of 15 s were used and 256 scans were collected. The content of hydroxyl groups was obtained by integration of the following spectral regions: internal standard (152.4-151.3 ppm), total aliphatic -OH (150.0-144.6 ppm), total phenolic -OH (144.6-137.0 ppm) and carboxylic acids (136.0-133.6 ppm).

Size-Exclusion Chromatography (SEC) was performed on a Dionex UltiMate 3000 system (Thermo Fisher Scientific, Germany), including degasser, autosampler, column oven, UV detector, and refractive index (RI) detector (Shodex RI-101) according to [19]. Dry lignin samples were dissolved in DMSO/LiBr (0.5%). Prior to SEC analysis, the solutions were filtered through a 0.45 μm PTFE syringe filter. Separation was performed on three Agilent PolarGel M columns (7.5 × 300 mm) with dimethyl sulfoxide (DMSO) containing LiBr (0.5% w/v) as the mobile phase. Columns were calibrated with polystyrene sulfonate standards of known molecular weight: $M_w = 1100, 1920, 3610, 6520, 14900, 29100, 63900, 148000 \text{ g}\cdot\text{mol}^{-1}$, $\bar{M}_n < 1.20$. The analysis parameters were: flow rate $0.5 \text{ mL}\cdot\text{min}^{-1}$; column temperature 40°C; injection volume 10 μL. Data evaluation was performed with Chromeleon software, version 6.80.

The differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) were carried out using NETZSCH STA 409 PG instrument in nitrogen atmosphere. The temperature range was 30–500°C, the heating rate $10^\circ\text{C}\cdot\text{min}^{-1}$, the purge gas velocity 25 ml·min⁻¹, and the sample weight 5-10 mg.

Oxyalkylation of lignin

Lignin (1.0 g; approx. 6 mmol -OH·g⁻¹) was dissolved in approx. 6 g of propylene carbonate (PC) or glycerol

carbonate (GC), and approx. 90 mg of K_2CO_3 were added. The mixture was allowed to react at 170°C and 140°C, in case of PC and GC, respectively, for 3 h under stirring in N_2 atmosphere. After the completion of the reaction, the mixture was cooled to room temperature and added to the 10-fold amount of deionized acidified (pH 2) water. The precipitated product was isolated and thoroughly washed with 5×50 ml water by means of centrifugation. The isolated product was first freeze-dried and finally dried in a vacuum oven at 40°C.

Alkylation

Methylation and isopropylation of hydroxy groups was done with the corresponding alkyl halides according to a procedure adopted from [20]. Complete or partial derivatization was achieved by using either a strong or a weak base catalyst, e.g. NaOH or K_2CO_3 . Lignin was dissolved in DMSO, finely ground basic catalyst and the corresponding alkyl halide were added (8h, RT). Ethylation of lignins was performed with diethyl sulfates according to [21]. A lignin sample was dissolved in acetone and 30% NaOH solution was slowly added with vigorous stirring. Dialkyl sulfate was added dropwise to the lignin solution. The temperature of the reaction medium was kept at around 20 °C. The mixing was continued for 16 hours. Acetone was partially evaporated on a rotary evaporator. Further isolation was the same for all alkylation experiments, i.e. the lignin solution was diluted with water 3-4 times and acidified with 1 M HCl solution to pH 2. The precipitated lignin was centrifuged off, thoroughly washed with excess deionized water until almost pH-neutral, and freeze-dried.

Acetylation

Isolated lignins were quantitatively acetylated by adding a mixture of freshly distilled acetic anhydride and dry pyridine (4.7:4.0 v/v, respectively) and stirring for 10 days at room temperature in the dark, according to [21].

Ultrafiltration

Sequential lignin ultrafiltration (U.F.) has been done according to [22] using a stirred ultrafiltration cell (Model 8200, 200 mL, Millipore Amicon). Regenerated cellulose (RC) membranes with polypropylene support from Millipore Corp. (USA) were used (thickness: 230 μ m, diameter: 63.5 mm). Three suitable membranes were selected, producing four lignin fractions, i.e.: >100, 100-30, 30-1 and <1 kDa.

Indulin lignin was dissolved in water at pH 12, which was adjusted with 1M NaOH. The ultrafiltration pro-

cess was started with the membrane having the highest cutoff, followed consecutively by filtration through membranes with decreasing cutoff. Each filtration step was stopped when the color of the permeate became almost colorless. Approximately two liters of water with pH 12 were used for automatic refilling of the cell containing the retentate, to ensure complete fractionation. The permeates were concentrated on a rotary evaporator at 40°C and used for the next step of fractionation. The retentates and the permeate remaining after the last step of fractionation were acidified to pH 2 with 1 M HCl. The precipitated lignin fractions were isolated by centrifugation, thoroughly washed with deionized water and lyophilized to a constant weight.

Bonding strength development tested on wood

To evaluate the bonding strength of the freshly cured adhesives, a self-constructed bonding strength tester was used, according to [12]. The adhesive formulations were tested on birch veneer with a thickness of 1.5 mm and an overlapping area of 10 x 34 mm. 114 $g \cdot m^{-2}$ adhesive were applied on the wood stripes and pressed at 120°C for 5 minutes. This test was used as a fast comparison of the bonding strength of different lignin/pMDI binder combinations. The homogeneity and applicability of the formulations were evaluated by visual inspection and microscopy.

Visual evaluation of resin mixtures

In addition to the macroscopic optical assessment of the adhesive mixtures, microscopic images were also taken for analysis. The evaluation was carried out using a light microscopy with software support (Olympus digital microscope DSX-1000, Olympus Hamburg, Germany). The images were taken from samples on object slides at 20x and 30x magnification using transmitted light.

Particle board production and testing

Particle boards with dimensions of 50x50x1.4 cm^3 were pressed in a laboratory press (G. Siempelkamp GmbH & CO. KG., Krefeld, Germany). The two-component adhesive was sprayed onto middle-layer particles with an air gun and then manually distributed into a pressing mold. After hot-pressing at 220°C using a press factor of 9.3 $s \cdot mm^{-1}$, the test boards were conditioned for 14 days at a standard climate (20°C and 65% relative humidity). The target density of the particleboards was 650 $g \cdot cm^{-3}$. The determination of internal bond strength perpendicular to the plane (IB) was done according to EN319 on a universal testing machine (Shimadzu Europe GmbH, Duisburg, Germany) [23].

Results and Discussion

The general requirements for the binder formulation in wood particle boards had to meet following requirements: a low viscosity (<1500 mPa·s), homogeneity, reasonably high content of lignin (at least 20–30% w/w), sufficiently long shelf life of the final formulation, no malodorous smell and cost-efficient preparation procedure. Integration of technical lignin into the existing pMDI adhesive system usually relies on several conditions, such as lignin reactivity, ability to form a homogeneous mixture or solution, stability of the chemical and physical properties and others. In order to meet the above mentioned requirements, different lignin modifications, such as alkylation, oxyalkylation and acetylation, were tested [1], [6]. To investigate the influence of the molecular weight of lignin, indulin was fractionated by ultrafiltration and the fractions prepared were partially alkylated and tested in several formulations. In addition, a high-speed homogenization approach was investigated. The tests were benchmarked against pure pMDI and also non-modified lignins.

Oxyalkylation

Technical lignins contain considerable amounts of aromatic and aliphatic hydroxyl groups, and can, therefore, be applied as a polyol in polyurethane formulations. However, direct application does not guarantee the desired behavior and acceptable adhesive performance. Therefore, it was suggested to modify lignin by means of an oxyalkylation reaction leading to the formation of so-called chain-extended hydroxyalkylated lignins [1]. This lignin modification uses a substitution of aromatic hydroxyls with an aliphatic chain carrying aliphatic hydroxyl groups. The latter are supposed to be more reactive in the reaction with pMDI than the original aromatic hydroxyls. Lignin oxyalkylation has already been confirmed to be effective in lignin-polyurethane synthesis [1].

The conventional approach to oxyalkylation involves a reaction with different alkylene oxides, such as propylene oxide [24], [25]. Necessary precautions upon handling the volatile, flammable, carcinogenic propylene oxide made this approach less attractive, especially considering an industrial perspective. However, recently it was proposed to substitute alkylene oxides with cyclic aromatic carbonates possessing low toxicity, high boiling point, biodegradability and other “green” chemical properties [26]–[28].

A range of lignin samples was oxyalkylated with propylene carbonate (PC) and glycerol 1,2-carbonate (GC) according to a procedure adopted from literature (Table 1 and 2, samples 1–9) [28]. The concept of this lignin modification for adhesive preparation was not just an increase of lignin reactivity, but also the simultaneous preparation of a more homogeneous liquid lignin polyol formulation.

Due to the formation of new OH groups, multi-oxyalkylation was reported to be a side reaction. The extent of this unwanted pathway strongly depends on the reaction conditions, i.e., catalyst, temperature, time etc. In practice, if the reaction conditions applied are not optimized for a specific lignin, not just an additional consumption of cyclic aromatic carbonate, but also a noticeable increase of the lignin’s molecular weight, which causes e.g., an undesired increase in viscosity, must be expected [29].

The analysis of the hydroxyl and carboxyl groups in the oxyalkylated samples was performed by means of ³¹P NMR [17], [18]. The comparison of the originally present hydroxy and carboxy groups with their content and composition after oxyalkylation confirmed complete substitution of aromatic hydroxy and carboxy groups and a doubling of the necessary aliphatic hydroxyls in all lignins investigated (Table 1). At the same time, a decrease in the total hydroxy groups content indicated a lignin polymerization reaction during oxyalkylation. This observation was confirmed by analysis of the molecular weight distribution (Table 2) [19], [30].

Targeting the increase in reactive aliphatic hydroxyl groups in lignin, also a set of experiments on oxyalkylation of lignin with glycerol carbonate was performed. Due to the additional hydroxy group present in glycerol carbonate, the alkyl chain introduced into the lignin eventually contains two aliphatic hydroxyl groups. As anticipated, the content of aliphatic hydroxy groups was approximately two times higher than upon oxyalkylation with propylene carbonate (Table 1, samples 3, 6 and 9). Significant increase (approximately four times) of the molar mass showed the extent of the undesired polymerisation, which appeared to be about two times larger than upon oxyalkylation with propylene carbonate (Table 2, samples 3, 6 and 9).

Thus, the efficiency of the oxyalkylation of lignin with propylene and glycerol carbonate was considered successful and quite promising for certain applications. The concept was modified in order to im-

Table 1: Content of hydroxyl and carboxyl groups (mmol·g⁻¹) in lignins before and after chemical modifications

Sample		Aliphatic -OH	Aromatic -OH	-COOH
(1)	Indulin	2.16	3.56	0.30
(2)	Indulin (PC)	3.88	0.00	0.00
(3)	Indulin (GC)	5.55	0.00	0.00
(4)	Lignin-A	2.14	4.19	0.60
(5)	Lignin-A (PC)	3.42	0.00	0.00
(6)	Lignin-A (GC)	8.45	0.00	0.00
(7)	Lignin-B	1.74	4.37	0.63
(8)	Lignin-B (PC)	3.64	0.00	0.00
(9)	Lignin-B (GC)	5.70	0.00	0.00
(10)	Indulin homogenized in (PC)	2.49	3.88	0.24
(11)	Indulin methylated	0.17	0.05	0.00
(12)	Indulin methylated partially	1.43	0.23	0.02
(13)	Indulin ethylated completely	0.22	0.12	0.36
(14)	Indulin ethylated partially 90%	0.26	0.27	0.33
(15)	Indulin ethylated partially 80%	0.47	0.54	0.36
(16)	Indulin ethylated partially 60%	0.82	1.28	0.35
(17)	Lignin-B ethylated completely	0.15	0.12	0.53
(18)	Indulin isopropylated	1.00	0.13	0.02
(19)	Lignin-B isopropylated	0.60	0.12	0.10
(20)	Indulin acetylated	0.08	0.23	0.43
(21)	Lignin-B acetylated	0.07	0.21	0.38
(22)	Indulin U.F. >100 kDa	1.93	2.95	0.54
(23)	Indulin >100 kDa methylated partially	1.55	0.22	0.03
(24)	Indulin U.F. 100-30 kDa	3.02	3.62	0.40
(25)	Indulin U.F. 100-30 kDa methylated partially	1.30	0.22	0.05
(26)	Indulin U.F. 30-1 kDa	1.95	3.61	0.84
(27)	Indulin U.F. 30-1 kDa methylated partially	1.24	0.28	0.06
(28)	Indulin U.F. <1 kDa	1.57	3.49	1.29
(29)	Indulin U.F. <1 kDa methylated partially	0.79	0.18	0.02
(30)	LMW lignin-A	1.34	4.44	0.81
(31)	LMW lignin-A methylated partially 85%	0.34	0.50	0.51
(32)	LMW lignin-A methylated partially 50%	0.68	2.23	0.52
(33)	LMW lignin-B	1.17	4.05	0.66
(34)	LMW lignin-B ethylated partially 11%	0.75	3.89	0.10

Table 2: Statistical moments of molar mass distribution of lignins before and after derivatization based on PSS calibration (note that all statistical moments are largely underestimated by this calibration).

Sample		Mn	Mp	Mw	Mz	Mw/Mn
(1)	Indulin	170	1000	3900	17800	22.9
(2)	Indulin PC	1100	2800	17150	108400	15.6
(3)	Indulin GC	1700	7400	20500	110200	12.1
(4)	Lignin-A	100	750	2700	14800	27.0
(5)	Lignin-A (PC)	950	2900	7400	29000	7.8
(6)	Lignin-A (GC)	1200	3400	14800	118800	12.3
(7)	Lignin-B	950	2100	5200	20300	5.5
(8)	Lignin-B (PC)	950	2500	8800	42000	9.3
(9)	Lignin-B (GC)	1500	3800	19000	127000	12.7
(22)	Indulin U.F. >100 kDa	1923	6000	13500	82590	7.0
(24)	Indulin U.F. 100-30 kDa	1772	2740	3530	6050	2.0
(26)	Indulin U.F. 30-1 kDa	735	1190	1410	2325	1.9
(28)	Indulin U.F. <1 kDa	270	315	500	940	1.9
(30)	LMW lignin-A	480	1215	2031	6586	4.2
(33)	LMW lignin-B	393	473	1300	8600	3.3

prove the overall economy by avoiding a very high demand of carbonates. In general, a low lignin dosage combined with additional costs for carbonates will not be economically successful.

Further experiments have shown that under the reaction conditions recommended in the literature, the only viable ratio between lignin and propylene or glycerol carbonate is 1:2. A higher content of lignin is not possible due to the very high viscosity of the resulting mixture.

The oxyalkylation of lignin and the behavior of carbonates at the selected ratio were additionally investigated by means of a simultaneous temperature analyzer (STA). In those experiments the oxyalkylation reaction conditions were accurately simulated. It was shown that oxyalkylation and/or condensation occur also without the commonly used K_2CO_3 catalyst, just being driven by external heating. Similar TG and DSC patterns were observed for PC and GC blank reactions, which have suggested that the self-condensation reaction of propylene and glycerol carbonates may occur even at moderate temperatures (100°C), especially in the presence of a catalyst.

Moreover, the presence of catalyst was found to play a crucial role with respect to the “pot life” of the final adhesive mixture. As it was observed, the presence of even minor amounts of catalyst in the final formula-

tion with pMDI dramatically increased the curing rate, leaving nearly no time slot for the resin to be applied.

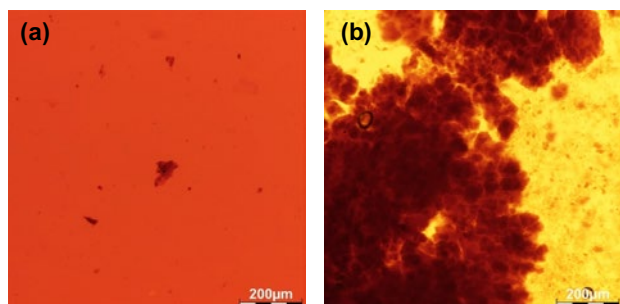
An attempt to run lignin oxyalkylation with propylene or glycerol carbonates without catalyst at a ratio 1:2 under otherwise identical conditions was tested. The products were isolated by precipitation in water and characterized by ^{31}P NMR (Table 1, sample 10). As anticipated, the content of lignin hydroxy groups has almost not increased, which indicated that lignin has experienced homogenization rather than the desired chemical modification. Meanwhile, based on STA experiments, the carbonates underwent self-condensation to certain degree, which eventually noticeably increased the viscosity of the polyol prepared.

Lignin Homogenization

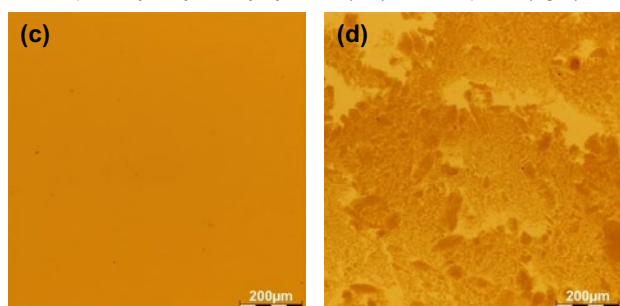
Application of a solvent is highly important not just for lignin homogenization, but also for the regulation of the viscosity of the final adhesive. At the same time, the selected solvent should not react with lignin or pMDI at ambient conditions before the adhesive is applied.

Experiments have shown that lignins can be successfully homogenized in various solvents, such as PC, GC, PEG and PEGDGE, even without application of long-term heating and mixing (Figure 1). Moreover,

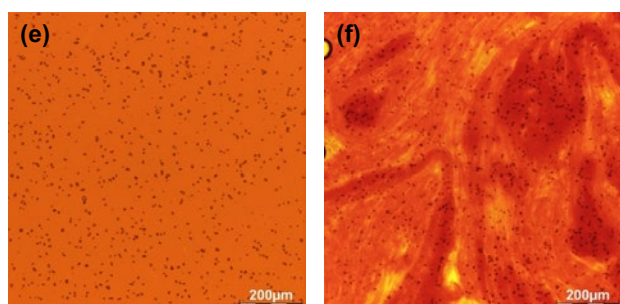
Indulin (1) in PC (left) and PC/pMDI (right)



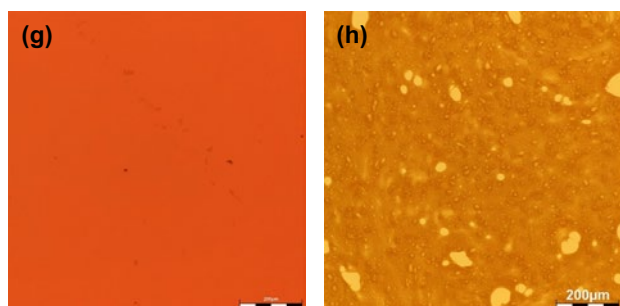
Indulin partially ethylated (15) in PC (left) and PC/pMDI (right)



LMW lignin-B (33) in PC (left) and PC/pMDI (right)



LMW lignin-B partially ethylated (34) in PC (left) and PC/pMDI (right)



LMW lignin-B (33) in pMDI (left) and LMW lignin-B partially ethylated (34) in pMDI (right)

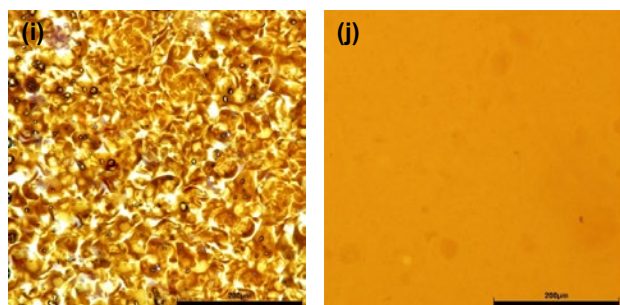


Figure 1: Microscopic pictures of lignin samples being homogenized in the PC, PC/pMDI and pMDI.

those solvents may additionally act as crosslinkers upon adhesive curing. However, not all of these solvents were found to be suitable for the preparation of pMDI formulations. For example, PEGDGE, being a very good solvent for kraft lignin, could not at all provide a stable homogeneous adhesive when lignin-PEGDGE was mixed with pMDI.

Lignin polyols were prepared by homogenizing lignins in a corresponding solvent at a 1:2 ratio, and then the lignin polyols were intensively mixed with pMDI at a 1:1 ratio and immediately the bonding strength after hot pressing was tested with bonding strength tester. Taking into account that the tensile shear strength of pMDI binders depends significantly on the press temperature and the moisture content of the veneers, those two parameters were strictly controlled at the optimized levels [13].

Though all tests showed fairly high tensile shear strength compared to just pMDI applied as sole adhesive, e.g., reaching 5.7 and 3.8 N·mm⁻² in case of PC and GC, respectively, they also revealed that lignin polyol – pMDI formulations had a rather low shelf life and tended to react and re-slurry after short standing (Figure 1, a and b). This phenomenon negatively influenced the overall adhesive performance, bringing it to a state of unacceptably high viscosity, which to some extent would render the adhesive inapplicable in wood particle board production. Thus, it was concluded that the lignin polyol-pMDI adhesives required fundamental optimisation of the proportions, utilization of some viscosity reducers or application of specifically selected or chemically modified lignins.

Complete and Partial Alkylation of Lignin

It is known that lignins have amphiphilic properties mainly due to the more hydrophobic aromatic and aliphatic skeleton on the one side and numerous hydrophilic hydroxy, carboxy and other functional groups on the other side. It was necessary to investigate the level of influence of hydrophilic groups on adhesive preparation and behaviour. For this purpose, a hydrophobization of lignin by alkylation and acetylation was performed. It was expected that such modifications would not just improve lignin homogeneity in pMDI, but at the same time might increase lignin

reactivity due to its better dissolution and thus accessibility. Thus, lignin samples were modified by means of complete and partial alkylation with dimethyl, diethyl and diisopropyl sulfates (Table 1, samples 11-19) [21], [25], [31]. The degree of alkylation was controlled by the amount of the derivatizing agent and implementation of basic auxiliaries, NaOH and K_2CO_3 . While NaOH allowed for complete -OH and -COOH group derivatization due to its high basicity, K_2CO_3 as a much weaker base permitted alkylation only at the more acidic aromatic hydroxy and carboxy groups.

In order to investigate if the alkyl chain length and branching have some influence on the lignin solubility, suspendability and eventually reactivity, a set of reactions with diethyl and isopropyl alkylating agents was carried out to obtain ethylated and isopropylated lignins, respectively (Table 1, samples 13-19).

Lignin modification by acetylation with acetic anhydride was selected as an alternative to methylation, providing completely derivatized hydroxy groups and improved lignin solubility in non-polar solvents (Table 1, samples 20-21) [32]. Acetylation was further used to confirm the blocking of hydroxyl groups and thus improvement of hydrophobic interactions in the pMDI system.

Both complete and partial lignin alkylation as well as acetylation made the lignins noticeably more suspendable and miscible in polyols, such as PC and GC, which allowed a significant reduction of the PC portion (Figure 1, c, d, g, h and j). Moreover, it was observed that already the partially alkylated lignins start to completely dissolve in just pMDI at quite high proportions (Figure 1, j). Completely ethylated and partially isopropylated lignins required some short-term, moderate heating (e.g. 50°C) to facilitate dissolution in pMDI.

Based on previous experiments, PC was chosen for lignin homogenization as the cheapest and most available reagent on an industrial scale. Modified lignin: PC polyols were prepared first in ratios of 1:2 or 1:1 and then mixed with pMDI in proportions of 1:1 or 3:1, which resulted in 20, 25 and approximately 37% of lignin in the final formulations ((lignin:PC):pMDI = (1:2):3, (1:2):1 and (1:1):2, (1:1):0.67), based on dry mass. The performance of the adhesives prepared was evaluated by means of tensile shear strength. Nearly all adhesive systems tested demonstrated significantly better performance compared to just neat pMDI. The performance of the partially

ethylated lignin similar or even slightly better than that of completely methylated lignin. The decrease of PC considerably raised the viscosity of the adhesives, but did not influence the strength of the binder as much as the amount of pMDI. The average tensile shear strength was approx. 7.8 and dropped by about 25% down to 5.9 $N \cdot mm^{-2}$, when pMDI was reduced two times.

The performance of the adhesives containing ethylated lignins was quite similar to that with methylated lignins. It was confirmed that the partially ethylated lignins formed homogeneous and stable adhesive mixtures which had a relatively low viscosity, on average ~ 1200 mPa·s, and therefore they were much more convenient to be applied on the wood surface. The tensile shear strength of the freshly cured adhesive with (lignin:PC):pMDI ratio (1:1):2 clearly demonstrated that approximately 60% masking of the hydroxy groups is already sufficient to form a homogeneous formulation providing even higher tensile shear strength than that obtained with completely ethylated lignin (Table 1, Figure 2).

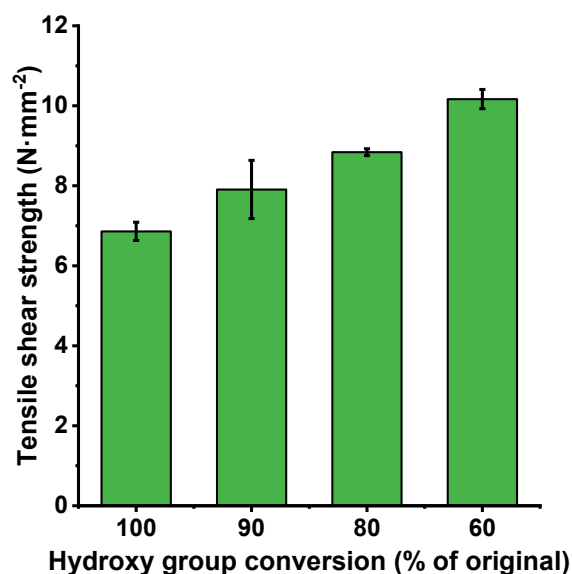


Figure 2: Evaluation and comparison of adhesive performance containing perethylated and partially ethylated Indulin with (lignin:PC):pMDI ratio (1:1):2

Compared to methylated and acetylated samples, the isopropylated lignin – PC – pMDI formulations obtained (at the same ratios used with other lignins) showed a comparably low viscosity, on average approx. 600 mPa·s. The tensile shear strength was quite similar for all lignins and similar to that obtained with methylated and ethylated lignins.

As anticipated, lignin acetylation, which allowed complete derivatization of all hydroxy groups, confirmed the positive effect of hydrophobization. All adhesive systems containing acetylated lignins with (lignin:PC):pMDI ratio (1:1):2 showed a very good lignin homogenization capability and formation of stable formulations in PC and pMDI with comparably moderate viscosity (1300 mPa·s), similar to that obtained with ethylated lignins. A subsequent testing of the tensile shear strength demonstrated high strength values for all adhesives, which in average reached 7.4 N·mm⁻² at 100% wood failure.

Though alkylation and acetylation of lignin as pre-treatment steps prior to adhesive preparation cannot be applied in a large-scale production due to the high price of reagents and a possible malodorous smell of the product, they unambiguously indicated the positive effect of the modification of hydroxyl groups on the viscosity of the pMDI adhesive system.

Fractionation of Lignin

One of the most crucial lignin characteristics that influences solubility and reactivity is the molar mass and its distribution. In order to verify the influence of lignin molecular weight on its homogenization in a solvent and further in pMDI, and to estimate the efficiency of the corresponding adhesive, several lignin fractions out of Indulin with relatively narrow molar mass distributions were prepared.

There are several techniques available for lignin fractionation [22], [33]–[35]. Ultrafiltration through a membrane of known cut-off can be considered as one of the most powerful and straightforward methods. The average yields of fractions >100, 100-30, 30-1 and <1 kDa determined in two parallel experiments were 43.2, 22.6, 12.7 and 5.7% of dry mass of starting Indulin sample, respectively.

Size-exclusion chromatography of the fractions confirmed an efficient fractionation and a narrow molar mass distribution (Table 1 and 2, samples 22, 24, 26 and 28) [19], [30]. As anticipated, the determined molecular weight distribution of the lignin fractions did not perfectly correspond to the molecular weight cut-off of ultrafiltration membranes applied, however, a strong correlation was evident [22]. Also, as expected, the content of hydroxyl groups changed depending on the change in molecular weight (Table 1 and 2) [22]. This was especially evident in the case of the fraction smaller than 1 kDa. The lignin fractions obtained were further tested in various formulations with pMDI.

A set of lignin fractions prepared was additionally modified by means of partial methylation as described before. Analysis of functional groups confirmed a nearly complete methylation of aromatic hydroxyl and carboxyl groups and approximately 25-50% (depending on the molecular weight of the fraction) of aliphatic hydroxyl groups (Table 1, samples 23, 25, 27 and 29).

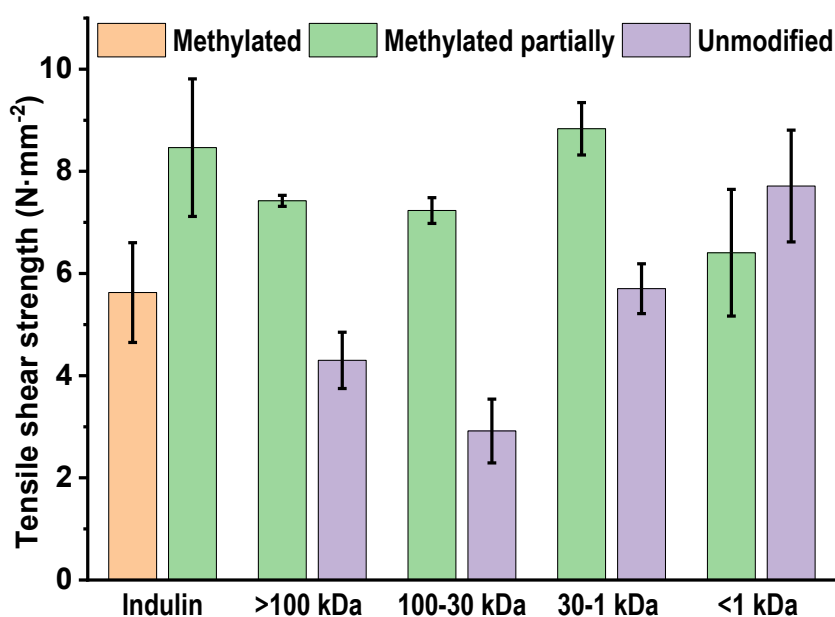


Figure 3: Tensile shear strength determined for methylated and partially methylated unfractionated Indulin (ratio of (lignin:PC):pMDI (1:1):1), its fractions and partially alkylated fractions

Indulin lignin fractions prepared directly after ultra-filtration and those after partial methylation were homogenized in PC at the ratio of 1:1 and then mixed with pMDI at the ratio of 1:1 (viz. lignin polyol: pMDI).

Good homogeneity in PC and then in pMDI was observed only in case of low molecular weight fractions below 1 kDa and 1-30 kDa, especially after partial methylation. All other fractions, when dissolved in PC, aggregated after pMDI addition, leading to phase separation and difficulties in applying them to the wood surface. Such behavior can be explained by the strong influence of lignin molecular weight on its solubility and insufficient dosage of the semi-polar PC solvent in the mixture. Nevertheless, it was possible to apply each adhesive formulation on wood to perform tensile shear strength test for bonding strength comparison (Figure 3). The tensile shear strength results showed very high values for the Indulin reference. However, it must be emphasized that applying the reference formulation to a wooden surface resulted in a non-homogeneous, clumpy surface, which makes industrial implementation practically impossible with general equipment used currently in particle board production. Only with the partially methylated lignin, a uniform application of the lignin-pMDI resin became possible and satisfactory strength values were achieved.

The low-molecular weight lignin fractions after partial methylation showed the best performance in the binder. The results for partially methylated lignin represent a significant improvement of adhesive formulation performances. This effect was much larger for the high molar mass fractions.

However, it was quite important to further corroborate

the effect of complete or partial alkylation of lignin and the influence of molar mass on real industrial lignin samples. Various technical lignin samples supplied from different pulp mills were screened to match the desired low molecular weight. LMW lignin-A (30) had a weight-average molecular weight of approximately 2000 g·mol⁻¹ (Table 2). A good miscibility in PC and then in pMDI was observed after partial ethylation (85 and 50% hydroxy group conversion), offering adhesive formulations with reasonably low viscosity of 1400 mPa·s. The strength test demonstrated that both adhesives provided high tensile shear strength of up to 7.7 N·mm⁻² with 100% wood failure and confirmed that for such LMW lignin-A already 50% of hydroxy group derivatization was sufficient to achieve adhesive with good performance.

Particle Board Pressing and Testing

Though ethylation of lignin with diethyl sulphate might be considered less attractive as a pre-treatment step prior to adhesive preparation in the light of modern biorefinery and “green chemistry” approaches, it was highly important to evaluate the influence of the lignin alkylation degree on the lignin-PC-pMDI adhesive performance, to be tested by the most realistic method, i.e., particle board pressing itself.

Experiments on modified lignins homogenization in PC and then in pMDI at previously optimized ratios clearly demonstrated that complete alkylation was not required and that in the case of implementation of LMW lignin it was possible to achieve a good compromise between lignin molecular weight and its hydrophobicity, sufficient to allow preparation of a homogeneous and stable adhesive formulation. Additional technical lignin screening allowed finding

Table 3: Formulation tested and particle board characteristics

Formulation		Ratio	Adhesive amount	pMDI amount	Average board density	Average internal bond strength
			% w/w on dry wood	% w/w on dry wood	kg·m ⁻³	N·mm ⁻²
pMDI Reference (1)		-	4	2	621	0.51
pMDI Reference (2)		-	2	4	626	0.39
(a)	pMDI:PC	3:1	4	3	659	0.66
(b)	pMDI:PC	1:1	4	2	682	0.57
(c)	pMDI:PC:Indulin partially ethylated	1:1:1	4	1.3	629	0.52
(d)	pMDI:PC:LMW lignin-B ethylated (partially 11%)	1:1:1	4	1.3	650	0.50

a sample LMW lignin-B (33) with even smaller molecular weight compared to the one (30) discussed above (Table 2). Thus, two lignin samples were prepared, a partially ethylated Indulin (15) and LMW lignin-B (34) with 80 and 11% hydroxyl group masking, respectively (Table 1, Figure 1, c, d, g and h). The effect of implementation of PC without lignin in the formulation was investigated (Table 3). All boards prepared surpassed the required strength criterion for P2 class boards (furniture and interior design in dry conditions). A two-fold decrease of applied pMDI reduced the bonding strength by 20% (Table 3). At the same time, it was observed that addition of even small portions of propylene carbonate increased adhesive bonding strength significantly. Though bonding strengths of adhesives containing lignins were somewhat lower compared to pMDI-PC formulations, it was possible to achieve a significant reduction of pMDI and PC (Table 3).

Conclusions

Our study has demonstrated a strong interconnection between lignin properties and the final pMDI adhesive formulation. It was shown that not every technical lignin would be appropriate in such an application. A wide range of technical lignin specimens was prepared and examined, and various chemical modifications, namely fractionation, oxypropylation, acetylation, methylation, ethylation and *iso*-propylation were evaluated. Obviously, not all common concepts discussed in the literature, regarding what the best properties of lignin applied in polyurethane formulations should be, were applicable.

Lignin oxyalkylation usually is intended to improve lignin reactivity towards isocyanate groups present, in particular in pMDI. However, our tests showed that this approach has the least attractiveness and application prospects in particle board production.

A more viable approach for a considerable reduction of pMDI in the particle board production has been proposed: utilization of technical kraft lignin and application of a cyclic carbonate, in particular propylene carbonate, as a solvent, diluter and reagent at the same time. A preferably low-molecular weight isolated kraft lignin can be easily dissolved in an equal amount of carbonate and then homogenized in pMDI. The formulations prepared for use as a binder in particle boards have shown superior properties and allowed noticeable reduction of pMDI consumption.

Another crucial issue studied within this research, which dramatically influences the overall adhesive performance, was the ratio of components and the way the adhesive system was prepared. Mechanical homogenization is a good alternative to the chemical pre-treatment of lignin and, in combination with the use of certain diluents, can provide formulations of acceptable viscosity.

Tensile shear strength tests and orientation experiments provided first insights how to utilize lignin in its genuine form in pMDI formulations. The decrease of pMDI demand while improving the bonding strength was confirmed to be possible, although with the need to use a solvent, such as propylene carbonate, to achieve the desirable homogeneity and improved viscosity. The results allowed a better grasp of ideas regarding what lignin characteristics should look like and which issues would be critical upon adhesive preparation.

Acknowledgement

The authors are grateful for the generous financial support by Fritz Egger GmbH & Co. OG. Markus Bacher is greatly acknowledged for ³¹P NMR analyses of lignins.

References

- [1] C. Xu and F. Ferdosian, 'Lignin-Based Polyurethane (PU) Resins and Foams', in *Conversion of Lignin into Bio-Based Chemicals and Materials*, Berlin, Heidelberg: Springer Berlin Heidelberg, 2017, pp. 133–156. doi: 10.1007/978-3-662-54959-9_8.
- [2] A. Vishtal and A. Kraslawski, 'Challenges in industrial applications of technical lignins', *BioRes*, vol. 6, no. 3, pp. 3547–3568, Jun. 2011, doi: 10.15376/biores.6.3.3547-3568.
- [3] M. Alinejad *et al.*, 'Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives', *Polymers*, vol. 11, no. 7, p. 1202, Jul. 2019, doi: 10.3390/polym11071202.
- [4] P. Tomani, P. Axegård, N. Berglin, A. Lovell, and D. Nordgren, 'Integration of lignin removal into a kraft pulp mill and use of lignin as a biofuel', *Cellulose Chemistry and Technology*, vol. 45, no. 7–8, pp. 533–540, 2011.
- [5] F. Ferdosian, Z. Pan, G. Gao, and B. Zhao, 'Bio-based adhesives and evaluation for wood com-

- posites application', *Polymers*, vol. 9, no. 2, p. 70, 2017.
- [6] V. K. Thakur, M. K. Thakur, P. Raghavan, and M. R. Kessler, 'Progress in Green Polymer Composites from Lignin for Multifunctional Applications: A Review', *ACS Sustainable Chem. Eng.*, vol. 2, no. 5, pp. 1072–1092, May 2014, doi: 10.1021/sc500087z.
- [7] A. F. Ang, Z. Ashaari, S. H. Lee, P. Md Tahir, and R. Halis, 'Lignin-based copolymer adhesives for composite wood panels – A review', *International Journal of Adhesion and Adhesives*, vol. 95, p. 102408, Dec. 2019, doi: 10.1016/j.ijadhadh.2019.102408.
- [8] S. Laurichesse and L. Avérous, 'Chemical modification of lignins: Towards biobased polymers', *Progress in Polymer Science*, vol. 39, no. 7, pp. 1266–1290, Jul. 2014, doi: 10.1016/j.progpolymsci.2013.11.004.
- [9] P. Solt, A.-S. Jääskeläinen, P. Lingenfelter, J. Konnerth, and H. W. G. van Herwijnen, 'Impact of Molecular Weight of Kraft Lignin on Adhesive Performance of Lignin-Based Phenol-Formaldehyde Resins*', *Forest Products Journal*, vol. 68, no. 4, pp. 365–371, Jan. 2018, doi: 10.13073/FPJ-D-17-00079.
- [10] P. Buono, A. Duval, P. Verge, L. Averous, and Y. Habibi, 'New Insights on the Chemical Modification of Lignin: Acetylation versus Silylation', *ACS Sustainable Chem. Eng.*, vol. 4, no. 10, pp. 5212–5222, Oct. 2016, doi: 10.1021/acssuschemeng.6b00903.
- [11] E. A. B. da Silva *et al.*, 'An integrated process to produce vanillin and lignin-based polyurethanes from Kraft lignin', *Chemical Engineering Research and Design*, vol. 87, no. 9, pp. 1276–1292, Sep. 2009, doi: 10.1016/j.cherd.2009.05.008.
- [12] P. Solt, S. Libowitzky, H. W. G. van Herwijnen, and J. Konnerth, 'Improved method for analyzing cohesive strength development of pMDI', *Wood Sci Technol*, vol. 54, no. 1, pp. 7–17, Jan. 2020, doi: 10.1007/s00226-019-01143-7.
- [13] G. He and N. Yan, 'Effect of moisture content on curing kinetics of pMDI resin and wood mixtures', *International Journal of Adhesion and Adhesives*, vol. 25, no. 5, pp. 450–455, Oct. 2005, doi: 10.1016/j.ijadhadh.2004.12.002.
- [14] D. J. Yelle, J. Ralph, and C. R. Frihart, 'Delineating pMDI model reactions with loblolly pine via solution-state NMR spectroscopy. Part 1. Catalyzed reactions with wood models and wood polymers', *Holzforschung*, vol. 65, no. 2, Mar. 2011, doi: 10.1515/hf.2011.028.
- [15] D. J. Yelle, J. Ralph, and C. R. Frihart, 'Delineating pMDI model reactions with loblolly pine via solution-state NMR spectroscopy. Part 2. Non-catalyzed reactions with the wood cell wall', *Holzforschung*, vol. 65, no. 2, Mar. 2011, doi: 10.1515/hf.2011.029.
- [16] P. Solt *et al.*, 'Technological performance of formaldehyde-free adhesive alternatives for particleboard industry', *International Journal of Adhesion and Adhesives*, vol. 94, pp. 99–131, Oct. 2019, doi: 10.1016/j.ijadhadh.2019.04.007.
- [17] P. Korntner, I. Summerskii, M. Bacher, T. Rosenau, and A. Potthast, 'Characterization of technical lignins by NMR spectroscopy: optimization of functional group analysis by ^{31}P NMR spectroscopy', *Holzforschung*, vol. 69, no. 6, pp. 807–814, Aug. 2015, doi: 10.1515/hf-2014-0281.
- [18] G. K. Wurzer *et al.*, 'A general solvent system for the analysis of lignosulfonates by ^{31}P NMR', *Anal. Methods*, vol. 13, no. 45, pp. 5502–5508, 2021, doi: 10.1039/D1AY01241J.
- [19] G. Zinovyev *et al.*, 'Getting Closer to Absolute Molar Masses of Technical Lignins', *ChemSusChem*, vol. 11, no. 18, pp. 3259–3268, Sep. 2018, doi: 10.1002/cssc.201801177.
- [20] I. Ciucanu and C. E. Costello, 'Elimination of Oxidative Degradation during the per-O-Methylation of Carbohydrates', *J. Am. Chem. Soc.*, vol. 125, no. 52, pp. 16213–16219, Dec. 2003, doi: 10.1021/ja035660t.
- [21] G. F. Zakis, *Functional analysis of lignins and their derivatives*. Atlanta, Ga: TAPPI Press, 1994.
- [22] G. Zinovyev, I. Summerskii, P. Korntner, I. Sulaeva, T. Rosenau, and A. Potthast, 'Molar mass-dependent profiles of functional groups and carbohydrates in kraft lignin', *Journal of Wood Chemistry and Technology*, vol. 37, no. 3, pp. 171–183, May 2017, doi: 10.1080/02773813.2016.1253103.
- [23] EN 319, 'Particle boards and fibre boards - determination of tensile strength perpendicular to the plane of the board.', European Committee for Standardisation, Brussels, 1993.
- [24] C. A. Cateto, M. F. Barreiro, A. E. Rodrigues, and M. N. Belgacem, 'Optimization Study of Lignin Oxypropylation in View of the Preparation of Polyurethane Rigid Foams', *Ind. Eng. Chem. Res.*, vol. 48, no. 5, pp. 2583–2589, Mar. 2009, doi: 10.1021/ie801251r.
- [25] H. Sadeghifar, C. Cui, and D. S. Argyropoulos, 'Toward Thermoplastic Lignin Polymers. Part 1. Selective Masking of Phenolic Hydroxyl Groups in Kraft Lignins via Methylation and Oxypropyl-

- ation Chemistries’, *Ind. Eng. Chem. Res.*, vol. 51, no. 51, pp. 16713–16720, Dec. 2012, doi: 10.1021/ie301848j.
- [26] I. Kühnel, B. Saake, and R. Lehnen, ‘Oxyalkylation of lignin with propylene carbonate: Influence of reaction parameters on the ensuing bio-based polyols’, *Industrial Crops and Products*, vol. 101, pp. 75–83, Jul. 2017, doi: 10.1016/j.indcrop.2017.03.002.
- [27] I. Kühnel, B. Saake, and R. Lehnen, ‘Comparison of different cyclic organic carbonates in the oxyalkylation of various types of lignin’, *Reactive and Functional Polymers*, vol. 120, pp. 83–91, Nov. 2017, doi: 10.1016/j.reactfunctpolym.2017.09.011.
- [28] I. Kühnel, J. Podschun, B. Saake, and R. Lehnen, ‘Synthesis of lignin polyols via oxyalkylation with propylene carbonate’, *Holzforschung*, vol. 69, no. 5, pp. 531–538, Jul. 2015, doi: 10.1515/hf-2014-0068.
- [29] F. R. Vieira, A. Barros-Timmons, D. V. Evtuguin, and P. C. O. R. Pinto, ‘Oxyalkylation of Ligno-boost™ Kraft Lignin with Propylene Carbonate: Design of Experiments towards Synthesis Optimization’, *Materials*, vol. 15, no. 5, p. 1925, Mar. 2022, doi: 10.3390/ma15051925.
- [30] I. Sulaeva, G. Zinovyev, J.-M. Plankeele, I. Sumerskii, T. Rosenau, and A. Potthast, ‘Fast Track to Molar-Mass Distributions of Technical Lignins’, *ChemSusChem*, vol. 10, no. 3, pp. 629–635, Feb. 2017, doi: 10.1002/cssc.201601517.
- [31] M. Selva and A. Perosa, ‘Green chemistry metrics: a comparative evaluation of dimethyl carbonate, methyl iodide, dimethyl sulfate and methanol as methylating agents’, *Green Chem.*, vol. 10, no. 4, p. 457, 2008, doi: 10.1039/b713985c.
- [32] K. Lundquist, ‘Proton (1H) NMR Spectroscopy’, in *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 1992, pp. 242–249. doi: 10.1007/978-3-642-74065-7_17.
- [33] S. Y. Lin and C. W. Dence, Eds., *Methods in lignin chemistry*. Berlin Heidelberg: Springer, 1992.
- [34] J. S. Rodrigues, V. Lima, L. C. P. Araújo, and V. R. Botaro, ‘Lignin Fractionation Methods: Can Lignin Fractions Be Separated in a True Industrial Process?’, *Ind. Eng. Chem. Res.*, vol. 60, no. 30, pp. 10863–10881, Aug. 2021, doi: 10.1021/acs.iecr.1c01704.
- [35] H. Sadeghifar and A. Ragauskas, ‘Perspective on Technical Lignin Fractionation’, *ACS Sustainable Chem. Eng.*, vol. 8, no. 22, pp. 8086–8101, Jun. 2020, doi: 10.1021/acssuschemeng.0c01348.