

# Ligneous resolite adhesives for exterior-grade plywood

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**Abstract** The performance of lignin–phenol–formaldehyde (LPF) resolite adhesives was investigated for exterior-grade plywood manufacture using commercial pine kraft lignin to replace 40 wt% of phenol. Furthermore, the implementation of a lignin methylation step prior to resolite cooking was tested aiming to activate lignin towards the electrophilic aromatic addition of formaldehyde and to improve thus the performance of the respective adhesive. Comprehensive monitoring of the resolite cooking process and characterization of the obtained resins confirmed a significant network expanding effect of lignin. This is evident from the fast increase of viscosity which occurs, however, at the expense of cross-link density, as reflected by the somewhat longer B-time measured for both types of ligneous PF resins. Evaluation of bonding strength development using a bond strength development test confirmed that the less dense network of LPF resins translates into delayed bond formation compared to the PF reference resin. Methylation of lignin prior to resolite cooking had no significant impact on bond formation as evident from the very similar behaviour during the bond strength development test. However, both the studied LPF resins turned out to be suitable adhesives for the manufacture of plywood panels for outdoor usage.

Specimen prepared from beech veneers fulfilled the respective standards as determined by shear strength and bending strength tests.

## 1 Introduction

Phenol–formaldehyde (PF) resoles constitute a major class of adhesives that finds wide use in the manufacture of exterior-grade plywood, laminated veneer lumber and glue laminated timber. Lignin is the second most abundant biopolymer on earth next to cellulose and the main by-product of the wood pulping industry. Its assumed comparatively low price, the high content of phenolic moieties along with environmental considerations render lignin a suitable substitute for phenol in the manufacture of phenol formaldehyde type resins and adhesives, respectively (Pizzi 2006; Ghorbani et al. 2016). However, widespread commercialization has not been achieved yet due to two main reasons. One was the missing large volume availability of lignin with a fixed cost structure. For the most predominant kraft process, Lora (2008) identified only one mill producing kraft lignin located in the US. However, this situation might change now as a couple of mills have announced serious interest in providing kraft lignin, and additionally lignin extraction technologies on an industrial scale become commercially available (e.g. Ligno-Boost technology, Valmet, Espoo, Finland). Consequently in the last years further mills started providing kraft lignin on industrial scale (e.g. Domtar, US; Stora Enso and UPM, Europe). As second reason, it is well known that lignin is inferior to phenol with regard to reactivity (Pizzi 2013), i.e. towards electrophilic aromatic addition of formaldehyde. This is mainly due to fewer reactive sites per aromatic moieties available in lignin, lower amount of free phenolic groups and the sterical hindrance of lignin molecules that altogether

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lead to a lower network density (Pizzi 1994; Vazquez et al. 1995). To overcome these obstacles, several approaches have been proposed as reviewed by Hu et al. (2011) aiming at reduction of sterical hindrance by selective lignin degradation (Cheng 2011), increase of the number of reactive sites, such as by demethoxylation or demethylation, or by introduction of reactive functionalities capable of establishing additional intermolecular bonds (Vazquez et al. 1999; Hu et al. 2011). Further treatments were proposed, such as a re-activation of lignin with a sodium hydroxide as proposed by Chen (1995). Lignin methylation is frequently recommended for pine kraft lignin (Zhao et al. 1994; Hu et al. 2011) due to the higher content of activated aromatic moieties for electrophilic aromatic substitution at moderate sterical hindrance, and higher content of free phenolic hydroxyl groups (Tejado et al. 2007; Malutan et al. 2008a; Passauer et al. 2011).

For plywood applications, research on lignin in phenolic adhesives has a long history as summarized by Gardner and Sellers (1986) and plenty of additional literature on the topic is available in the meantime. When it comes to utilization of kraft lignin still a couple of works were performed and also some satisfying results could be achieved in the past. Gardner and Sellers (1986) reported in their own findings on shear strength values achieved using LPF adhesive with 25% kraft lignin as phenol replacement to be in a similar range compared to PF resin. Olivares et al. (1995) were able to produce plywood using beside other resource again kraft lignin at a level of 15% phenol replacement resulting in adhesives with comparably low solid contents (< 30%). In a range of studies also higher phenol replacement levels were analysed. Chen (1995) used up to 40% re-activated kraft lignin as phenol replacement and concluded their performance mainly from wood failure amount. Even higher levels were analysed by Klasnja and Kopitovic (1992) using hardwood kraft lignin and Danielson and Simonson (1998) using softwood kraft lignin, both produced plywood with satisfactory shear strength properties up to 50% phenol replacement. A recent study, aiming at analysing various filter systems used after the precipitation step, reported again the possibility of manufacturing plywood using 30% kraft lignin as phenol replacement without major change in shear strength properties (Kouisni et al. 2011). However, some of the here mentioned work used only very thin panels or only single veneer sheets combined with comparably high hot-pressing temperatures, which is favourable for the typically required higher curing temperatures of lignin containing adhesives. For thicker plywood panels, such high temperatures may not be achieved in the bond-lines located in the centre of the boards and properties may tend to suffer.

Motivated by the prospect of reasonable kraft lignin availability, this work investigates the adhesive properties of lignin–phenol–formaldehyde resole resins with the aim

of achieving considerable substitution levels of 40 wt% of phenol by pine kraft lignin. This lignin type has recently been additionally identified as best performing commercial lignin in resoles synthesis (Ghorbani et al. 2016). According to Pizzi (2013), some American plywood mills may apply between 20 and 30% pre-methylolated lignin in PF adhesives. The need of this frequently proposed supplementary step of methylation should also be compared to the use of unmodified kraft lignin using a co-polymerization approach.

As the speed of bond strength development is a critical factor for the processing speed of panel producing plants emphasis was made to precisely monitor this parameter as it is hardly available in comparable studies using kraft lignin. Additionally, the suitability of these unmodified adhesives (no addition of additives such as extenders or accelerators) for manufacturing exterior-grade plywood panels was analysed. Respective materials prepared from lignin-free counterparts were used as reference samples.

## 2 Materials and methods

### 2.1 Material

Pine kraft lignin Indulin AT™ was purchased from Mead Westvaco Corp (Richmond, SC, USA). Phenol ( $\geq 99.5\%$ ), formaldehyde (37% aqueous solution, formalin), isopropanol, distilled water, hydroxylamine hydrochloride, sodium hydroxide solution ( $1 \text{ mol L}^{-1}$ ) and hydrochloric acid ( $1 \text{ mol L}^{-1}$ ) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Sodium hydroxide pellets (97%) were obtained from Sigma-Aldrich Co. LCC (Steinheim, Germany). Bond strength development tests were conducted using beech veneer strips ( $147 \times 20 \times 0.58 \text{ mm}^3$ ) stored previously at  $20 \text{ }^\circ\text{C}$  and 65% relative humidity. The preparation of plywood was accomplished using beech veneers with a dimension of  $500 \times 500 \times 3 \text{ mm}^3$  which had been stored at the above standard climate until equilibrium moisture content was reached.

### 2.2 Methylation of lignin

According to the procedure reported elsewhere (Malutan et al. 2008b), 112.5 g of lignin was placed in three-neck round-bottom flask and dissolved in 291 g aqueous NaOH solution 3% (wt/wt) corresponding to a NaOH/lignin ratio of 0.08 (wt/wt) at  $25 \text{ }^\circ\text{C}$ . The flask was equipped with a condenser, electronic temperature controller, and magnetic stirring bar. 78.45 g formaldehyde solution (37%) corresponding to a formaldehyde/lignin ratio of 0.258 (wt/wt) was added at room temperature. The mixture was then heated up to  $55 \text{ }^\circ\text{C}$  to start methylation. Free formaldehyde content was measured every 50 min until a constant

value was obtained (Malutan et al. 2008b). The total reaction time was 5 h. At that point the ratio of lignin to consumed formaldehyde was 0.07 wt/wt (0.22 mol HCHO per 100 g lignin). The reaction product was precipitated by adding 1N hydrochloric acid until a pH of 1.5–2 was reached. The crude methylolated lignin was centrifuged at 2500 rpm for 10 min, washed three times with distilled water and then freeze-dried.

## 2.3 Preparation of resole resin

### 2.3.1 Preparation of phenol–formaldehyde (PF) resin

PF resin was prepared according to the procedure described in previous work (Ghorbani et al. 2016). In brief, 58.42 g of solid crystalline phenol and 15.07 g of aqueous sodium hydroxide (50 wt%) was placed in a 500-mL three-neck flask equipped with a condenser, electronic temperature controller and Heidolph™ RZR Overhead Stirrer Impellers—Blade and Half-Moon Styles (Carl Roth GmbH & Co. KG, Karlsruhe, Germany). The molar ratio of sodium hydroxide to phenol was 0.3. The mixture was heated to 65 °C, then 115 mL aqueous formaldehyde (37 wt%) corresponding to a formaldehyde to phenol molar ratio of 2.5, was added using an automatic burette (TitroLine® 6000/7000) at a flow rate of 8.43 mL min<sup>-1</sup>. The temperature was then increased to 80 °C and viscosity measurement was started after 1 h. The cooking was stopped at the viscosity of 150 mPa s and the resin cooled down using an ice bath.

### 2.3.2 Preparation of lignin–phenol–formaldehyde (PK-LPF and mPK-LPF) resins

LPF resin was prepared according to the above general procedure but adapted for the co-polymerization of lignin as detailed elsewhere (Ghorbani et al. 2016). In an attempt to increase the efficiency of formaldehyde usage its amount required to react with lignin (40 wt% phenol replacement) was recalculated based on the conducted lignin methylation experiment where only 0.22 mol formaldehyde per 100 g lignin had been consumed. Therefore, 72.83 mL aqueous formaldehyde (37%) was added for cooking PK-LPF resin. For cooking mPK-LPF resin where methylolated lignin was used to replace phenol, the amount of formaldehyde was reduced to the remaining 60 wt% of phenol. For both PK-LPF and mPK-LPF resins, the lignin co-monomers were added portion-wise to the alkaline mixture of phenol and sodium hydroxide at 65 °C.

## 2.4 Characterisation of resin

Viscosity was measured according to DIN 16916-2 (1987) using cooled (20 °C) aliquots (1.1 mL) of the

pre-condensates. A cone-plate rheometer (Bohlin CVO; Malvern Instruments Limited, Malvern, UK) at a shear rate of 200 s<sup>-1</sup> equipped with a temperature control unit was used.

Free formaldehyde content was determined according to ISO 11402 (2004) by a reaction with hydroxylamine hydrochloride and back-titration of the released HCl using 1 M NaOH. In brief, a well-defined amount of resin (5.0 ± 0.2 g) was dissolved in 50 mL of a mixture consisting of isopropanol and water (3:1 v/v). The pH of this mixture was adjusted to 3.5 with 1 M hydrochloric acid using a TitroLine® 6000/7000 titrator (SI Analytics, Germany). Then 25 mL of hydroxylamine hydrochloride solution (10 wt%) was added to the solution and stirred for 10 min. Then, the solution was immediately back-titrated to pH 3 using 1 M aqueous sodium hydroxide.

Solid content was determined according to ISO 3251 (2008). All samples were initially cured and equilibrated in a ventilated oven at 135 °C.

The time required to reach the B-stage of resin curing (B-time) was measured according to DIN 16916 (1987) using a self-designed equipment capable of fulfilling the standard requirements of such a device. The device consisted of a heated aluminium plate with a depression (diameter 25 and 5 mm depth) on it and a Pt100 temperature sensor for precise temperature control. Aliquots (500 mg) of the PF and LPF resins, respectively, were placed inside the depression at a plate temperature of 100 °C which was controlled at an accuracy of ±0.5 °C. A glass rod was used to stir the sample for 1 min. Then, the sample was stirred every minute for 10 s until the B-stage was reached. B-stage time was recorded when the resin sample was not stringy anymore and tore off at the end of the glass rod while it was pulled out. The test was performed at 100 °C instead of 130 °C as suggested in the standard procedure as such high temperatures are hardly achievable in solid wood bonding.

To analyse the percentage of soluble fraction in the cured resins, an acetone extraction was conducted by a method based on ASTM D 494 (2004). The resin was cured at a temperature of 110 °C for 1 h and pulverized with a micro-fine grinding drive (IKA MF10 basic). The milled resin was then fractionated with a sieve Nos. 120 (125 µm) and dried at 103 °C for 4 h. Cellulose extraction thimbles were dried under the same conditions as the resins, filled with 3 g of the adhesive powder and plugged with cotton wool. For the extraction setup, a round-bottom flask was filled with 250 mL acetone and the thimble was placed in a 100 mL Soxhlet extractor. The resin powder was then extracted for 48 h, as proposed in previous work (So and Rudin 1990; Schmidt and Frazier 1998). Subsequently, the thimble—including the insoluble resin and the extractive was dried and weighed to determine the soluble amount of the cured adhesives.

Bonding strength development was monitored using a bond strength development test (inspired by Humphrey 1990; ASTM D7998-15 2015) performed by a self-constructed device. This self-constructed analogue device capable of assessing the development of bonding strength during hot pressing of resin joints was mounted onto a Zwick/Roell Z100 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany) using a controlled hot press temperature of 120 °C. The veneer lap joints were prepared with gluing two beech veneer strips with an overlap length of 4 mm using a spread rate of 200 g m<sup>-2</sup> and a relative pressure of 1.4 N mm<sup>-2</sup> (Eder 2014). Tensile shear strength was measured in hot state immediately after the selected pressing time i.e. 30, 60, 90, 120, 240, 360, 420, 480, and 720 s. For each bond formation under a certain hot pressing time, eight specimens were tested.

### 2.5 Plywood preparation

Five veneers were laid cross-wise over each other. Resin was applied to one adherent at a spread rate of 200 g m<sup>-2</sup> for a single glue-line. Hot-pressing was performed at 120 °C applying a specific pressure of 2 MPa. The particular hot pressing time was assumed for each type of resin based on the time determined by bond strength development test to achieve a maximum strength value, multiplied by a “safety factor” of 3 in order to definitely achieve a state of full curing, plus a required heat conduction time of estimated 1 min mm<sup>-1</sup>. Finally 36 min pressing time were chosen for PF and 66 min for both types of LPF resins. The plywood panels were cut into two groups of bending test specimens (in fibre direction and perpendicular to fibre direction) with the dimension of 300 × 50 × 14 mm<sup>3</sup> as well as tensile shear specimens with the dimension of 100 × 25 × 14 mm<sup>3</sup> including the necessary saw kerfs for the defined shear plane according to EN 314-2 (1993).

### 2.6 Properties of plywood

Tensile shear tests were performed according to EN 314-1 (2004) using a Zwick/Roell Z100 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany). According to the standard, saw kerfs were varied in depth in order to assess all single bond-lines, also those located close to the centre of the plywood. The pre-treatments which specify the requirements for bonding classes of plywood for exterior use (class 3) were carried out according to EN 314-2 (1993).

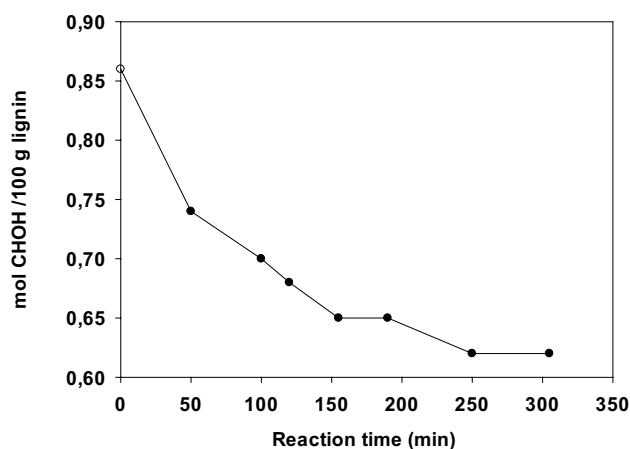
Three-point bending strength (modulus of rupture, MOR) and modulus of elasticity (MOE) were determined

according to EN 310 (1993) using again above mentioned Zwick/Roell Z100 universal testing machine.

## 3 Results and discussion

Earlier studies comparing the reactivity of different types of commercial lignins towards electrophilic addition of formaldehyde have shown that the obtained liginous A-stage resoles (ca. 1000 mPa·s) featured significantly higher contents of free formaldehyde not consumed during resin cooking compared to their lignin-free counterparts (Ghorbani et al. 2016). This result had been explained by the fact that the preferred reaction of formaldehyde with phenol, which is more reactive, has more reactive sites per aromatic unit and is much less sterically demanding which translates into a higher frequency at which formaldehyde molecules can approach those reactive sites. The increasing molecular weight of the resole molecules along with the declining formaldehyde concentration additionally hampers the involvement of lignin in the network formation. Lignin methylation prior to resin cooking has been therefore tested to promote the introduction of functional groups and to maximize the efficiency of the added formaldehyde during cooking of LPF resins. Figure 1 illustrates the formaldehyde consumption by lignin during a reaction time of 4 h and a temperature of 55 °C. The reaction time varies with chosen reaction temperature (Malutan et al. 2008b; William 2014).

The properties of the two LPF and the PF reference resins are compiled in Table 1. The cooking time required to reach the intended target viscosity of 150 mPa·s was confirmed to be significantly shorter for the LPF resins. This is well in line with previous observations (Danielson and Simonson 1998) and is attributed to the bigger size of the lignin molecules compared to phenol leading to a faster network



**Fig. 1** Formaldehyde (CHOH) consumption during methylation of lignin at 55 °C

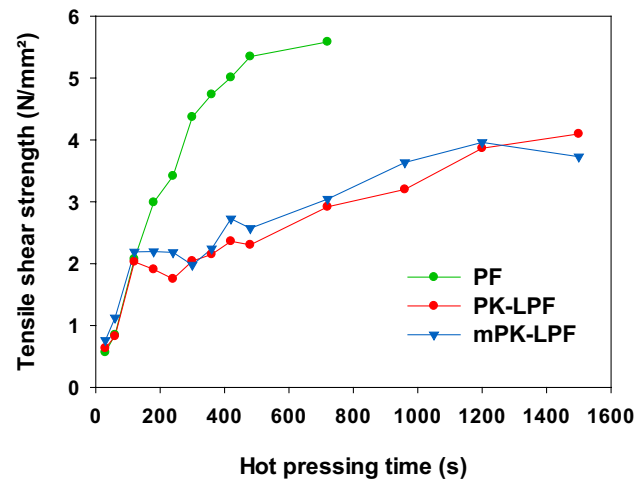
**Table 1** Properties of resins with no lignin (PF), pine kraft lignin (PK-LPF) and methylolated pine kraft lignin (mPK-LPF)

Resin type	Cooking time	Viscosity (mPa·s)	Free formaldehyde (wt%)	B-time	Soluble fraction (wt%)
PF	2 h 35 min	145	1.8	9 min 25 s	1.4
PK-LPF	34 min	150	1.2	11 min 47 s	3.1
mPK-LPF	32 min	143	1.2	11 min 25 s	2.5

expansion for the case of LPFs (Ghorbani et al. 2016). Both final pH (9.9–10.1) and solid content (45.1–47.3 wt%) of the resin did not vary significantly. Different to the former study (Ghorbani et al. 2016) where a higher free formaldehyde content (FFC) was consistently found for all lignin containing resole resins (target viscosity 1000 mPa·s), a lower FFC value was determined in this study for both of the LPF resoles compared to the reference PF resin (*cf.* Table 1) as the formaldehyde content was adapted for LPF resins as described in the methods section. However, it needs to be mentioned that the viscosity of all resins was much lower than in the above-mentioned study.

B-time, i.e. the curing time at a given temperature (100 °C in this study) after which resins of known concentration change to the B-state, was as expected somewhat longer (120–142 s) compared to the PF reference resin (Table 1). Possible reasons are dominated by sterical hindrance and lower amount of functional groups entering cross-linking reactions. Virtually no differences in B-time were observed between the two studied ligneous (PK-LPF, mPK-LPF) resins. The soluble fraction determined by acetone extraction (Table 1) was found to be 1.4% for neat PF resins, which is in line with values reported in literature for corresponding adhesives (e.g. Schmidt and Frazier 1998). The same method and also solvent were used for analysing LPF adhesives. Blind extraction tests on pure lignin powder applying again the same procedure as for adhesive powder resulted in a lignin solubility of approx. 46%. Thus, hot acetone is clearly not capable of fully dissolving unbonded lignin, but may act as a first indicator to determine probable differences in lignin incorporation quality. As can be found in Table 1, the LPF adhesives have higher soluble fractions compared to the neat PF adhesive. By comparing the two LPF adhesives the one using methylolated lignin showed a slightly lower amount of soluble fraction in the cured adhesive, what may be interpreted as a somewhat better incorporation of lignin in the adhesive network.

Within the first 150 s, bond strength development was well in line for the different adhesive types until reaching the considerable level of 2 N mm<sup>-2</sup>. At this strength level various adhesives already fail in fully cured state (e.g. Danielson and Simonson 1998). Passing this strength level, LPF adhesives slowdown drastically in bond strength development but have still the potential to double the measured

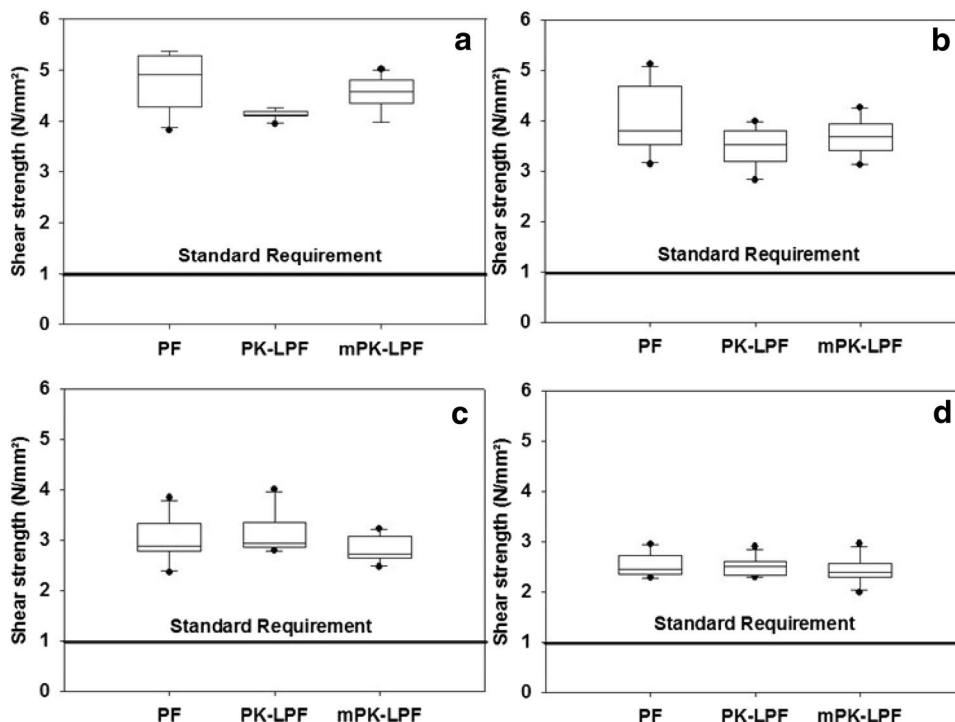


**Fig. 2** Impact of pressing time on tensile shear strength development of beech veneer lap joints prepared at 120 °C as monitored using a bond strength development test

tensile-shear strength measured in hot state (Fig. 2). It has to be mentioned that no type of accelerator was used for adhesive synthesis, but their utilization may be helpful if further increase in curing speed is desired (Trosa and Pizzi 1998). Pre-methylolation did neither translate into faster nor superior performance in terms of tensile shear strength of adhesive joints between beech veneer strips compared to resins that were obtained by copolymerisation of phenol and un-modified lignin under otherwise identical conditions. This is somehow in contrast with results from Vazquez et al. (1997) who found evidence of increased reactivity of methylolated lignin based on <sup>13</sup>C NMR spectra, using lignin from acetic pulping. The current observations imply furthermore that the reaction of formaldehyde with unmodified lignin (and phenol) at higher temperature (65 °C/80 °C during resin synthesis instead of 55 °C during pre-methylolation) generates an amount of hydroxymethyl groups sufficient to form mechanical equally performing resins.

According to the intended use of ligneous PF adhesives for the preparation of plywood, respective materials were prepared from five alternating cross-wise oriented beech veneers that were glued together with the different types of resole adhesives obtained in this work. Quality assessment of these materials was conducted in two ways: one set of

**Fig. 3** Shear strength of plywood boards prepared using lignin-free phenol-formaldehyde adhesive resins (PF), as well as ligneous resins substituting 40 wt% of phenol by pine kraft lignin (PK-LPF) or by methylolated pine kraft lignin (mPK-LPF). The treatments included: standard climate (20 °C, relative humidity of 65%) (a), immersion in water at 20 °C for 24 h (b), immersion in boiling water for 4 h, then drying in an oven for 16 h at 60 °C, then immersion in boiling water for 4 h followed by cooling in water 20 °C for 1 h (c), immersion in boiling water for 72 h followed by cooling in water at 20 °C for 1 h (d). The results are based on ten replicas per adhesive type

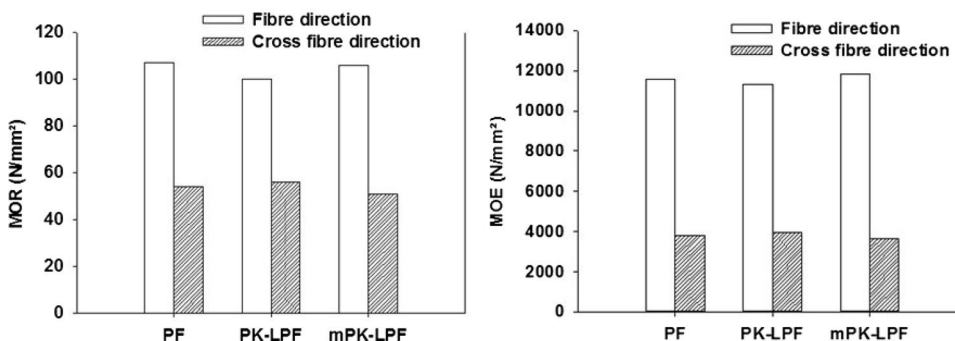


specimen (10 replicates) was just equilibrated in standard climate at 20 °C and a relative humidity of 65% (Fig. 3a) and three sets were subjected to different treatments as required by EN 314-1 (2004). These treatments comprise immersion in water at 20 °C for 24 h (Fig. 3b), immersion in boiling water for 4 h followed by drying in an oven for 16 h at 60 °C, re-immersion in boiling water for 4 h and eventual cooling in water (20 °C) for 1 h (Fig. 3c), and immersion in boiling water for 72 h followed by cooling in water at 20 °C for 1 h (Fig. 3d).

Shear strength measurements revealed that all prepared plywood boards surpassed distinctly the EN 314-1 (2004) 1 N mm<sup>-2</sup>—shown in Fig. 3a–d as solid lines—independently from the harshness of the applied treatment and by assessing all bond-lines (close to surface and core layers). The latter indicates that also bond-lines located in the core region of the panel, which typically exhibit lower glue-line

temperature, are sufficiently cured and able to withstand the harsh treatments. This is some improvement or extends previous studies which usually test 3-ply plywood (e.g. Danielson and Simonson 1998; Klasnja and Kopitovic 1992) combined with high hot pressing temperature resulting in correspondingly high and possibly not representative glue line temperature. Again adhesives using pre-methylolated lignin do not show any advantage over the in-situ modified kraft lignin. As wood failure turned out to be the dominating failure mode approving the sufficient strength of the tested resins, it is safe to conclude that all plywood samples prepared using LPF adhesives for gluing where 40 wt% of phenol had been replaced by lignin are suitable even for outdoor application. Similar findings were reported in other studies using phenol substitution degrees between 15% (Olivares et al. 1995) and 30% (Kouisni et al. 2011) by kraft lignin for plywood application.

**Fig. 4** Three-point bending strength (modulus of rupture, MOR) and modulus of elasticity (MOE) of plywood boards prepared using lignin-free phenol-formaldehyde adhesive resins (PF), as well as ligneous resins substituting 40 wt% of phenol by pine kraft lignin (PK-LPF) and by methylolated pine kraft lignin (mPK-LPF)



Three-point bending strength (modulus of rupture, MOR) and modulus of elasticity (MOE) of all tested plywood boards are shown in Fig. 4. It is apparent that the absolute values for both MOR as well as MOE are relatively high which is mainly due to the high density of the chosen hardwood species beech (Green et al. 2010; Cihad Bal and Bektas 2014). Even though the values should be treated with care due to the limited number of specimens tested per fibre direction and adhesive ( $n = 2$ ), the observed bending behaviour was quite similar for all plywood boards bonded with the different resins, as failure again occurred predominantly in the wood veneers and not in the glue lines. A distinct difference between the results in fibre direction and perpendicular to fibre direction is also evident, which is clearly the result of both significantly higher mechanical strength and stiffness of the outermost veneer layers in fibre direction (Green et al. 2010).

#### 4 Conclusion

Substitution of phenol by 40 wt% of pine kraft lignin affords lignin–phenol–formaldehyde resole resins of laboratory type (not including any type of additives as used for commercial products) that can be used as adhesives in exterior-grade plywood production. This has been confirmed by respective mechanical testing according to EN 314-1 which sets a shear strength limit value that has been surpassed by all plywood boards tested in this study. This was also the case for resins prepared from the same amount of pre-methylolated pine kraft lignin. However, this additional step turned out to offer no advantages in terms of bonding strength development nor regarding processing time of LPF resins. However, incorporation into the adhesive network seemed to be somewhat better for methylolated lignin as a lower soluble fraction was observed for this lignin type.

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