**ORIGINAL ARTICLE**

# The synthesis of maleated nanolignin–polyvinyl alcohol–hexamine resin as a cold-setting wood adhesive

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## Abstract

This work reports the development of a cold-setting plywood adhesive based on polyvinyl alcohol (PVOH), maleated nanolignin, and hexamine. The influence of the maleated nanolignin content (10, 15, and 20 wt%) and cold-pressing time (3, 6, 12 and 24 h)  on the properties of the resin and the plywood panels bonded with it was investigated. Some physicochemical, structural and thermal properties of the synthesized resins were determined. The water absorption and shear strength of the plywood panels bonded with the resins were also measured according to the relevant standard methods. FTIR analysis indicated that the amount of the –OH at 3420 cm$^{-1}$ band and the C=O groups at 1740 cm$^{-1}$ band increased in the resins with  increasing proportion of maleic anhydride-treated nanolignin from 10 to 20 wt%. Based on the physicochemical results obtained, the modification of nanolignin by maleic anhydride accelerates the gelation time and increases the viscosity and solids content of the resin compared to when virgin nanolignin is used. DSC analysis shows that the addition of maleated nanolignin significantly decreases the curing temperature of the resin from 56 to 48 °C. Based on the analysis of the panel results, higher mechanical strength (shear strength, MOE and MOR) and dimensional stability were obtained by treating nanolignin with maleic anhydride. The addition of 20 wt% maleated nanolignin in the adhesive while using a cold-pressing time of 24 h produced plywood which satisfies standard requirements.

## 1 Introduction

Today, more than 90% of plywood panels are bonded with urea–formaldehyde (UF) resins (Younesi-Kordkheili and Pizzi 2018). Although the use of UF resins as a wood adhesives has several advantages, the resulting high formaldehyde emission, low chemical bond resistance to water and the need for high temperature curing are the main problems of UF resin. For these reasons, nowadays bio-based wood adhesives have been more researched due to the increased environmental awareness, the need for more sustainable wood-based products and the stringent legislative requirements related to hazardous formaldehyde emission from wood composites (Younesi-Kordkheili 2022; Ganewatta et al. 2019). As one of the most important bio-sourced materials, lignin is considered to be the second most abundant aromatic polymer in nature (Younesi-Kordkheili et al. 2017; Garlapati et al. 2020; Rico-García et al. 2020). Although the specific phenolic structure of lignin provides high hydrophobicity, its sterically hindered aromatic structure decreases its reactivity. Thus, to obtain a wood adhesive of high quality, previous works have indicated that lignin should be used as a part of synthetic resins formulation. There are several research works on "green", hot-setting wood adhesives based on lignin (Younesi-Kordkheili and Pizzi 2020, 2017; Siahkamari et al. 2022). Thus, due to increasing energy costs, the rapid development of engineered wood products and biorefinery concept (maximum utilization of the waste of pulp and paper industries), the interest in developing environment friendly cold-setting wood panel adhesives based on lignin is growing. To prepare cold-setting wood

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adhesives, chemical modification of lignin before its utilization in wood adhesives is necessary. Younesi-Kordkheili and Pizzi (2022) indicated that one of the best methods to decrease heterogeneity and polydispersity as well as increase reactivity of lignin is changing it to maleated nanoparticles. They indicated that lower formaldehyde emission and higher mechanical strength and dimensional stability were obtained by treating nanolignin with maleic anhydride in lignin-urea–formaldehyde (LUF) resins. However, modified UF resins by maleated nanolignin, as they still contain formaldehyde, are still toxic and also need a higher temperature to cure than pure UF resins.

Conversely, previous work has shown that another alternative to decrease toxicity is substitution of formaldehyde by hexamine in the production of wood adhesives (Lubis et al. 2022). Hexamine is linked to lignin units both by covalent and ionic bonding (Dunky 2021). However the reactivity of hexamine is lower than that of formaldehyde. Moreover, the rate of increase of the adhesion strength when hexamine is used is lower than for formaldehyde. Thus, to obtain cold-setting wood panel adhesives based on lignin, it is necessary to use "green" additives in the maleated nanolignin/hexamine mixture. Poly(vinyl alcohol) (PVOH) is one of the non-toxic and relatively low cost adhesives that the wood industry has used for decades. It is a water-soluble high molecular mass polymer which is widely used for its excellent performances and relatively low cost. In the research work presented here, where the aim was to enhance the link of maleated nanolignin with hexamine, PVOH was used to promote more hydroxy (−OH) groups in the system. Bortolatto et al. (2022) indicated that PVOH as a highly polarity polymer, is used in polymer blends with natural polymeric lignin. It is expected that the blending of PVOH, maleated nanolignin, and hexamine could provide an alternative cold-setting wood adhesive. Lubis et al. (2022) indicated that it is possible to prepare environment friendly plywood bonded with PVOH–lignin–hexamine-based adhesives using cold pressing as an alternative to conventional hot-pressed plywood. However, they indicated that an increasing lignin content lowers the mechanical strength of the prepared plywood. Therefore, the aim of this research was development of new, high quality bio-based cold-setting adhesives based on modified nanolignin.

So far extensive work has been conducted to investigate hot-setting wood adhesives based on modified lignin. However, there is no information on wood adhesives based on PVOH, maleated nanolignin and hexamine. Therefore, the work presented here aimed to develop an alternative cold-setting wood adhesive for plywood based on PVOH, maleated nanolignin, and hexamine. The influence of maleated nanolignin content and cold pressing time on the properties of the synthesized resin and associated plywood panels bonded with it were also investigated.

## 2 Materials and methods

### 2.1 Materials

Soda lignin was extracted from sugarcane bagasse with a soda pulping process by a pulp and paper industrial mill (Haft tape, Iran). Bagasse soda black liquor with pH = 13 and 40% consistency as source of lignin was prepared. Lignin was extracted from black liquor by acidic method. For such a purpose, soda lignin was precipitated from black liquor by adding very slowly concentrated (36N) sulphuric acid, until the pH of the resultant solution was close to 2. The precipitate was then thoroughly washed with water until the pH of the rinse was close to 6. Finally, the obtained lignin was dried in an oven at 60 °C for 24 h, after which a dark-brown powder was recovered. Maleic anhydride and other chemical materials used were acquired from Merck Co.

### 2.2 Methods

#### 2.2.1 Preparation and characterization of nanolignin

Nanolignin was obtained according to the method of Gao et al. (2020). The specific surface area and average pore diameter of lignin and nanolignin were measured at 200 °C by BET method and is reported in Table 1.

#### 2.2.2 Modification of nanolignin

Maleated nanolignin was obtained according to the method of Gao et al. (2020). DMSO was used to dissolve sufficient nanolignin in a glass reactor equipped with reflux condenser and mechanical stirring. 400 μL 1-methylimidazole was then added dropwise under continuous stirring to catalyze nanolignin esterification, immediately followed by 40 g maleic anhydride. The mixture was then heated to 80 °C under continuous mechanical stirring for 3 h. After cooling, the maleated nanolignin was then recovered by precipitating it at pH 3. The unreacted maleic anhydride was then eliminated by continuous washing with water. Finally, the residual solids were oven dried at 60 °C.

**Table 1** Specific surface area, average pore volume, and pore size of nanolignin

| Sample | Specific surface area (m² g⁻¹) | Average pore volume (cm³ g⁻¹) | Average pore size (nm) |
|---|---|---|---|
| Lignin | 0.05371 | 0.0007 | 8.85 ± 0.13 |
| Nanolignin | 6.1766 ± 0.2 | 0.0098 | 5.99 ± 0.1 |

### 2.2.3 Preparation of PVOH-maleated nanolignin- hexamine adhesives

Prior to the blending process, lignin solution was prepared by mixing nanolignin/maleated nanolignin in acetone at a ratio of 1:10. Furthermore, PVOH beads were dissolved in distilled water at 80 °C to obtain a PVOH solution of 15% w/v and hexamine 15% w/v was prepared by dissolved hexamine powder in distilled water at $27 \pm 2$ °C. The mixing process of adhesive was conducted at a temperature of $27 \pm 2$ °C under a stirring rate of 300 rpm according to the formulation in Table 2.

### 2.2.4 FTIR analysis

Structural changes in nanolignin before and after reaction with maleic anhydride as well as the functional groups of PVOH–maleated nanolignin–hexamine based adhesive at different maleated nanolignin contents were determined by Fourier transform infrared spectrometry (FTIR). FTIR spectra were obtained from pellets of KBr with %1 by weight of powdered resins between 400 and 4000 cm$^{-1}$ wave number.

### 2.2.5 DSC analysis

The curing process of PVOH–maleated nanolignin–hexamine-based adhesive at different nanolignin contents was tested by DSC with a NETZSCH DSC 200 F3 Model thermal analyzer. The DSC scans were recorded at a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 60 cm$^3$/min. To determine the curing temperature of the resins, about 5 mg of freeze-dried sample was added to the aluminum pan. Then, the samples were heated from ambient temperature (25 °C) to 120 °C under nitrogen atmosphere. The DSC cups were closed during the whole temperature range investigated.

**Table 2** Formulation of PVOH–lignin–hexamine-based adhesive at different lignin contents

| Code | PVOH (%) | Nanolignin content (%) | Maleated nanolignin (%) | Hexamine (%) |
|---|---|---|---|---|
| LPH10 | 75 | 10 | – | 15 |
| LPH15 | 70 | 15 | – | 15 |
| LPH20 | 65 | 20 | – | 15 |
| mLPH10 | 75 | – | 10 | 15 |
| mLPH15 | 70 | – | 15 | 15 |
| mLPH20 | 65 | – | 20 | 15 |

### 2.2.6 Physicochemical tests

The solid content of the adhesives was determined according to ASTM D 4426-93. The density of the liquid resin was obtained by density hydrometer. A rotational rheometer was used to determine the viscosity of the resin. A gel time meter was utilized to measure the gel time of PVOH/maleated nanolignin/hexamine adhesives at different lignin contents at $27 \pm 2$ °C. Three replicates for each sample was made.

### 2.2.7 Plywood panel manufacturing

The details of the plywood panel manufacturing methods were presented in a previous study (Younesi-Kordkheili and Pizzi 2018). Beech (*Fagus orientalis*) layers with dimensions of 240 mm * 200 mm * 2 mm were prepared and dried to a moisture content of less than 6 mass percentage for manufacturing three-layer plywood. For this purpose, both faces of the veneer in the middle layer were coated with 250 g/m$^2$ resin. The three layers were assembled and hot-pressed at 70 °C and the maximum pressure of 1 MPa for 10 min. Three panels were prepared for each resin. Preparation of the samples for shear strength and water absorption measurement was started 24 h after pressing.

### 2.2.8 Panel testing

The samples were conditioned at a temperature of 23 °C $\pm$ 2 °C and a relative humidity of 60% $\pm$ 5% for 2 weeks. Shear specimens were prepared from each board to examine shear strength according to ASTM D 906-98. Water absorption tests were performed according to ASTM D4442-07. Five specimens were tested for each resin.

### 2.2.9 Statistical analysis

The mean values of the mechanical properties of plywood were compared using analysis of variance (ANOVA), and the Duncan multiple range test at $\alpha = 0.05$ was performed to determine the optimum maleated nanolignin content and pressing time for plywood.

## 3 Results and discussion

### 3.1 FTIR analysis

The infrared spectra of the nanolignin before and after modification with maleic anhydride are shown in Fig. 1. A comparison between the IR spectra of nanolignin and maleated nanolignin indicated that the intensity of the 1700 cm$^{-1}$ band to COOH increased in the maleated nanolignin, a clear indication of the anhydride ring opening to form maleic acid.
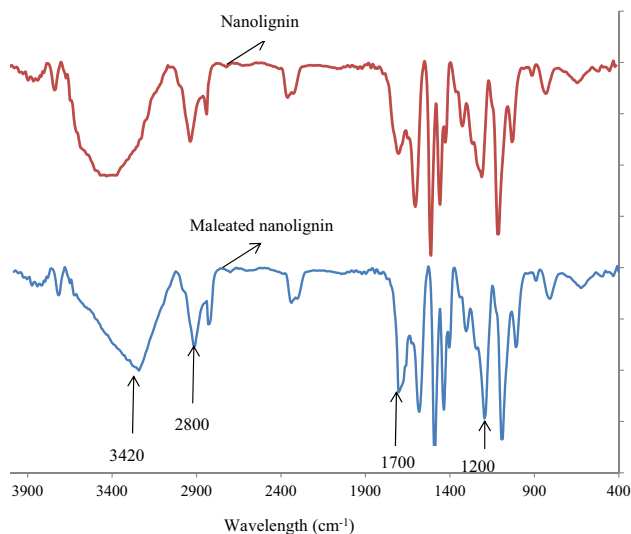
**Fig. 1** FTIR analysis of nanolignin and maleated nanolignin



**Fig. 2** FTIR analysis of PVOH–maleated nanolignin–hexamine resin at different lignin content

The intensity of the 2800 cm$^{-1}$ band related to the C–O groups and 1200 cm$^{-1}$ band assigned to the C=C bonds increases in modified nanolignin, again due to the addition of maleic anhydride. Furthermore, the nanolignin modified with the maleic anhydride showed a smaller peak at 3420 cm$^{-1}$ (the hydroxyl group) than the neat nanolignin. The decreasing intensity of –OH groups is probably due to the esterification reaction of free –OHs of lignin by the carboxylic acid functions of maleic acid generated by the hydrolysis of maleic anhydride and confirms that chemical reactions have occurred and that maleate groups or carbonyl groups replace the hydroxyl groups in the nanolignin structure.

Moreover, the alteration in functional groups of PVOH–maleated nanolignin–hexamine adhesives at different maleated nanolignin contents after curing was observed in Fig. 2. The wavenumber at 3300 cm$^{-1}$ showed a secondary amine peak resulting from the reaction of PVOH–maleated nanolignin with hexamine. Hexamine can form covalent bonds with the functional groups of the maleated nanolignin. In the resin with 20% maleated nanolignin, the proportion of −OH groups was much greater compared to the resin with 10% modified nanolignin. Equally, the band at 1740 cm$^{-1}$ related to the C=O group of an aldehyde (resulting from the decomposition of hexamine at high temperatures) in the mLPH resin with 20% maleated nanolignin was higher than the one in the 15% and 10% modified nanolignin cases, respectively. According to the FTIR it is possible that three main reaction sequences occur (Fig. 3): One is the reaction of crosslinking of the lignin with maleic anhydride, and the second one is the cross-linking by esterification with maleic acid of both the polyvinyl alcohol and lignin, thus with the maleic acid functioning as the cross-linker (Fig. 3a). By
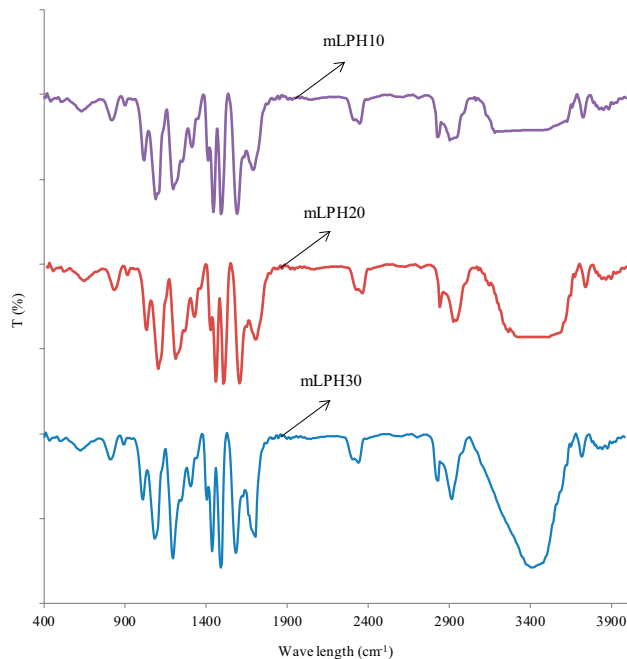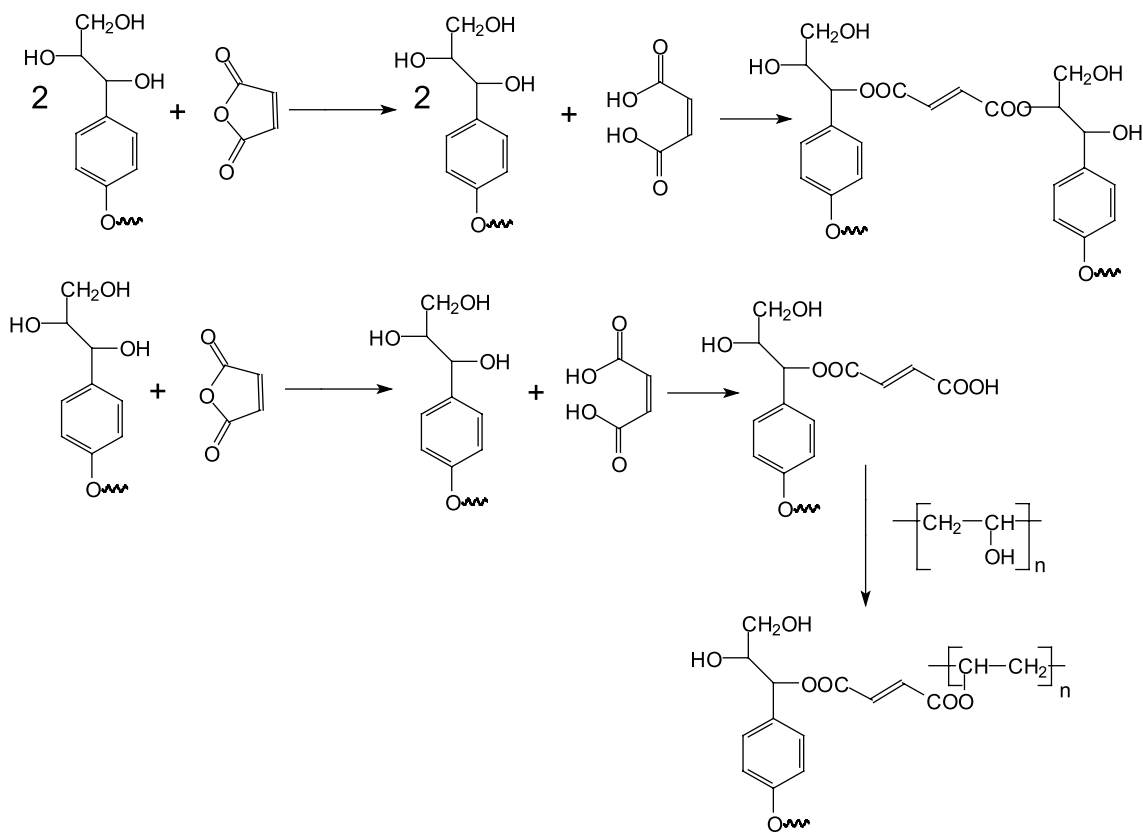
addition of hexamine the reactions (b) do occur (Fig. 3b) (Kamoun and Pizzi 2000a, 2000b; Kamoun et al. 2003).

## 3.2 DSC analysis

DSC analysis of virgin LPH15 as control and mLPH adhesives with 10, 15 and 20% maleated nanolignin contents was done to investigate the resins thermal curing behavior (Fig. 4). Figure 4 shows that all the resins with any of the amounts of maleated nanolignin have a lower temperature peak (Tp) than that of the control sample. This can be attributed to the faster condensation of the mLPH resin due to its high carboxyl content compared to LPH. Moreover, the presence of carboxylic acid (COOH) groups gives faster condensation as there are more sites for active cross-linking through the additional mechanism already outlined (Younesi-Kordkheili and Pizzi 2022). Figure 4 also shows that the Tp value continuously decreases from 56 to 48 °C by increasing in the adhesive the amount of maleated nanolignin from 10 to 20%. These results were confirmed by gel time measurements, which decreased on incorporation of maleated nanolignin into the resin structure. The high rate of curing for the mLPH resin indicated that incorporation of maleated nanolignin accelerates the curing of resin and this can be attributed to fast condensation of mLPH resin due to its high functional groups content in comparison with LPH resin. Decrease in the curing temperature of the resin is very favorable due to the lower energy prospective consumption in the wood industry.

a

By addition of hexamine the following reactions do occur
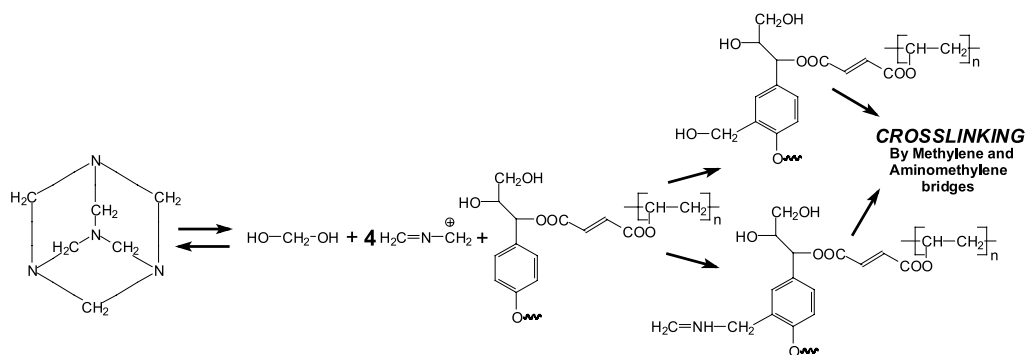


b

**Fig. 3** Schematic of the possible reactions between the elements

## 3.3 Physicochemical analysis of resin prepared

The main properties of the adhesives prepared at different unmodified nanolignin and maleated nanolignin contents are summarized in Table 3. The solids content and viscosity of PVOH–lignin–hexamine-based adhesives were decreased by increasing the amount of neat nanolignin from 10 to 20%. By incorporating high amount of nanolignin into the resin, the density of the adhesive probably decreases and hence the resin with 20% nanolignin exhibits the lowest solid content. Conversely, greater solids content and viscosity can be observed by increasing maleated nanolignin content. The results showed that the resin with 20% virgin nanolignin exhibited the lowest solids content (17%) and
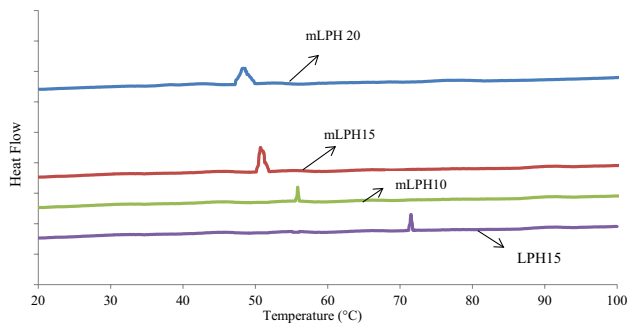
**Fig. 4** DSC analysis of the prepared resin

**Table 3** Physicochemical properties of PVOH–lignin–hexamine resin

| Nanolignin content (%) | Viscosity(mPa s) | Solid content (%) | Gel time(h) |
|---|---|---|---|
| mLPH10 | $2402 \pm 65$ | $26 \pm 0.3$ | nd[a] |
| mLPH15 | $2873 \pm 80$ | $28 \pm 0.2$ | nd |
| mLPH20 | $3200 \pm 23$ | $31 \pm 0.4$ | 16 |
| LPH10 | $1898 \pm 47$ | $22 \pm 0.1$ | nd |
| LPH15 | $1578 \pm 62$ | $20 \pm 0.3$ | nd |
| LPH20 | $1365 \pm 38$ | $17 \pm 0.2$ | nd |

[a]Not detected

viscosity (1365 mPa s) while the resin containing 20% modified nanolignin had the highest solid content (31%) and viscosity (3200 mPa s) among all synthesized resins. Higher viscosity of the resins with maleated nanolignin compared to those with unmodified nanolignin can be explained by the high level of chemical bridges between the elements by the esterification of nanolignin. The gelation time of the adhesives prepared are shown in Table 3. The gelation time of

virgin LPH adhesives at different lignin contents could not be detected, meaning that the gelation process of the adhesive is over 17 h. For mLPH with 10% and 20% maleated nanolignin the gel time cannot be determined too. However the resins with 20% maleated nanolignin exhibited gelation time of about 16 h.

### 3.4 Plywood panel properties

The physical and mechanical properties of the plywood bonded with PVOH–lignin-hexamine blends at different contents of maleated nanolignin and different pressing times were evaluated according to JAS No. 233:2003 (Table 4; Figs. 5, 6). The shear strength and associated wood failure percentages of plywood increased by adding a higher maleated nanolignin content and longer pressing time (Figs. 5, 6). The lowest shear strength value of 0.23 MPa and wood failure percentage (10%) was obtained for control plywood panels at 3 h press time. The highest one was obtained for the plywood bonded with 20% maleated nanolignin after cold pressing for 24 h, with shear strength value of 0.82 MPa and wood failure percentages of 80%. Chemical modification of nanolignin by maleic anhydride increases its reactivity, shortened the cold-pressing time and improves the bonding strength of the plywood panels. Reduction of pressing time is very important for industry as it can increase the production capacities for manufacturing plywood panels by cold pressing. The result of wood failure percentages also inferred that a higher maleated nanolignin content and longer pressing time enhanced the adhesion strength and increased the percentage wood failure.

The bending strength of plywood bonded with PVOH–lignin–hexamine blends at different modified nanolignin contents and prepared for different pressing times are

**Table 4** Properties of plywood bonded with PVOH–lignin–hexamine-based adhesives at different maleated lignin contents and pressing times

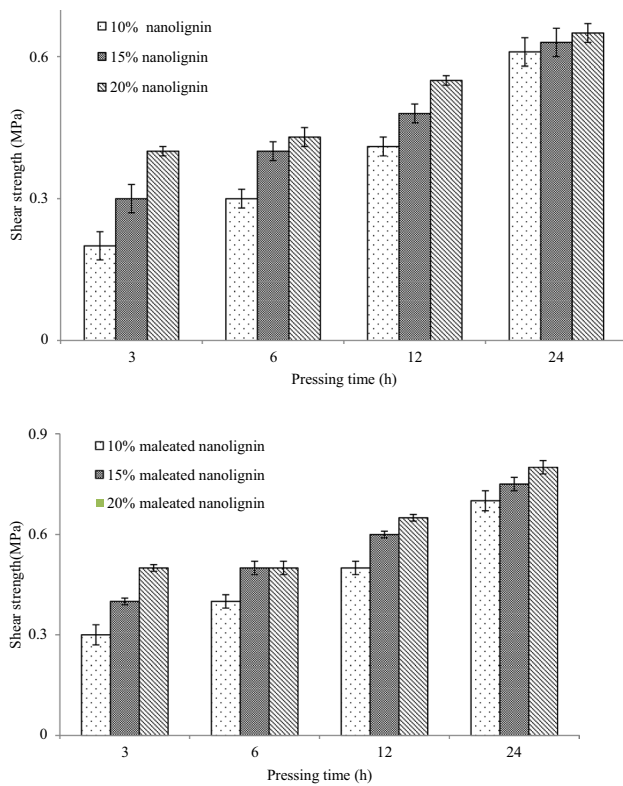| Nanolignin content (%) | Pressing time (h) | Density (g/cm³) | MOE (MPa) | MOR (MPa) | Water absorption (%) |
|---|---|---|---|---|---|
| Control (LPH15) | 12 | 0.42 | $2130 \pm 50$ | $15 \pm 1$ | $16 \pm 0.8$ |
| 10 | 3 | 0.42 | $2220 \pm 55$ | $17 \pm 2$ | $13 \pm 0.5$ |
| | 6 | 0.42 | $2431 \pm 26$ | $19 \pm 3$ | $12 \pm 0.3$ |
| | 12 | 0.42 | $2514 \pm 24$ | $22 \pm 1$ | $10 \pm 0.7$ |
| | 24 | 0.42 | $2626 \pm 14$ | $23 \pm 3$ | $9 \pm 0.4$ |
| 15 | 3 | 0.42 | $2303 \pm 44$ | $18 \pm 1$ | $12 \pm 0.3$ |
| | 6 | 0.42 | $2490 \pm 12$ | $20 \pm 3$ | $11 \pm 0.1$ |
| | 12 | 0.42 | $2603 \pm 25$ | $23 \pm 2$ | $9 \pm 0.3$ |
| | 24 | 0.42 | $2733 \pm 14$ | $25 \pm 1$ | $8 \pm 0.2$ |
| 20 | 3 | 0.42 | $2403 \pm 15$ | $19 \pm 3$ | $11 \pm 0.3$ |
| | 6 | 0.42 | $2522 \pm 45$ | $22 \pm 1$ | $9 \pm 0.2$ |
| | 12 | 0.42 | $2703 \pm 24$ | $25 \pm 3$ | $7 \pm 0.2$ |
| | 24 | 0.42 | $2873 \pm 44$ | $27 \pm 2$ | $6 \pm 0.1$ |

**Fig. 5** Influence of different nanolignin contents on the shear strength of plywood at different pressing times
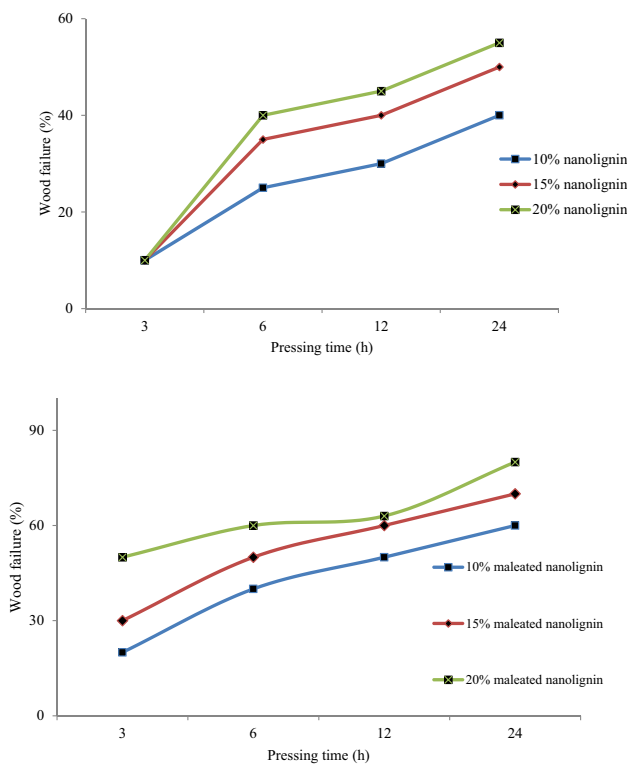


**Fig. 6** Influence of different nanolignin contents on the wood failure of plywood at different pressing times

shown in Table 4. The properties of the LPH resin with 15% nanolignin as a control sample were also reported in Table 4. The result showed that adding a higher maleated nanolignin content and increasing the pressing time did not affect the density of the manufactured plywood panels. The results showed that MOE and MOR values of plywood increased by adding a higher modified nanolignin content and a longer pressing times. The highest MOR (27 MPa) and MOE (2873 MPa) values were obtained for plywood bonded with PVOH–hexamine and 20% maleated nanolignin after cold pressing for 24 h. The results implied that increasing the maleated nanolignin content increased the cohesion strength of the PVOH–lignin–hexamine-based adhesives. This result was supported by the solids content and the average viscosity of the adhesive, which increased with higher addition of maleated nanolignin. Makri et al. (2022) and Sun et al. (2015) indicated that the tensile strength and Young's modulus of the bio-based poly(lactic acid) (PLA) composite were significantly improved by the addition of nanolignin, due to the rigidity of the lignin's structure, which consists of highly concentrated benzene rings, as well as due to stereocomplexation, which promotes the load transfer.

The water absorption of the panels after 24 h soaking in distilled water is reported in Table 4. It can be seen that increasing the amount of maleated lignin nanoparticles decreased the water absorption of the panels. Improving dimensional stability of the plywood panels by increasing content of nanolignin can be due to the hydrophobic nature of lignin (Younesi-Kordkheili and Pizzi 2023). In Table 4, the panels bonded with the mLPH resin have lower water absorption compared to those made from the LPH resin with 15% nanolignin. The lower water absorption of the panels made from mLPH can be attributed to the difference in the type and the amount of bridges formed between the reactive sites compared to LPH resin. Younesi-Kordkheili and Pizzi (2022) showed that the addition of maleated lignin to thermoset resins can increase dimensional stability of the panels bonded with them. They also indicated that lower water absorption was obtained by progressively increasing the lignin nanoparticles proportion in phenol-lignin-glyoxal resin (Younesi-Kordkheili and Pizzi 2023). Finally it must be noted that it is possible that the lignin recovered using acidification and water washing method may still have some ash. Also, soda pulping of bagasse should result in recovered lignin that may contain xylan depending on pulping conditions. The amount of xylan and ash can significantly influence the properties of lignin which were not quantified in this research.

# 4 Conclusion

In the research work presented here a cold-setting plywood adhesive was developed based on PVOH–maleated nanol-ignin–hexamine blends. The influence of maleated nanol-ignin content (10%, 15%, and 20%) and cold-pressing time (3, 6, 12, and 24 h) on physical, thermal, and mechanical properties of plywood was investigated. This study showed that an increased maleated nanolignin content increased the solids content and viscosity of the adhesive. Thermal behavior analysis indicated that increasing maleated nanol-ignin content from 10 to 20% progressively decreases the peak temperature of the resins prepared. The addition of 20% maleated nanolignin in the adhesive and using cold-pressing times of 24 h can produce plywood with physical and mechanical properties which meet the EN standard requirements. Based on the finding of this research work, it is then possible to manufacture environment friendly ply-wood panels bonded with PVOH–maleated nanolignin–hex-amine-based adhesive also by a cold-pressing process.

## Declarations

## References

Bortolatto R, Bittencourt PRS, Yamashita F (2022) Biodegradable composites of starch/polyvinyl alcohol/soybean hull (*Glycine max* L.) produced by thermoplastic injection. J Appl Polym Sci 139(23):1–25

Dunky M (2021) Wood adhesives based on natural resources: a critical review: part III tannin- and lignin-based adhesives. In: Mittal KL (ed) Progress in adhesion and adhesives, vol 6. Wiley, Hoboken, pp 383–529

Ganewatta MS, Lokupitiya HN, Tang C (2019) Lignin biopolymers in the age of controlled polymerization. Polymers 11(7):1–44

Gao S, Liu Y, Wang C, Chu F, Xu F, Zhang D (2020) Structures, prop-erties and potential applications of corncob residue modified by carboxymethylation. Polymers 12(3):1–15

Garlapati VK, Chandel AK, Kumar SJ, Sharma S, Sevda S, Ingle AP, Pant D (2020) Circular economy aspects of lignin: towards a lignocellulose biorefinery. Renew Sustain Energy Rev 130(109977):1–21

Kamoun C, Pizzi A (2000a) Mechanism of hexamine as a non-aldehyde polycondensation hardener, Part 1, hexamine decomposition and reactive intermediates. Holzforschung 52(1):16–19

Kamoun C, Pizzi A (2000b) Mechanism of hexamine as a non-aldehyde polycondensation hardener, Part 2: recomposition of intermediate reactive compound, Part 2: hexamine recomposition and reactive intermediates. Holzforschung 52(3):66–67

Kamoun C, Pizzi A, Zanetti M (2003) Upgrading of MUF resins by buffering additives—Part 1: hexamine sulphate effect and its lim-its. J Appl Polym Sci 90(1):203–214

Lubis MAR, Labib A, Akbar F, Nuryawan A, Antov P, Kristak L, Papadopoulus N, Pizzi A (2022) Influence of lignin content and pressing time on plywood properties bonded with cold-setting adhesive based on poly (vinyl alcohol), lignin, and hexamine. Polymers 14(10):1–19

Makri SP, Xanthopoulou E, Klonos P, Grigoropoulos A, Kyritsis A, Tsachouridis K, Anastasiou A, Deligkiozi L, Nikolaidis N, Biki-aris DN (2022) Effect of micro- and nano-lignin on the thermal, mechanical, and antioxidant properties of biobased PLA–lignin composite films. Polymers 14(23):1–25

Rico-García D, Ruiz-Rubio L, Pérez-Alvarez L, Hernández-Olmos SL, Guerrero-Ramírez GL, Vilas-Vilela JL (2020) Lignin-based hydrogels: synthesis and applications. Polymers 12(1):1–23

Siahkamari M, Emmanuel S, DB H, Nejad M (2022) Lignin-glyoxal: a fully biobased formaldehyde-free wood adhesive for interior engi-neered wood products. ACS Sus Chem Eng 10(11):3430–3441

Sun Y, Yang L, Lu X, He C (2015) Biodegradable and renewable poly(lactide)–lignin composites: synthesis, interface and tough-ening mechanism. J Mater Chem A 3(7):3699–3709

Younesi-Kordkheili H (2022) Maleated lignin coreaction with phenol-formaldehyde resins for improved wood adhesives performance. Int J Adhes Adhes 113(103080):1–6

Younesi-Kordkheili H, Pizzi A (2017) A comparison between lignin modified by ionic liquids and glyoxalated lignin as modifiers of urea-formaldehyde resin. J Adhes 93(14):1120–1130

Younesi-Kordkheili H, Pizzi A (2018) Improving the physical and mechanical properties of particleboards made from urea–glyoxal resin by addition of pMDI. Eur J Wood Prod 76(6):871–876

Younesi-Kordkheili H, Pizzi A (2020) Improving the properties of urea-lignin-glyoxal resin as a wood adhesive by small addition of epoxy. Int J Adhes Adhes 102(2):1–6

Younesi-Kordkheili H, Pizzi A (2022) Nanolignin, a coupling bio-agent for wood-plastic composites. J Renew Mater 11(5):2075–2083

Younesi-Kordkheili H, Pizzi A (2023) Improving the properties of phenol-lignin-glyoxal as a wood adhesive by lignin nanoparticles. Eur J Wood Prod 81:507–512

Younesi-Kordkheili H, Kazemi-Najafi S, Behroz R (2017) Influence of nanoclay on urea-glyoxalated lignin-formaldehyde resins for wood adhesive. J Adhes 93(6):431–443