Bio-based Adhesive Mixtures of Pine Tannin and Different Types of Lignins

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Tannins and lignins, which are natural phenolic compounds, are gaining substantial interest in biobased wood adhesive research. In this study, several different biobased tannin-lignin-hexamine adhesive mixtures were prepared and compared in a lap-joint shear strength test. In the first part, the suitability of different types of kraft and organosolv lignins as part of the mixture used in the production of biobased adhesives (in combination with pine tannins) were observed. It was found that biobased adhesive mixtures containing kraft lignins performed significantly better than those that contained organosolv lignins. In the second part, unmodified kraft lignins were mixed with pine tannin in different proportions, ranging from 0% to 100%. The pressing parameters were set to 150 °C for 15 min after performing oscillatory tests with a rheometer. Pure tannin adhesives performed the best, but no significant differences or a trend line were observed among adhesives containing different proportions of tannins and lignins.

Keywords: Lignin; Tannin; Wood adhesives; Pressing parameters; Degree of cure; Rheometer; Shear strength

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INTRODUCTION

Biobased adhesives derived from natural sources are gaining substantial interest due to the environmental concerns related to synthetic adhesives. Due to their phenolic origin and wide natural abundance, tannins and lignins are considered to be promising natural components for the replacement of synthetic adhesives. It was determined that the side products of the European wood and paper industry, which are now burned for energy production, contain higher amounts of lignins and tannins in comparison to the synthetic adhesives (in terms of mass) that are produced in Europe. This makes the holistic replacement of synthetic adhesives with biobased tannin-lignin adhesives possible (Saražin *et al.* 2020).

The first research works on the use of tannins in wood adhesives were performed in 1950 by Dalton (Pizzi 1978). Since then, much work has been done on improving tannin adhesive formulations. The first decades of studies were mostly dedicated to replacing part of the phenol and resorcinol in phenol (resorcinol) formaldehyde adhesives. However, later research also focused on the production of tannin adhesives without the addition of formaldehyde. The most commonly used hardeners then were hexamethylenetetramine (hexamine), glyoxal, and furfuryl alcohol (Pizzi 2016). One of the most promising formulations from that era is the pine/pecan tannin adhesive with a 6.5% addition of hexamine, which was also used industrially (Pizzi *et al.* 1997).

Tannins from wood and bark are divided into two classes of chemical compounds: hydrolysable tannins and condensed tannins. Less reactive hydrolysable chestnut tannins were considered as promising for adhesive formulations in some past research applications (Thebault *et al.* 2014; Ghahri and Pizzi 2018; Marini *et al.* 2020). Due to their higher reactivity, condensed tannins are more appropriate for usage in adhesive production than hydrolysable tannins. From European tree species, condensed tannins can be extracted from the bark of major coniferous species, *e.g.*, pine (*Pinus* sp.), spruce (*Picea sp.*), fir (*Abies alba*), larch (*Larix decidua*), and Douglas fir (*Pseudotsuga menziesii*) (Fengel and Wegener 1989; Bianchi *et al.* 2015). However, the bark of these tree species contain a smaller amount of tannins and most need to be further purified, which makes the extraction more expensive, in comparison to the quebracho (*Schinopsis* sp.), mimosa (*Acacia mearnsii*), and chestnut (*Castanea sativa*) extraction processes.

Since condensed tannins from European tree species are relatively expensive for large-scale adhesive production, cheaper technical lignins started to gain attention in the 1980s. Large quantities of technical lignin are produced as a side product of the pulp and paper industry. Since lignins are less reactive than tannins, they were primarily used as an additive to other adhesives. The reactivity of lignins can be increased with chemical (Krzysik and Young 1986; El Mansouri *et al.* 2007) or enzymatic (Batog *et al.* 2008) modification. The most appropriate technical lignins for large-scale adhesive production are produced by the kraft process (El Mansouri and Salvado 2006). Later research studies were successful in increasing the added amount of lignins up to 50% for a tannin adhesive mixture (Mansouri *et al*. 2011; Navarrete *et al.* 2012). Due to its lower reactivity, which resulted in needing longer pressing times, lignins were only used industrially at a small level as the additive to formaldehyde-based adhesives (Pizzi 2016).

The development of new adhesive formulations and their successful application in the wood industry required the characterizing of the curing process and later defining the optimal pressing parameters. Several such studies were carried out on commercial synthetic adhesives, but only a few were performed on biobased ones. The curing process characterization of biobased adhesive materials was studied with liquefied wood (Ugovšek and Šernek 2013), tannin adhesives (Pizzi and van der Spuy 1980; Garnier *et al.* 2002a,b), tannin foams (Basso *et al.* 2013; Čop *et al.* 2015), tannin based epoxy resin (Benyahya *et al.* 2014), and lignin-based epoxy resin (Ferdosian *et al.* 2015).

The first aim of this study was to explore the suitability of different types of lignins for the production of biobased adhesives in combination with tannins and to select the most promising lignin. The second aim was to determine the impact of the mixing ratio of the biobased adhesives (the selected lignin to tannin ratio) on the shear strength of the adhesive bond.

EXPERIMENTAL

The research was divided into two parts. In the first part, pine tannin and commercially available technical lignins with several modifications were used. The biobased tannin-lignin adhesive mixtures were prepared with each type of lignin, and then the screening test was performed to define which lignin was the most suitable for preparation of a biobased tannin-lignin adhesive. In the second part, the most promising type of lignin was studied further in terms of its suitability for biobased adhesive development. The properties of the adhesive, *i.e.*, the pH value, water content, and pressing parameters were optimized, and then the research focused on the influence that the ratio of tannins to lignins in the adhesive mixture had on the bonding performance.

Materials

The components used in the preparation of the biobased adhesive formulations were as follows: pine tannin (T) powder (92% to 94% polyphenolic content) (Phenopin, DRT, Dax, France), 40% water solution of hexamine (99% pure hexamethylenetetramine) (Carlo Erba Reagents S.A.S., Val de Reuil, France), 33% water solution of NaOH (99% pure sodium hydroxide) (Fischer Scientific, Loughborough, U. K.), and different types of lignins:

- Kraft lignins (KL) tradename Indulin AT (LOT: KH22M, Ingevity Corporation, North Charleston, SC)
- Oxypropylated kraft lignins (PKL) were generated *via* an addition reaction with propylene oxide and KL in an alkaline solution (Fraunhofer ICT, Pfinztal, Germany)
- Glycidolated kraft lignins (GKL) were generated *via* an addition reaction with 2,3-epoxy -1-propanol (glycidol) and KL in an alkaline solution (Fraunhofer ICT, Pfinztal, Germany)
- The soluble kraft lignin fraction (KLsol) was generated using a successive precipitation process using water/acetone mixtures and water as a non-solvent (Fraunhofer ICT, Pfinztal, Germany)
- Organosolv lignins (OL) were generated *via* the acid-catalyzed ethanol/water organosolv-cooking of standard beechwood chips (Fraunhofer CBP, Leuna, Germany)
- Oxypropylated organosolv lignins (POL) were generated *via* an addition reaction with propylene oxide on OL in alkaline solution (Fraunhofer ICT, Pfinztal, Germany)
- Glycidolated organosolv lignins (GOL) were generated *via* an addition reaction with 2,3-epoxy -1-propanol (glycidol) and OL in an alkaline solution (Fraunhofer ICT, Pfinztal, Germany)

First Part – Screening Test for Lignin Selection

Preparation of biobased adhesives from tannins and different types of lignins

The adhesive mixtures from the first part of the research are presented in Table 1.

Table 1. Tested Biobased Adhesives Produced from Tannins and Different Types of Lignins

Adhesive Name	Adhesive pH Value	Tannin : Lignin : Hexamine Dry Weight Ratio
T-KL	12.7	50 : 50 : 6
T-PKL	12.6	
T-GKL	12.4	
T-KLsol	12.1	
T-OL	12.6	
T-POL	12.9	
T-GOL	13.1	

The mixtures were prepared according to the following steps: (1) 25 weight units of lignins were dissolved in 50 weight units of distilled water and then 25 weight units of tannins were added and mixed; (2) the pH value was increased to the range 12 to 13 *via* the addition of NaOH; (3) at the end of the pH increasing process 7.5 weight units of a 40% hexamine solution (6% dry weight of hexamine to the dry weight of the lignins and tannins) were added. Since the adhesive mixtures were not optimized regarding the water content and pH value, there were some difficulties with the solubility of all the components in water; however, the results were mutually comparable for the purpose of the screening test.

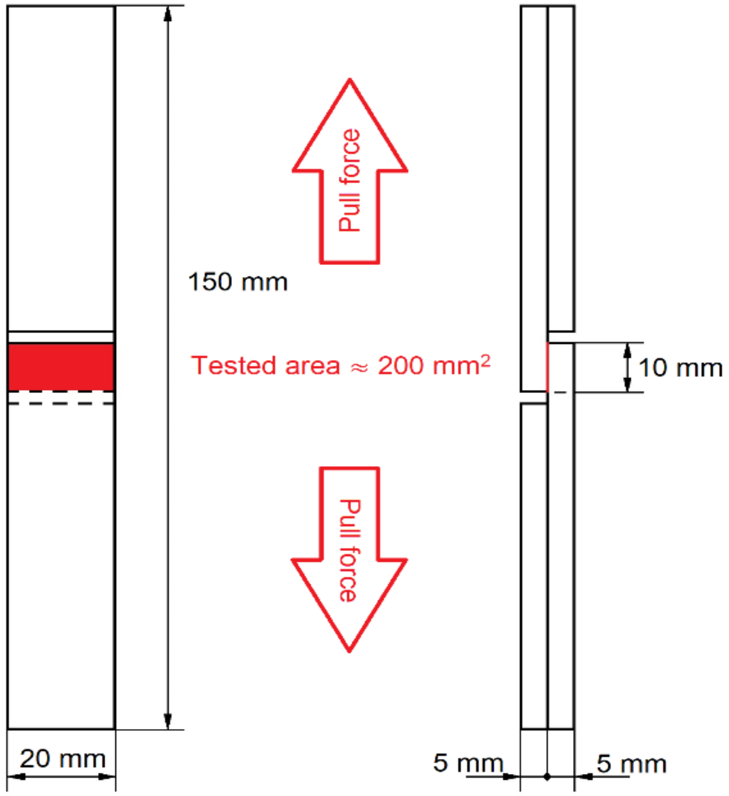

Fig. 1. Lap joint test piece (EN 205, 2016)

Shear strength test

The shear strength of the adhesive bonds was tested according to EN standard 205 (2016). Two 5 mm thick beech (*Fagus sylvatica*) lamellae, conditioned under standard atmospheric conditions at 20 °C and 65% relative humidity (20/65), were bonded in a hot press for 12 min at 170 °C and a pressure of 1.5 N/mm^2. Bio-based tannin-lignin adhesive was applied to both the lamellae (a total amount of 250 g/m^2). The prepared boards were cut into the lap joint test pieces (as shown in Fig. 1) and conditioned at standard atmospheric conditions (20/65) for 7 d.

After conditioning, 10 lap joint test pieces from each series were tested on a Zwick Z005 universal testing machine (Zwick Roell, Ulm, Germany). The constant movement of traverse (6 mm/min) applied force to the testing piece until rupture occurred. The maximum achieved force was measured and compared with the lap joint area, to express the shear strength in N/mm^2.

The shear strength data of each adhesive mixture tested were statistically analyzed using an ANOVA pairwise comparison with the other tested adhesive mixtures. The difference was expressed as statistically significant if the *p*-value was lower than 0.05.

Second Part – Defining the Optimal Tannin to Lignin Ratio

Preparation of biobased adhesives with different tannin to lignin ratios

To achieve appropriate solubility of the kraft lignins and pine tannins, the target pH value was decreased, and the water content in the mixture was increased (in comparison to the experiment in the first part). It was found that a pH value between 11 and 12 and a dry mass percentage of 40% was an adequate compromise for all the tested adhesive mixtures.

All the adhesive mixtures were prepared following same steps: (1) the lignins (if present in the mixture) were mixed in distilled water, then the tannins were added and mixed (40 weight units of lignin and tannin powder were dissolved in 60 weight units of water); (2) the pH value was adjusted to 11 to 12 *via* the addition of NaOH; (3) at the end of the pH increasing process a hexamine solution was added (6 weight units as 6% dry weight of hexamine to the dry weight of the lignins and tannins). Different adhesive mixtures were prepared with various ratios of tannins and lignins (as shown in Table 2). For comparison, a reference mixture (T100R), similar to the industrially applied adhesive from Pizzi *et al.* (1997) (with a pH value of 6.5), was also tested.

Table 2. Tested Biobased Adhesives with Different Tannin to Lignin Ratios

Adhesive Name	Tannin : Lignin : Hexamine Dry Weight Ratio	pH Value
T0-L100	0 : 100 : 6	11.6
T20-L80	20 : 80 : 6	11.7
T40-L60	40 : 60 : 6	11.3
T50-L50*	50 : 50 : 6	11.3
T60-L40	60 : 40 : 6	11.4
T80-L20	80 : 20 : 6	11.4
T100-L0	100 : 0 : 6	11.0
T100R	100 : 0 : 6	6.5
Note: * = Only used for rheology		

Determination of the pressing time and temperature

A pressing temperature of 150 °C was assumed to be sufficient, according to preliminary shear strength tests. In order to determine the pressing time, the temperature transition to the bond line in the hot press was recorded, and then the curing processes of the adhesives were examined *via* oscillatory tests on a rheometer.

The temperature transition from a hot press (with a pressing temperature of 150 °C) to the adhesive bond line was observed with a K-type thermocouple, placed in the central part of the bond line of the testing board, *i.e.*, two 5 mm thick beech lamellas. Oscillatory tests were carried with an ARES G2 rheometer (TA Instruments, New Castle, DE). Adhesive was applied to disposable aluminum discs (plates) with a 25 mm diameter. The parallel plate methodology was used with a gap of 0.5 mm. The sinusoidal oscillation frequency of the lower plate was 1 Hz, with a peak strain of 0.007.

Based on the temperature profile of the adhesive bond line during hot pressing, three characteristic temperatures (100 °C, 125 °C, and 150 °C) were defined as representative to describe the curing process of the tested adhesives, and these temperatures were further used as target temperatures for the oscillatory tests. Thus, three temperature regimes were included in the oscillatory tests; each started at the room temperature (25 °C) then the temperature was increased at a set heating rate of 60 °C/min to the target value and remained constant. The real temperature in the rheometer oven was observed *in situ*.

The resulting storage modulus (G'), expressed in MPa, was recalculated to the degree of cure ($\alpha(t)$), according to Eq. 1,

$$\alpha(t)_{REO} = 1 - \frac{G'_{max} - G'(t)}{G'_{max} - G'_{min}} \tag{1}$$

where G'_{min} and G'_{max} are the minimum and maximum storage shear modulus (G') and $G'(t)$ is the value of the storage modulus at time t (Čop *et al.* 2015).

The oscillatory tests were performed for the T100-L0, T50-L50, and T0-L100 adhesive mixtures. For pressing time determination, the average curves of all different adhesive mixtures were calculated. In the next step, the curves were tuned, taking into account the heating time of the rheometer oven and the actual heating process of the hot press.

Shear strength test

The shear strengths of the adhesive bonds were tested following the same procedure as described in the first part. The only difference was that the boards in the second part were larger and had different pressing conditions than in the first part. They were hot-pressed for 15 min at 150 °C and a pressure of 1.2 N/mm^2.

RESULTS AND DISCUSSION

Selection of the Most Promising Adhesive Mixture `

Shear strength of the biobased adhesive bonds synthesized from tannins and different types of lignins

The shear strength of the adhesive bonds of different biobased adhesives prepared from pine tannins and different types of lignins are shown in Fig. 2. In general, adhesive mixtures in which kraft lignins were used had a better performance than those made with organosolv lignins. The highest shear strength results were observed when either KLsol, GKL, or KL lignins was used in the adhesive mixture in combination with tannins.

The required threshold shear strength value for several wood adhesives (for structural and non-structural applications), after being conditioning at standard atmospheric conditions (20/65) is 10 N/mm^2. Although none of those mixtures achieved this threshold value, they all have the potential to meet this requirement with the optimization of the adhesive mixture and pressing parameters. The differences in shear strength among these adhesive mixtures were not significant (all p-values were greater than 0.85). The shear strength results for the mixtures that used PKLs or any of the organosolv lignins were significantly lower than the other mixtures (all p-values were less than 0.01) and were not sufficient for further development. Because less-modified lignins represent a more reasonable solution, in terms of economics and time, the decision was made to exclusively investigate unmodified kraft lignins (KL).

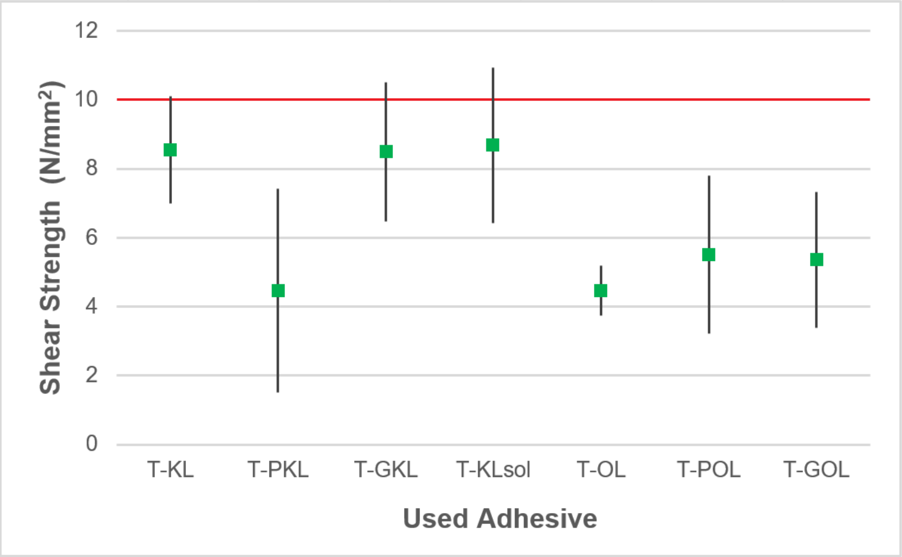

Fig. 2. Shear strength of the biobased adhesive bonds synthesized from tannins and different types of lignins

Influence of Tannin to Kraft Lignin Ratio on Adhesive Bond Performance

Temperature transition to the bond line in the hot press

The temperature in the adhesive bond line increased throughout the pressing process (as a function of time) and approached the press temperature (150 °C) at the end of pressing (Fig. 3). At the beginning, when the press closed, the temperature rapidly increased and reached 100 °C after 1.1 min. Then, a strong evaporation of water from the adhesive bond remarkably slowed down the increase of temperature, which slowly rose to 125 °C after 8.1 min and approached the press temperature (145.9 °C) after 15 min.

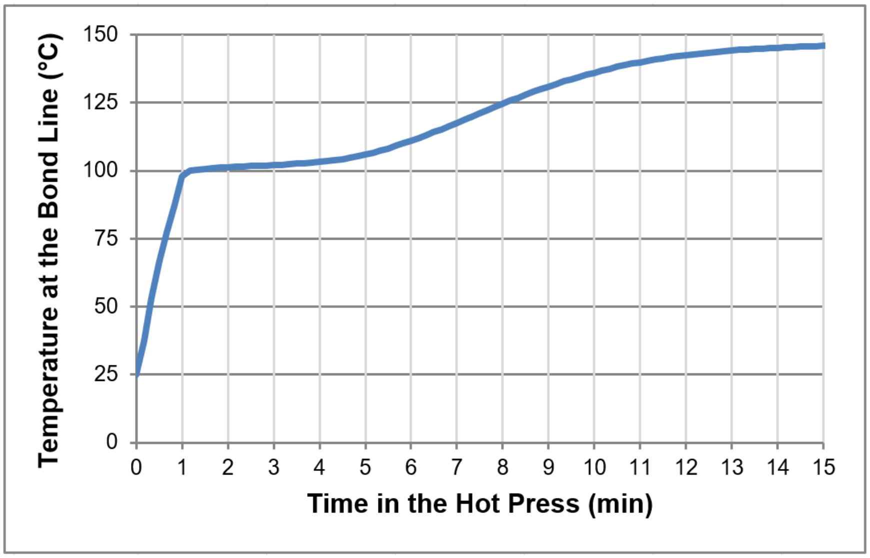

Fig. 3. Increase in the temperature inside the bond line during the hot pressing process

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Determination of the pressing time

For characterization of the curing process and determination of an appropriate pressing time, the average degree of cure among the T100-L0, T50-L50, and T0-L100 curves was calculated (Fig. 4). It was observed that at 150 °C most of the curing was done in the first 5 min from the onset of cure; however, at 125 °C and at 100 °C, the average values did not reach full cure of the adhesive in the observed time frame.

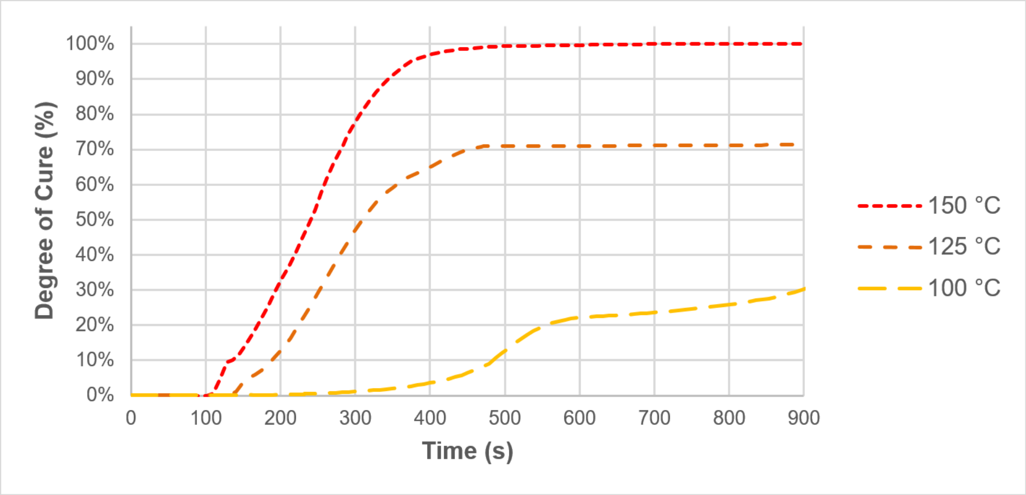

Fig. 4. Average degree of cure of the T100-L0, T50-L50, and T0-L100 adhesive mixtures at 100 °C, 125 °C, and 150 °C temperatures

On all performed measurements, the curing process started after the temperature reached 100 °C. This occurred after 2 min at a temperature of 150 °C and after 4 min at a temperature of 100 °C. This delay was later taken into account when defining an appropriate pressing time.

For the determination of a sufficient pressing time in a hot press, a combined curing profile was made based on the oscillatory test results (Fig. 5).

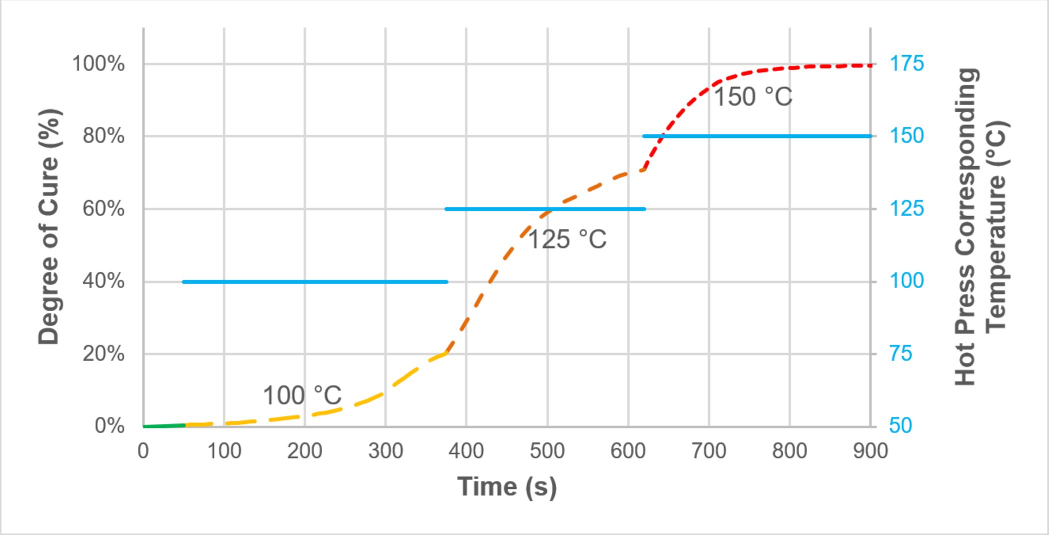

Fig. 5. Combined curing curve corresponding to its representative time/temperature intervals in the hot press

The oscillation curve obtained at 100 °C represented the curing process in the hot press at temperatures between 87.5 °C and 112.5 °C (between 50 s and 375 s); the oscillation curve obtained at 125 °C represented the curing process at temperatures between 112.5 °C and 137.5 °C (between 375 s and 620 s); and the oscillation curve obtained at 150 °C represented the curing process at temperatures greater than 137.5 °C.

Based on these assumptions, approximately 800 s at 150 °C was determined as sufficient time for the average adhesive to fully cure. The final pressing time was then set to be 15 min (900 s), which included for a delay in heating as well as for a safety reserve.

Shear strength of the biobased adhesives with different tannin to kraft lignin ratios

The shear strength results showed that the inclusion of lignins into an adhesive mixture with tannins had a great influence on the adhesive bond performance (as shown in Fig. 6). However, all panels bonded with the adhesive mixture with the presence of lignins did not reach the threshold value of 10 N/mm^2. Only two pure tannin adhesives (T100R and T100-L0) passed this requirement, and they significantly differed from all other mixtures containing lignins (all *p*-values were less than 0.001). No significant differences or a trend line among the adhesive mixtures with the presence of lignins were observed (all *p*-values were greater than 0.5).

However, the deficiency in shear strength of these adhesives to reach the threshold was approximately 10%, and it is assumed that with further optimization of the mixtures (water content and pH value adjustment) and pressing at higher temperatures, tannin-lignin adhesives have a potential for further development and application.

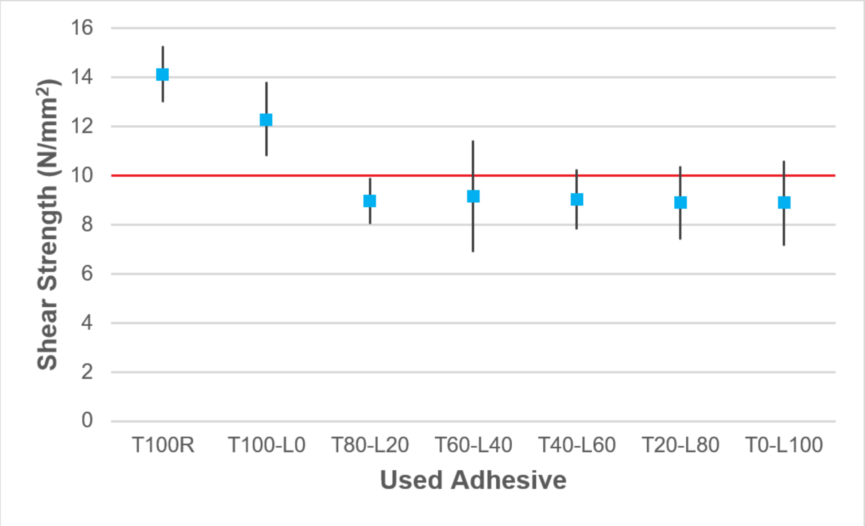

Fig. 6. Shear strength of the biobased adhesive bonds with different tannin to lignin ratios

CONCLUSIONS

1. Kraft lignins were more effective for biobased tannin-lignin adhesive preparation than organosolv lignins did. Adhesive mixtures with unmodified kraft lignins (KL), glycidolated kraft lignins (GKL), and the soluble fraction of kraft lignin (KLsol) showed similar shear strength results, which were significantly higher than all other adhesive mixtures with the presence of PKLs, OLs, GOLs, and POLs.

2. Pure tannin adhesives (T100-L0 and T100R) showed the best bonding performance. They achieved the threshold shear strength value of 10 N/mm^2 and had significantly higher shear strength values than the adhesive mixtures with the presence of lignins.
3. Increasing the proportion of lignins in the mixture did not influence the bonding performance of the adhesive. No significant difference or trend line was found among the T80-L20, T60-L40, T40-L60, T20-L80, and T0-L100 adhesive mixtures.

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