

# Crosslinking of Hardwood Lignin with Citric Acid for Sustainable Wood Adhesives

Ega Cyntia Watumlawar and Byung-Dae Park\*

*Department of Wood and Paper Science, Kyungpook National University, Daegu, 41566, Republic of Korea*

**Abstract:** The toxicity of petroleum-based crosslinkers raises health and environmental concerns, prompting interest in bio-based alternatives. This study reports the facile crosslinking of hardwood lignin (HWL) with citric acid (CA) as a bio-crosslinker for application as a lignin-based wood adhesive. HWL is characterized by GPC and DSC to determine its molecular weight and glass transition temperature, respectively. The successful crosslinking and esterification reactions of the HWL-CA-based resin are confirmed by the exothermic peaks observed in the DSC thermogram and by FT-IR analysis. The HWL-based adhesives with various proportions of CA meet the Korean standard shear strength requirement of 0.60 MPa, with 12% CA (HWL-CA12) giving the maximum value of 1.07 MPa. The successful surface modification of the veneer pre-treatment with CA is also confirmed by FT-IR analysis. Although the adhesive strength of the HWL-CA12 is decreased on the pre-treated veneer relative to the untreated veneer, it remains above the standard requirement on the veneers that were treated with 10% and 15% of CA. These findings demonstrate the potential of CA-crosslinked lignin as a sustainable alternative to petroleum-based wood adhesives.

**Keywords:** Crosslinking, Hardwood lignin, Citric acid, Wood adhesives.

## 1. INTRODUCTION

Lignin is the most abundant natural aromatic polymer and has attracted significant attention as a renewable raw material for various applications. It can be used as a sustainable feedstock for energy production, including the generation of biofuels and synthesis gases such as hydrogen [1]. In addition, lignin can be used in either its native or chemically modified forms for applications such as binders, emulsifiers, and components in composites and copolymers [2-5]. The effectiveness of these applications depends on the proportion of monolignol units, including syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) in the lignin, with these, in turn, depending on the type and source of the lignin. Thus, softwood lignin is widely used, due to its relatively high proportion of guaiacyl units, which make it generally more reactive [6], whereas the higher syringyl content of hardwood lignin makes it less reactive in many contexts. However, despite this limitation, recent studies have shown that hardwood lignin can be effectively utilized in the development of polyurethanes, hydrogels, and wood adhesives [7-9].

Environmental concerns about petroleum-based adhesives, particularly those containing formaldehyde, have accelerated interest in the use of lignin as a sustainable alternative. Lignin-based wood adhesives

have shown comparable and, in some cases, superior performance to that of conventional adhesives [10,11], with the crosslinking reaction playing a critical role in achieving a high performance. However, toxicity of commonly used synthetic crosslinkers such as epichlorohydrin, glyoxal, glutaraldehyde, epoxy, and formaldehyde raise significant environmental and health concerns [12-16]. Therefore, bio-based crosslinkers such as chitosan, furfuryl alcohol, and citric acid have emerged as safer and more environmentally friendly alternatives [11,17]. In particular, citric acid has shown potential as a green crosslinker for wood-based materials such as particleboard and plywood [18]. Citric acid is a naturally derived compound containing three carboxyl (COOH) groups, which can react with the hydroxyl (OH) groups in lignin to form ester bonds. However, this reaction typically requires elevated temperatures to proceed efficiently. Most previous studies have reported that temperatures above 100 °C are necessary to enable the reaction between citric acid and various biomaterials [19,20].

Hence, the present study investigates a facile method for crosslinking hardwood lignin with citric acid under room temperature conditions. This study also explores the effect of pre-treating the veneer with citric acid on the bonding performance. The esterification reaction and crosslinking between hardwood lignin and citric acid, along with the bonding between the citric acid-treated veneer and the crosslinked lignin, are examined.

\*Address correspondence to this author at the Department of Wood and Paper Science, Kyungpook National University, Daegu, 41566, Republic of Korea; E-mail: byungdae@knu.ac.kr

## 2. MATERIALS AND METHODS

### 2.1. Materials

Hardwood lignin (HWL) (birch wood) was purchased from 3PLINK International. Pyridine was obtained from Sigma Aldrich, USA. Hydrochloric acid (HCl) and acetic anhydride were obtained from Duksan Chemical, Korea. Citric acid (CA) was purchased from Daejung Chemical, Korea.

### 2.2. Methods

#### 2.2.1. Resin Preparation and Application

The preparation of the HWL-CA adhesive resin is shown schematically in Figure 1. First, oven-dried HWL was mixed with water at a lignin-to-water ratio of 1:3 and stirred at room temperature for 1 h. After that, various ratios of CA (12%, 15%, and 18% based on the total lignin mass) were added to the mixture and stirred at room temperature for 7 h until the desired viscosity of 200 mPa s was reached. The selection of CA concentration was based on preliminary trials. The resulting samples are designated hereafter as HWL-CA12, HWL-CA15, and HWL-CA18, respectively. These resins were each applied to untreated 150 mm x 150 mm x 2 mm veneers from radiata pine (*Pinus radiata*) at a glue spreading rate of 250 g/m<sup>2</sup> by using a rubber roller. The resin was then cold-pressed at 8.8 kPa for 15 min prior to hot pressing at 160 °C for 8 min at 1.5 MPa to examine the effect of CA proportion on the bonding performance.

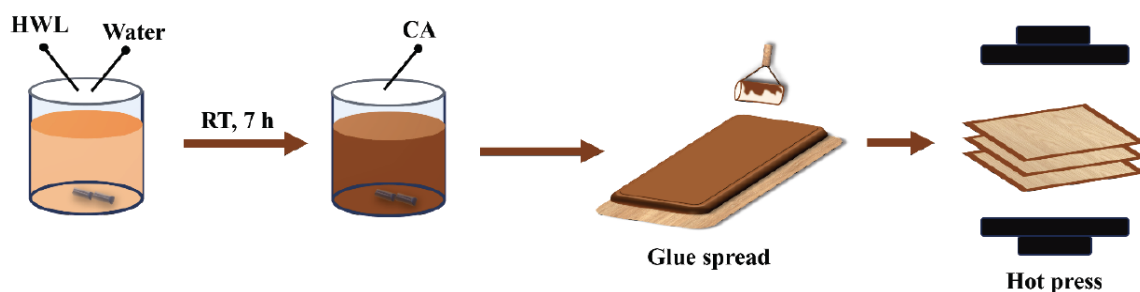


Figure 1: A schematic illustration of the HWL resin synthesis with CA.

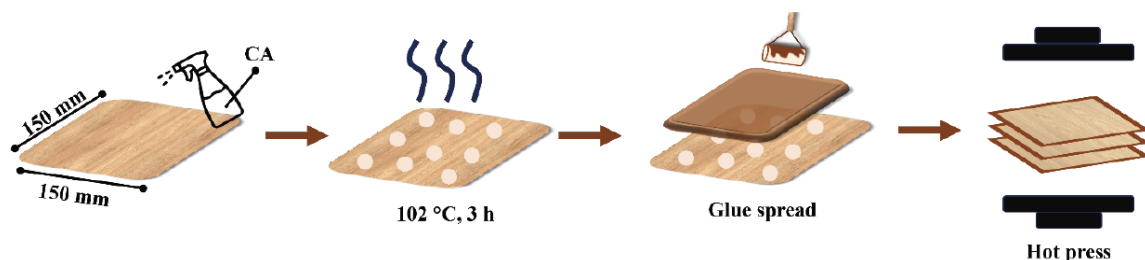


Figure 2: A schematic illustration of the veneer pre-treatment with CA and subsequent application of the HWL-CA12 adhesive.

The solid content (%) of the sample was measured in triplicate. Briefly, 1 g of resin was added to each labeled pan, placed in an oven at 105 °C for 3 h, and then weighed. The solid content was calculated by dividing the weight of the oven-dried resin by the initial weight of the resin and multiplying the result by 100%. The viscosity of the resin was determined using a Brookfield RVDV-II+ programmable viscometer with LV spindles at room temperature.

#### 2.2.2. Pre-Treatment of the Veneer

The methodology for pre-treating the veneer with CA is shown schematically in Figure 2. First, CA was dissolved in water to prepare 10%, 15%, and 20% (w/w) solutions. Each solution was then evenly sprayed onto the surface of a veneer at a glue spreading rate of 150 g/m<sup>2</sup> and dried in an oven at 102 °C for 3 h to set the reaction and control the moisture content. The resulting pre-treated veneer samples are designated hereafter as the T10, T15, and T20, respectively. After that, the HWL-CA12 resin was applied to each veneer at a glue spreading rate of 250 g/m<sup>2</sup> followed by cold and hot pressing to obtain the CA12-T10, CA12-T15, and CA12-T20, respectively.

### 2.3. Characterization

#### 2.3.1. Gel Permeation Chromatography (GPC)

The molecular weight of the HWL was determined via gel permeation chromatography; Waters Alliance e2695 system, Milford, MA, USA with a polystyrene

standard (molecular weight 1.06-2330 kDa). Prior to GPC, each sample was subjected to acetylation to enhance its solubility in tetrahydrofuran (THF). Approximately 2 mg of sample was dissolved in 1 mL of THF and then sonicated for 5 s before being filtered through a 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE) syringe filter. The GPC column temperature was 35 °C under an isocratic THF flow rate of 1 mL/min.

For the acetylation, 300 mg of lignin was stirred in 18 mL of 1:1 (v/v) pyridine:acetic anhydride at 200 rpm and room temperature for 48 h. The resulting solution was then poured into 250 mL of 0.1 N HCl to precipitate the product. The precipitate was collected by filtration using a 0.45  $\mu\text{m}$  Whatman nylon membrane. The lignin was then purified by washing three times with 0.01 N HCl and deionized water, followed by filtration.

### 2.3.2. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC; Discovery 25, TA instruments, New Castle, USA) was used to determine the glass transition temperature ( $T_g$ ) and exothermic reaction of the pristine HWL and the various HWL-CA resins. In the case of the HWL, the dried lignin sample (3-5 mg) was sealed in an aluminum pan with a lid and annealed by heating to 105 °C at a rate of 10 °C/min, followed by isothermal conditioning for 30 min before cooling to 0 °C. The DSC thermogram was then recorded by gradually increasing the temperature to 250 °C at a rate of 10 °C/min. For the HWL-CA resins, 10-12 mg of each sample was sealed in a high-pressure capsule pan to prevent water evaporation during the scan. The samples were then heated from 0 to 200 °C at a rate of 10 °C/min under a nitrogen flow of 50 mL/min.

### 2.3.3. FT-IR Spectroscopy

The properties of the HWL-CA based resins and CA-treated veneers were characterized by attenuated total reflectance infrared spectroscopy (ALPHA, Bruker Optics GmbH, Ettlingen, Germany). The Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000-400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and 32 scans. All FT-IR spectra were normalized for intensity comparison.

### 2.3.4. Adhesive Strength

All samples were conditioned for a minimum of 8 h before being cut and tested. The dry tensile shear strength (TSS) values of the plywood samples were measured according to a standard procedure (KS F 3101). Three specimens (25 mm x 80 mm x 6mm) of

each sample were recorded at a crosshead speed of 2mm/min using the peak load of a universal testing machine (H50KS, Hounsfield, Redhill, England).

## 3. RESULTS AND DISCUSSION

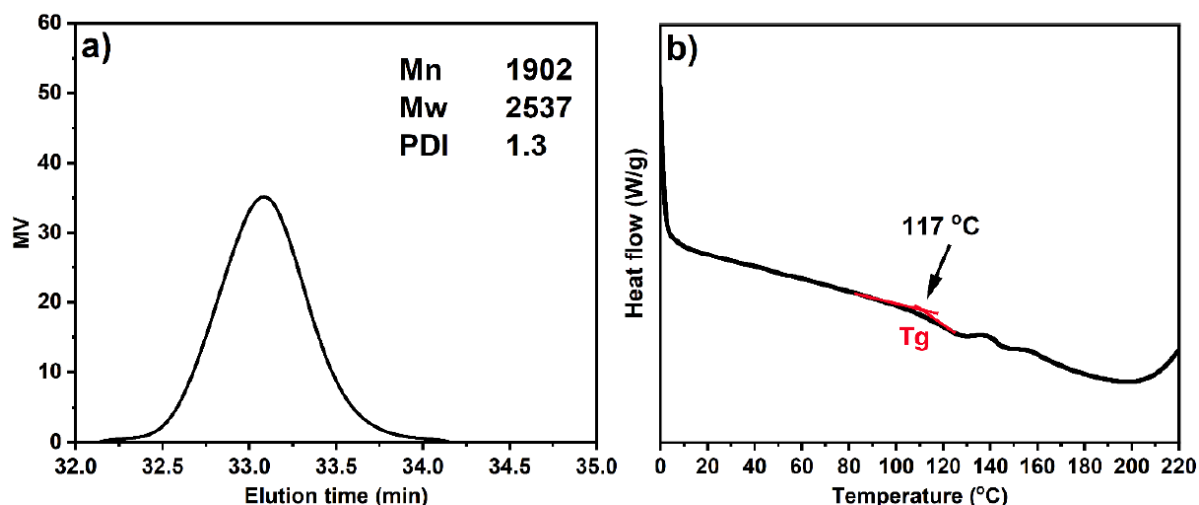
### 3.1. Properties of HWL

An understanding of the properties of raw materials prior to crosslinking is essential for optimizing the reaction conditions and achieving high-performance results. Hence, the material and thermal characteristics of the HWL are elucidated by its molecular weight (Mw) and glass transition temperature ( $T_g$ ) in Figure 3. Notably, the average Mw of HWL used herein is 2537 g/mol (Figure 3a), which is lower than that of other HWLs reported in the literature [21-23]. Such low Mw lignins typically exhibit a higher density of accessible ionizable groups, such as phenolic hydroxyl and carboxylic acid groups. These negatively charged functional groups contribute to a higher surface charge, thereby enhancing the electrostatic repulsion between particles and improving the colloidal stability compared to higher Mw lignins [23]. Moreover, the Mw influences both the recalcitrance of biomass and the potential for lignin valorization [21]. In addition, the HWL used herein exhibits a  $T_g$  of 117 °C (Figure 3b), which is relatively high compared to that of many conventional synthetic polymers [24]. The observed  $T_g$  is influenced by various factors, including functional groups, intermolecular bonding, thermal treatment, moisture content, impurities, and Mw [25]. Both the Mw and  $T_g$  suggest that the HWL possesses suitable characteristics for efficient crosslinking, particularly with CA, under mild conditions.

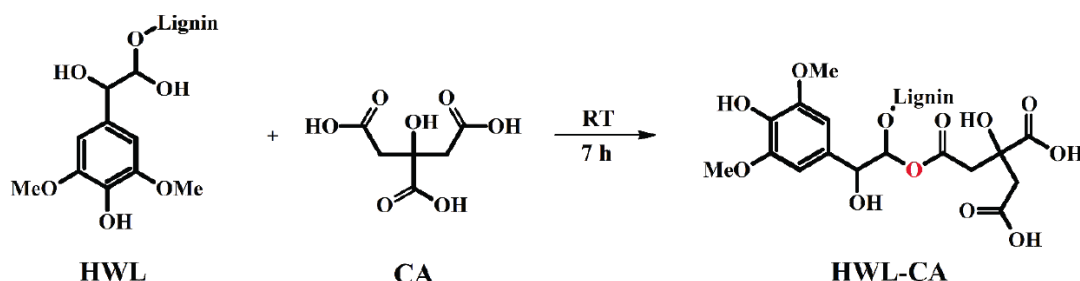
### 3.2. Crosslinking of HWL with CA

As shown schematically in Figure 4, the incorporation of HWL with CA is expected to result in the formation of a three-dimensional network via ester linkages between the carboxylic (-COOH) groups of CA and the aliphatic -OH groups of HWL.

The properties of the HWL-CA resins are summarized in Table 1. Here, both the solid content and viscosity are seen to increase with the increase in CA concentrations, giving maximum values of 26.5% and 650 mPa·s, respectively, for the HWL-CA18, and a minimum value of 24.4% and 250 mPa·s for the HWL-CA12. This increase in viscosity reflects enhanced intermolecular interaction and partial network formation at RT, suggesting a denser network due to ester and



**Figure 3:** Graphs of (a) the molecular weight (Mw) and (b) the glass transition temperature (T<sub>g</sub>) of the HWL.



**Figure 4:** The schematic reaction of HWL with CA.

hydrogen bonding interactions. These interactions reduce the mobility of lignin chains, leading to a more viscous resin. In addition, the solid contents are relatively low compared to those reported for petroleum-based adhesives, which typically exceed 40% [26,27]. The non-volatile solid content and viscosity clearly indicates a correlation between CA concentration and resin polymerization, with the increased viscosity and solid content of the HWL-CA18 likely arising from faster polymerization in the presence of the high concentration of CA. Nevertheless, all three HWL-CA resin remain in partially crosslinked state prior to exposure to the elevated temperatures required for full curing.

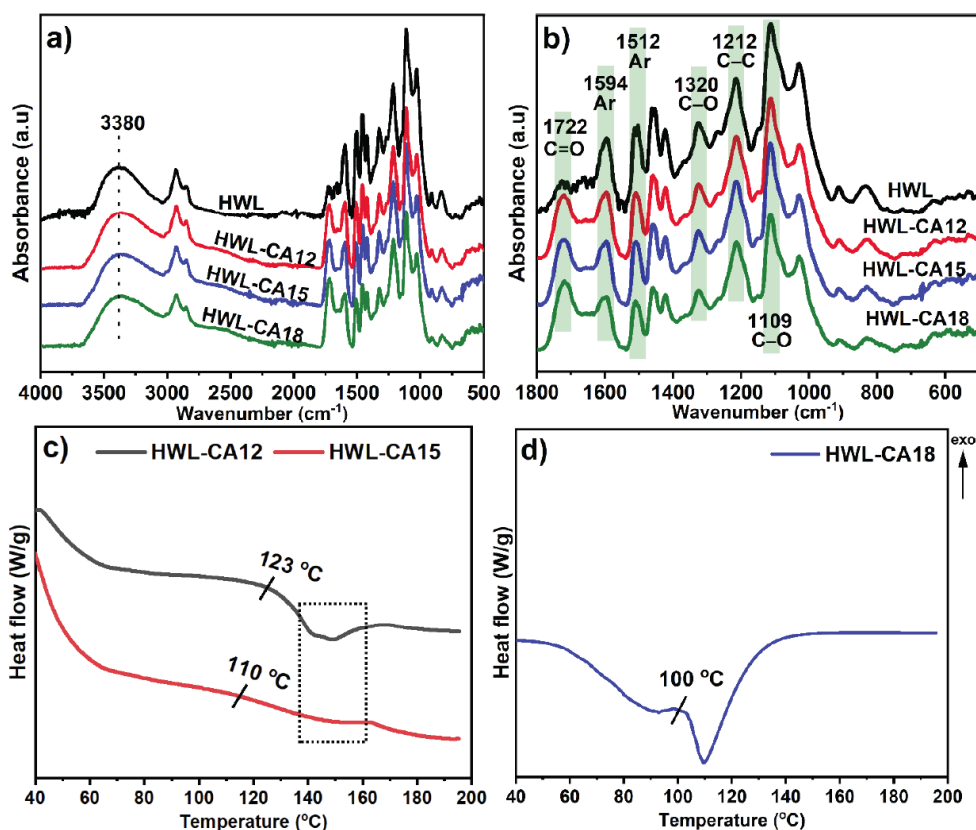
**Table 1: The Properties of Various HWL-CA Resins**

Sample	Solid content (%)	Viscosity (mPa s)
HWL-CA12	24.4	250
HWL-CA15	25.8	600
HWL-CA18	26.4	650

The esterification reaction of HWL with CA is confirmed by the FT-IR results in Figure 5a, and b.

Here, the broad band at 3380 cm<sup>-1</sup> is attributed to the -OH stretching vibrations and is clearly visible in all samples. Meanwhile, the peak at 1730 cm<sup>-1</sup> due to the carbonyl (C=O) stretching vibrations is seen to increase in intensity after CA addition, thereby confirming the incorporation of CA into the resin and supporting the occurrence of the esterification reaction. This is further confirmed by the enhanced peaks at 1320 and 1109 cm<sup>-1</sup>, which are associated with stretching vibrations of the ether and ester C-O bonds.

The effects of CA concentration on the curing behavior are revealed by the DSC results in Figure 5c and 5d. The addition of CA clearly influences the thermal behavior of each resin, particularly at elevated temperatures, with the presence of an exothermic peak indicating the occurrence of the crosslinking reaction in each sample [28]. The maximum curing temperatures are seen to be approximately 123 and 100 °C for the HWL-CA12 and HWL-CA18, respectively, while the HWL-CA15 exhibits a very small exothermic peak at around 110 °C. These results suggest that different reactions may occur depending on the relative amounts of available hydroxyl groups or other reactive structures within the resin. In addition, endothermic peaks



**Figure 5:** The FT-IR spectra (a and b) and DSC results (b and c) of the initial HWL and the various HWL-CA resins.

(indicated by the dotted rectangle in Figure 5c) are observed for both the HWL-CA12 and HWL-CA18. This can be attributed to the melting of CA molecules or CA-rich domains within the adhesive matrix. While melting is a physical phase transition, the CA molecules can undergo a thermally-induced chemical decomposition process known as thermolysis at higher temperatures [18,29]. Nevertheless, these results support the conclusion that crosslinking between HWL and CA can be initiated at room temperature, thus highlighting the potential of this system for the development of sustainable lignin-based wood adhesives.

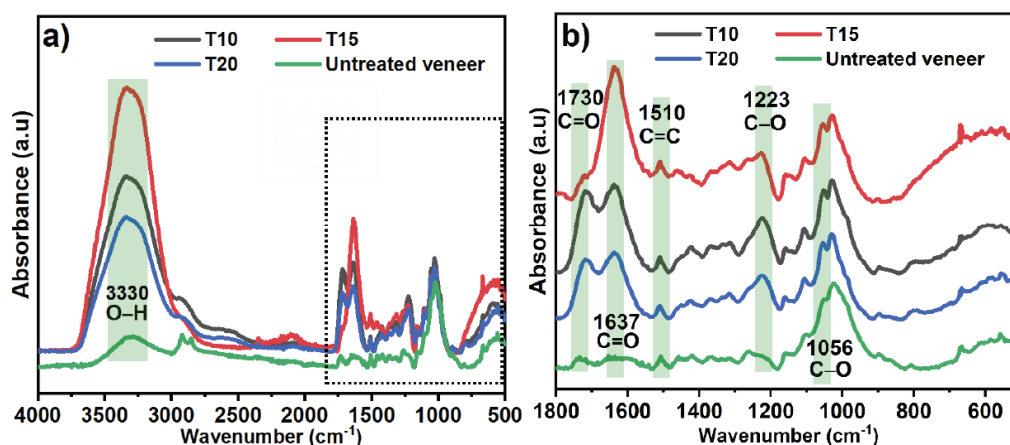
### 3.3. The Effects of Veneer Pre-Treatment with CA

Pre-treatment has offered valuable insights into enhancing the surface performance of wood materials, with CA being commonly used green solvent. As revealed by the FT-IR spectra in Figure 6, significant differences in chemical composition are observed for the CA-treated veneers compared to the untreated sample. Notably, the O-H stretching band at  $3300\text{ cm}^{-1}$  shows a clear increase in intensity after treatment (Figure 6a). Moreover, the zoomed-in view in Figure 6b reveals increased peak intensities at  $1730\text{ cm}^{-1}$  and  $1637\text{ cm}^{-1}$ , corresponding to the respective C=O stretching vibrations of holocellulose and lignin, and at  $1223\text{ cm}^{-1}$ ,

and  $1056\text{ cm}^{-1}$  due to the C=C and C-O stretching vibrations of wood [30,31]. Among the treated samples, the spectrum of the T15 exhibits the highest peak intensities, followed by T10 and T20. The enhanced absorbance in these regions confirms the esterification and etherification reactions between the -OH groups of wood components (cellulose, hemicellulose, and lignin) and -COOH groups of CA. These results suggest that dehydration condensation occurs during the reaction, which is consistent with previous findings [18,20,32].

### 3.4. Adhesion Performance

The adhesion performances of the various HWL-CA adhesives on the untreated veneers are demonstrated by the dry tensile shear strength (TSS) test results in Figure 7a. Here, the HWL-CA12 and HWL-CA18 exhibit comparable bonding strengths of 1.07 and 1.06 MPa, respectively, whereas the HWL-CA15 exhibits a significantly lower strength of 0.62 MPa. This may be attributable to an incomplete or less efficient crosslinking reaction, as suggested by the small exothermic peak in the abovementioned DSC thermogram (red profile, Figure 5b). The schematic reaction of crosslinking HWL-CA is provided in Figure 8. The results in Figure 7a indicate a non-uniform response to increasing CA concentrations, such that an

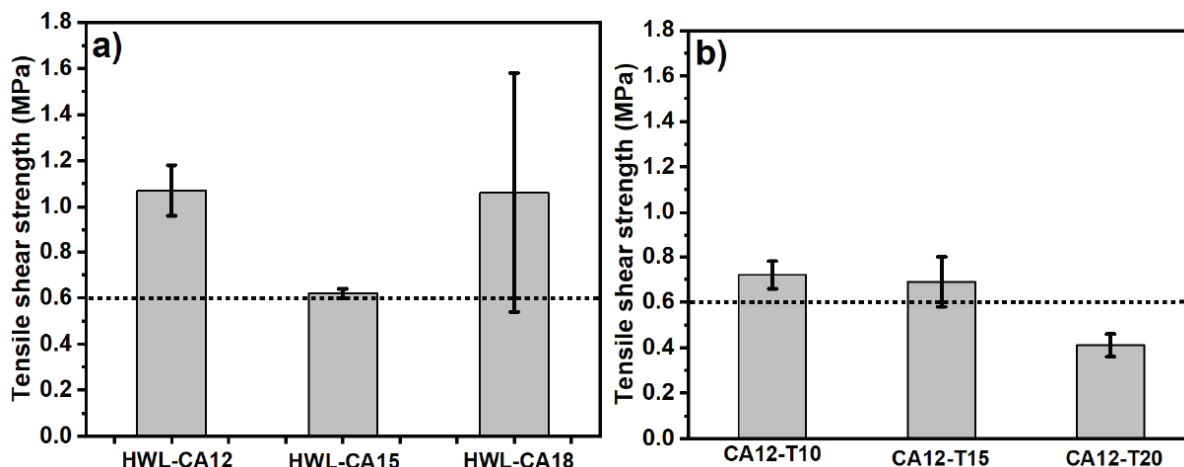


**Figure 6:** The FT-IR spectra of the untreated and CA-treated wood veneers.

optimal CA concentration is essential for effective crosslinking. This result may also be attributed to the availability of free hydroxyl groups in the lignin and on the wood surface, which are crucial for esterification with citric acid. Further, the adhesion strengths obtained herein are compared with those of previously-reported CA-based adhesives synthesized from various biomass sources in Table 2, thus highlighting the significant differences in performance and crosslinking strategies. Nevertheless, all of dry TSS values obtained in the present study exceed the minimum requirement of 0.60 MPa according to the Korean Standard (KS F 3101).

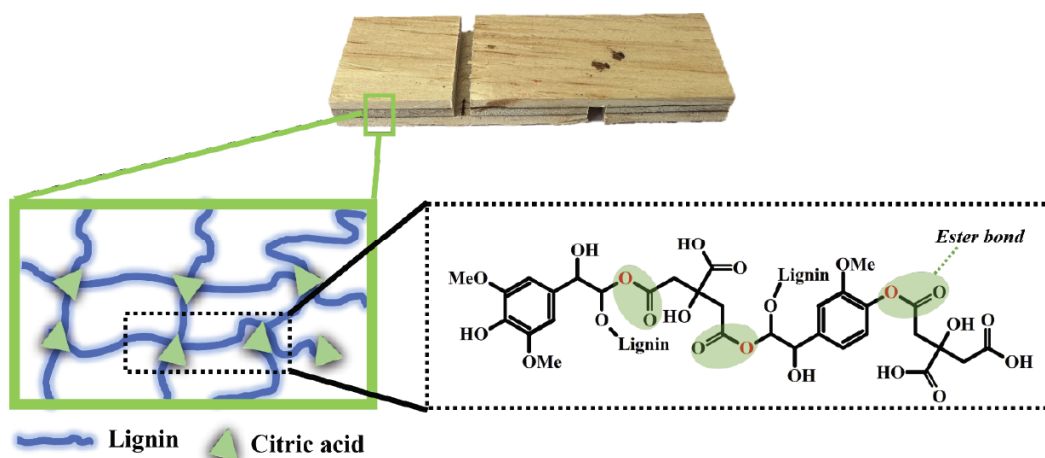
Notably, when the HWL-CA12 is applied to each CA-treated veneer (Figure 7b), the bonding strength is decreased compared to that of the HWL-CA12 with the untreated veneer. Specifically, the dry TSS values of the CA12-T10, CA12-T15, and CA12-TA20 are 0.72, 0.69, and 0.41 MPa, respectively, compared to 1.07 for the HWL-CA12. This unexpected reduction in adhesion strength may be attributed to excess CA on the veneer

surface, which could hinder the additional crosslinking and proper network formation during hot pressing. This explanation is further supported by the FT-IR spectra in Figure 6, where the highest peak intensities are observed for the T15 sample, followed by T10 and T20. In addition, excessive heat during pressing may lead to the degradation or over-crosslinking of reactive sites, thereby weakening the adhesive interface. Moreover, acid-induced surface changes may reduce porosity or wettability, impairing adhesive penetration and interlocking. These findings underscore the importance of optimizing the curing temperature and treatment conditions to improve the bonding performance of CA-treated veneers. Therefore, optimizing the pH to reduce the acidity of CA or introducing an intermediate primer layer could enhance the compatibility. Future work should address these issues. Furthermore, the lack of water resistance limits the performance of this adhesive. Nevertheless, both CA and lignin are inexpensive, renewable, and biodegradable, and the room-temperature preparation reduces energy input,



**Figure 7:** The TSS results for the HWL-CA resin applied to (a) the untreated and (b) CA-treated veneer.





**Figure 8:** The schematic reaction of HWL-CA crosslinking.

**Table 2:** A Comparison of the Present TSS Results with those Previously-Reported CA-Based Adhesives

Biomass	Reaction temp (°C)	Reaction time (h)	Dry TSS (MPa)	Ref.
Glucose	110	1	1.02	[19]
Corn starch	120	1	n/a	[20]
Chitosan	RT	n/a	2.10	[29]
Sucrose	90-100	1-4	n/a	[32]
Sucrose	100	2	~1.15	[33]
Tannin	RT	1	0.62	[34]
HWL	20-30	7	1.30	This study

making the process scalable and eco-friendly for industrial applications.

#### 4. CONCLUSIONS

Herein, the facile crosslinking of hardwood lignin (HWL) with the bio-based crosslinker citric acid (CA) was successfully demonstrated, and the effect of CA concentration on adhesion strength was investigated. In addition, the effect of pre-treating the veneer of CA was examined. The formation of the HWL-CA resin was confirmed by FT-IR analysis and by the appearance of an exothermic peak in the DSC results, which indicated the occurrence of esterification and crosslinking reactions. Furthermore, FT-IR analysis of the CA-treated veneers revealed chemical interaction between the wood components and CA. All of the HWL-CA adhesives met the dry tensile shear strength requirement (0.60 MPa) when applied to the untreated veneer, and the adhesive that was prepared using 12% CA maintained an acceptable adhesion strength when applied to 10% and 15% CA treated veneers. These findings support the potential of CA-crosslinked lignin

as a sustainable alternative to petroleum-based wood adhesives, thus offering a promising route toward greener adhesive technologies. Future work should explore other pathways to enhance flexibility and water resistance of the CA adhesive, primarily by incorporating other natural polymers for crosslinking with lignin. Furthermore, the long-term durability and industrial scalability of these bio-based adhesives should be thoroughly evaluated.

#### DECLARATION OF INTEREST

The authors declare that there are no conflicts of interest regarding this study.

#### ACKNOWLEDGEMENT

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