

Wood Adhesive from Lignin Biomass: Effects of Crosslinker and Nano-Reinforcement

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Abstract

Lignin accounts for about 30% of the dry mass of wood and provides rigidity and stability to woody plants. In pulping operations, lignin is removed to liberate the paper making fiber. Lignosulfonate is a byproduct of sulfite pulping. An estimated one million tons of lignosulfonate is produced annually. This byproduct is easily recoverable but underutilized. Due to the function of lignin as a natural binder of adjacent cells, lignin biomass has been investigated for wood adhesives. This study aims to improve the competitiveness of lignosulfonate-based adhesives by incorporating bio-based additives. The specific objective is to examine the effects of citric acid as a crosslinker and cellulose nanofiber as reinforcement.

To achieve the research objective, adhesives were prepared in various mass ratios of lignosulfonate, citric acid, and cellulose nanofiber. The adhesives were applied to wood surfaces and hot pressed to form single lap joints. Lap joint specimens were pulled apart to test for the shear bond strength of the adhesives. Results showed that the addition of citric acid increased the shear bond strength by 29% and the addition of cellulose nanofiber increased the shear bond strength by 27%. In wet conditions, lignosulfonate and citric acid did not perform nearly as well as phenol formaldehyde, but by incorporating 25% phenol formaldehyde to lignosulfonate and citric acid made the adhesive directly comparable to neat phenol formaldehyde. This suggests potential for lignosulfonate to significantly add bio-based content and reduce the non-renewable carbon in petroleum-based wood adhesives.

1. Introduction

Lignin is a natural aromatic polymer and is the second largest group of biopolymers on Earth after cellulose. Lignin is found in vascular plants (such as trees, shrubs, and grasses), with its largest presence found in wood (tree stems). Lignin contributes about 30% of the dry mass of wood, serving to provide rigidity and antimicrobial properties to trees.¹ As such, lignin is a large source of biomass waste from processing where wood is used for its cellulose portion in the manufacturing of products like specialty pulp, cellulosic ethanol, etc. Such an abundant bioresource, however, lignin is currently under-utilized for industrial applications.¹

Lignosulfonate is a type of major industrial lignin from the sulfite pulping of wood. It is more easily recoverable and more commercially available than kraft lignin (from alkaline kraft pulping) which is typically combusted for energy in the process of recovering pulping chemicals. Lignosulfonate has added advantages in its possession of anionic (negatively charged) sulfonate groups, making it useful where water-holding capacity (e.g., in concrete admixtures) and surfactant properties (e.g., as agrochemical dispersant) are desired.¹ With an estimated global production of one million tons per year,¹ it would be highly beneficial to further expand the applications of lignosulfonate to provide increased value and economic advantage to the pulping industry.

As lignin in its native form exists as a binding material between wood cell walls, there have been considerable research efforts in using lignin as a bio-renewable wood adhesive. Fossil-based thermosetting (heat-curable) resins in the market today are the current standard for use. Most wood adhesives are currently made using phenol, formaldehyde, and polyether polyols, with a considerable amount of solid waste and pollutants as byproducts.² In previous research, lignin has been used to substitute some of the adhesive raw materials, such as phenol and polyols, by harnessing the phenolic moiety and multiple hydroxyl groups of the lignin macromolecules. The resulted adhesives showed a high variability in performance depending on the fraction of lignin in the recipe and the type of lignin used.² Overall, more research is needed to allow viable use of lignin as a wood adhesive.

To address the underutilization of lignosulfonate, this study is aimed at improving its adhesive performance through successful crosslinking. Lignosulfonate is non-toxic and soluble in water, making it desirable for green processing. However, due to being water soluble, improving the wet performance of lignosulfonate-based adhesives is essential for use as a wood thermosetting adhesive. Crosslinking is known to improve wet performance, and as shown with starch (a hydroxyl containing polymer), this can be enabled using citric acid.³ Citric acid is a polycarboxylic acid found in oranges, limes, or other citrus fruits. Cellulose nanofiber, another biomaterial, was reported to strengthen epoxy thermoset resin.⁴ By incorporating citric acid and cellulose nanofiber as biobased additives and expanding on published efforts, the goal is to create from lignosulfonate an effective and eco-friendly wood adhesive.

2. Materials and Methods

2.1 Materials

Lignosulfonate (Fig. 1) was supplied by Sigma Aldrich in the form of lignosulfonic acid calcium salt (product number: 471054-100G). Citric acid (Fig. 2) was also supplied by Sigma Aldrich (product number: 251275-500G). Cellulose nanofiber was supplied by Sappi marketed as Valida S231C. Birch wood tongue depressors as a substrate used for bonding were supplied by Fisher Scientific (product number: 22363169). As a reference adhesive, phenol-formaldehyde resin used was from Hexion.

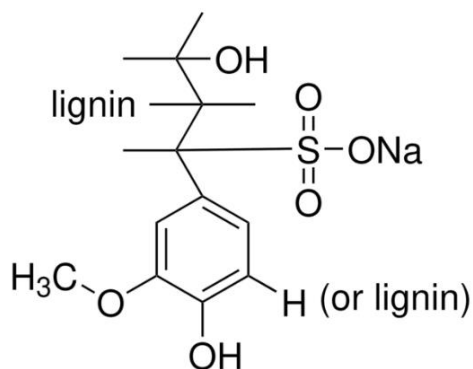


Figure 1. Lignosulfonic acid sodium salt.⁵

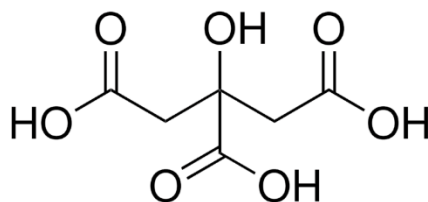


Figure 2. Citric acid.⁶

2.2 Preparation of Wood Test Strips

Test strips were first cut from tongue depressors to a size of 40 mm by 8.5 mm using a laser cutter (Full Spectrum Laser with LightBurn Software) (Fig. 3). Each tongue depressor yielded 3 identical test strips. A total of 24 test strips were prepared and placed into a desiccator until needed for use.



Figure 3. Full Spectrum Laser.

2.3 Preparation of Adhesives

Adhesives were prepared in various mass ratios of lignosulfonate, citric acid, and cellulose nanofiber. A single adhesive batch was to account for 20 lap shear (bonding) specimens at 30% solid content and a spread rate of 200 g solid/m². These parameters resulted in 0.221 g of solid per batch of adhesive.

When cellulose nanofiber was included in an adhesive, a stock suspension of the nanofibers was used that was prepared ahead of time. This suspension was created at 0.30% consistency. It was then homogenized by an Ultra Turrax at 10000 rpm for 10 minutes at creation followed by magnetic stirring before adhesive preparation.

When using phenol formaldehyde, a resin of 47% solid content was used. Adhesive batches of phenol formaldehyde were diluted to 30% solid content using water before application.

2.3 Creation of Lap Shear Specimens

Two wood test strips were placed on a balance and their combined mass was recorded. The adhesive was then applied either via pipette or laboratory spatula (depending on ease of spreading) at a rate of 200 g solid/m² (Fig. 4). For the area specified in this project (8.5 mm x 6.5 mm), this rate totaled 0.0368 g of adhesive per lap shear specimen. Test strips were assembled into specimens and hand pressed together momentarily before they were hot pressed at 1.2 MPa and 180°C for either 5 or 10 minutes. Bonded specimens were then brought to a conditioning

room set to 23°C and 50% relative humidity for 48 hours before testing. When wet testing was to be performed, lap shear specimens were moved after 46 hours of dry conditioning and waterlogged for 2 hours in a volumetric flask.

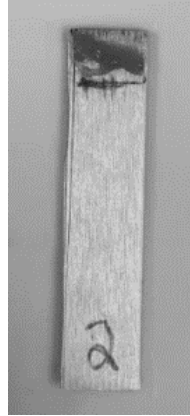


Figure 4. Unbonded lap shear specimen.

2.4 Tensile Testing of Lap Shear Specimens

A tensile test machine (Instron Model 68SC-05) was used in the conditioning room to test the shear bond strength of lap shear specimens (Fig. 5). Tensile grips with serrated jaws were used to avoid slippage of lap shear specimens during testing. A gauge length of 25.4 mm (1 in) and loading rate of 5.08 mm/min (0.2 in/min) was set. Time, force, and displacement data was collected. The shear bond strength was calculated by dividing the maximum force by the bond area ($\tau = F/A$). When wet testing was performed, lap shear specimens were lightly patted dried before tensile testing was conducted.

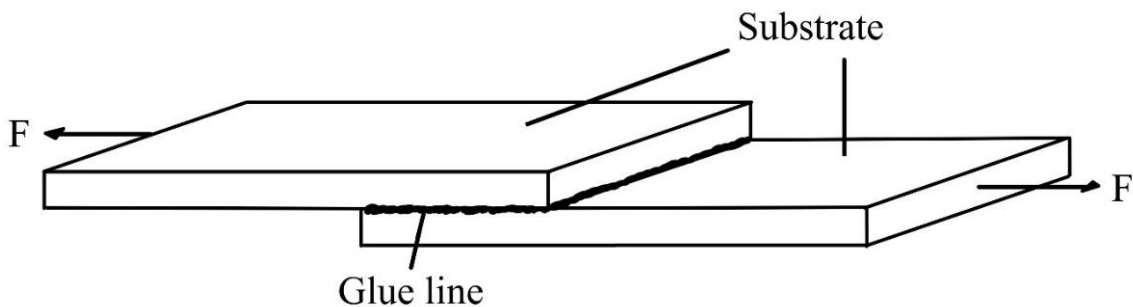


Figure 5. Lap shear specimen for shear bond test.

2.5 FTIR Analysis of Adhesive Samples

After tensile testing, broken specimens were scrapped of the glue line to be characterized through FT-IR spectroscopy using the attenuated total reflectance (ATR) mode. Peaks in the carbonyl range of 1680 cm^{-1} to 1750 cm^{-1} were analyzed for verification of crosslinking between lignosulfonate and citric acid (Fig. 6).^{7,8}

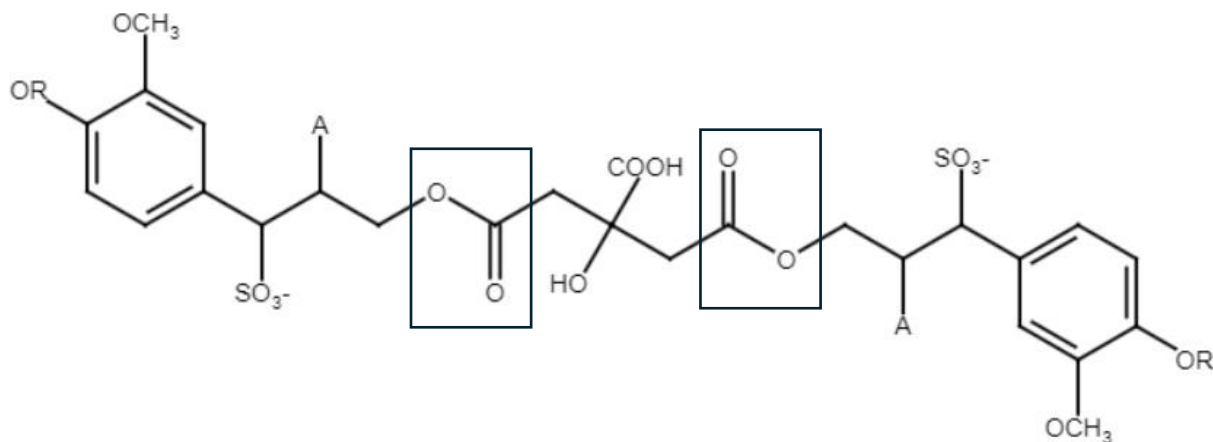


Figure 6. Proposed crosslinking product of lignosulfonate and citric acid (ester bond boxed).

3. Results and Discussion

For the ease of discussion, samples were labeled to show mass percents in the form of LS:CA:CNF where LS, CA, and CNF represent lignosulfonate, citric acid, and cellulose nanofiber respectively. The use of PF was used to represent phenol formaldehyde when present.

3.1 Effects of Citric Acid, Cellulose Nanofiber, and Hot Press Time on Dry Bond Strength

The addition of citric acid and cellulose nanofiber to lignosulfonate-based adhesives improved the shear bond strength (Fig. 7). Both citric acid (67:33:0) and cellulose nanofiber (90:0:10) individually improved the shear bond strength by approximately the same amount (27% and 29% respectively). Utilizing both additives (60:30:10) showed some additional improvement, however the improvement was not statistically significant to conclude optimal performance.

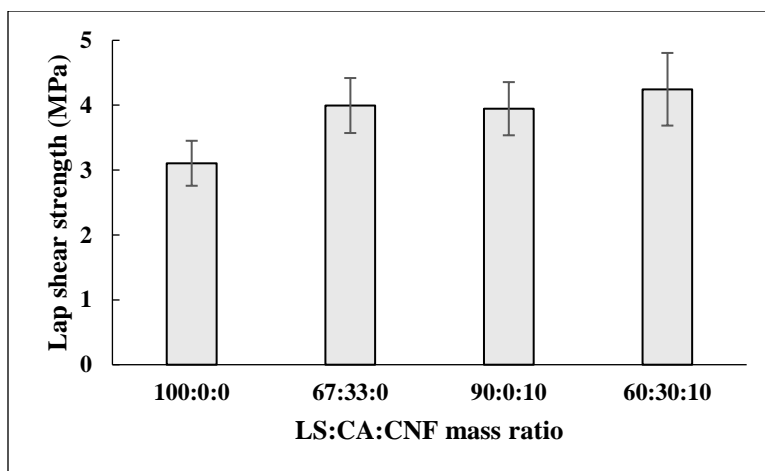


Figure 7. Effects of citric acid and cellulose nanofiber on dry shear bond strength with 10-minute curing.

The shear bond strength improvement (Fig. 7) by citric acid was due to crosslinking (to be verified later) with the formation of ester bonds between lignosulfonate and citric acid (Fig. 6). Cellulose nanofiber, being stiff and strong, improved the shear bond strength through sustaining a portion of the applied load.⁹ Through observation, cellulose nanofiber also increased the viscosity of the adhesive, conforming with a published report about its rheology modulating effect.¹⁰ It is hypothesized that the increase in viscosity reduced adhesive wicking into the wood substrate and minimized oozing out from the edges of the lap joints during hot pressing. This allowed appropriate amount of adhesive to remain in the joint, thereby avoiding starved glue joints.¹¹ On the other hand, adhesive wicking and oozing out was observed in the case of adhesive without cellulose nanofiber, and this might have compromised its shear bond strength.

The hot press time also played a crucial role in the shear bond strength (Fig. 8). Increasing the press time from 5 to 10 minutes is hypothesized to allow more time for crosslinking to occur resulting in better adhesive curing. When cellulose nanofiber was not present in adhesives (67:33:0), the effect of hot press time was seen to increase to a greater extent compared to when cellulose nanofiber was present (60:30:10). Interestingly, utilizing cellulose nanofiber at 5-minute curing was equivalent to increasing the hot press time to 10 minutes (67:33:0). In other words, there were two possible routes to further enhance the bond strength of citric acid-crosslinked adhesives, by increasing the hot press time or adding reinforcement with cellulose nanofiber.

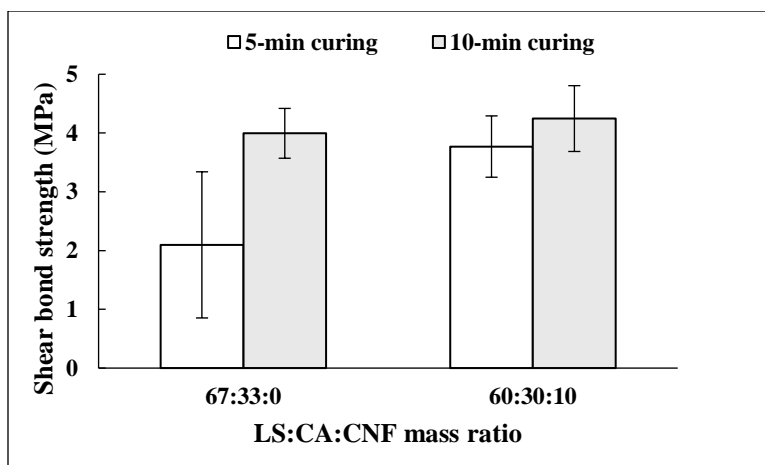


Figure 8. Effects of curing time on shear bond strength.

3.2 FTIR Analysis

The FT-IR study revealed that spectrum A (not containing citric acid) did not have a pronounced peak in the 1716 cm^{-1} - 1725 cm^{-1} range (marked in Fig. 9), whereas spectra B and C, both containing citric acid, showed a distinct peak in that range. This new peak appearance was due to C=O groups with the introduction of citric acid.⁸ The peak shift from 1716 cm^{-1} to 1725 cm^{-1} between spectrum B and spectrum C, whose difference was heating temperature (70°C and 180°C), was indicative of the transformation of carboxylic acid groups into ester bonds. Ester bonds are known to have a higher wavenumber due to the ester C=O stretching.^{7,8} With this information, alongside the increase in shear bond strength (Fig. 7), it was concluded that successful crosslinking between liginosulfonate and citric acid was accomplished.

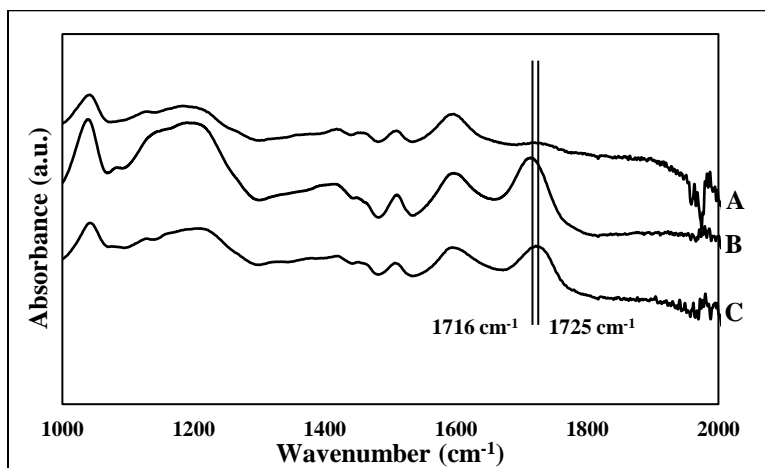


Figure 9. FT-IR spectra of scraped 100:0:0 adhesive (A), 67:33:0 solution dried at 70°C in beaker (B), scraped 67:33:0 adhesive (C).

3.3 Wet Bond Strength and Comparison to Phenol Formaldehyde

In wet conditions, lignosulfonate-based adhesives did not compete favorably against phenol formaldehyde. Neat lignosulfonate (lignosulfonate on its own) is dissolvable in water, which makes for a poor performing wood adhesive without any additives. Due to this, the study did not yield any testable lap shear specimens after waterlogging neat lignosulfonate (100:0:0) adhesives. Crosslinking (67:33:0) improved the wet performance slightly, but it was still outperformed significantly by neat phenol formaldehyde (PF) (Fig. 10).

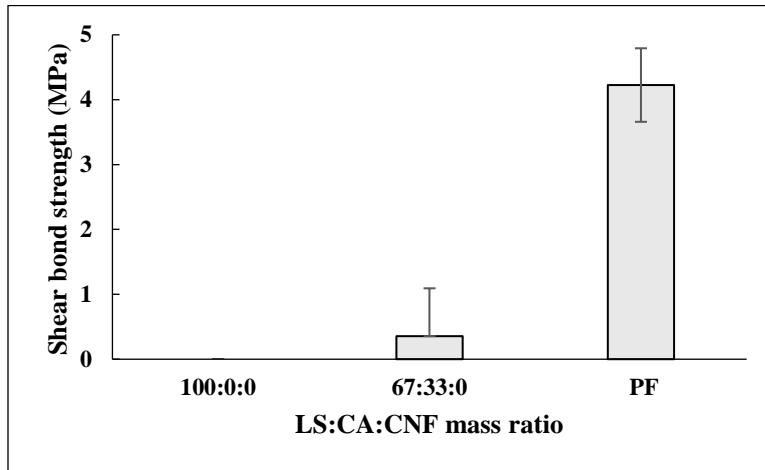


Figure 10. Shear bond strength in wet conditions with 10-minute curing.

Lignosulfonate-based adhesives were made more competitive by substituting 25% of the solid mass with phenol formaldehyde while maintaining the 2:1 ratio of lignosulfonate and citric acid. The resulting adhesive (50:25:25PF) exhibited massive improvement compared to 67:33:0 (Fig. 11) in both dry and wet conditions. Neat phenol formaldehyde was not tested in dry conditions and was therefore not included in the figure. Remarkably, the blended adhesive was comparable to neat phenol formaldehyde in wet bond strength. This was significant as only 25% of the adhesive was petroleum-based while achieving the same results.

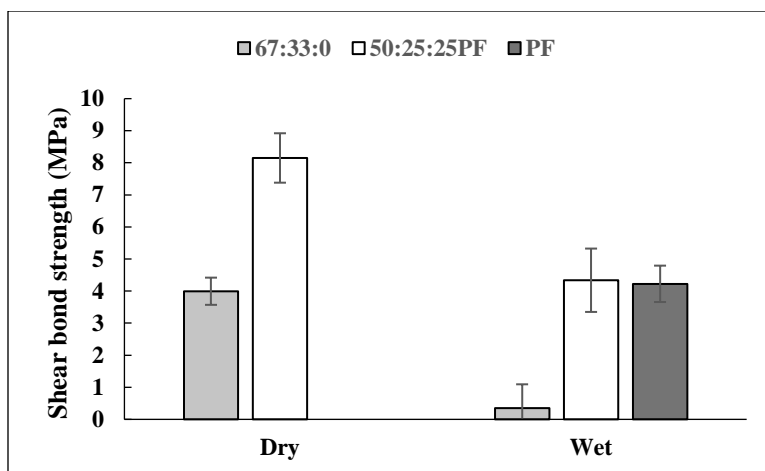


Figure 11. Shear bond strength of PF blended adhesive in dry and wet conditions with 10-minute curing.

4. Conclusion

The addition of citric acid and cellulose nanofiber was able to enhance the wood bonding ability of lignosulfonate by acting as a crosslinker and providing reinforcement. Citric acid was proven to crosslink with lignosulfonate via FT-IR spectroscopy and the effects were seen in the shear bond strength improvement. In wet conditions, lignosulfonate did not perform as well, especially compared to the commercial wood adhesive, phenol formaldehyde. When the bio-based adhesive was blended with phenol formaldehyde, it was comparable to neat phenol formaldehyde. The blend was nearly twice as strong as the fully bio-based adhesives in dry conditions and more than 10-fold stronger in wet conditions. These results show potential for the use of lignosulfonate to significantly add bio-based content and reduce the non-renewable carbon in petroleum-based wood adhesives.

5. Acknowledgement

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5. Appendix

Table 1. Average shear bond strengths and standard deviations.

Sample	Hot Press Time (min)	Condition	Average Shear Bond Strength (MPa)	Standard Deviation (MPa)
T	10	Dry	3.10	0.35
67:33:0	10	Dry	3.99	0.42
90:0:10	10	Dry	3.95	0.41
60:30:10	10	Dry	4.25	0.56
67:33:0	5	Dry	2.10	1.24
60:30:10	5	Dry	3.77	0.52
100:0:0	10	Wet	N/A	N/A
67:33:0	10	Wet	0.36	0.74
PF	10	Wet	4.23	0.57
50:25:25PF	10	Dry	8.15	0.77
50:25:25PF	10	Wet	4.34	0.99

6. References

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