



**Michigan
Technological
University**

Michigan Technological University
Digital Commons @ Michigan Tech

Michigan Tech Publications, Part 2

11-15-2023

Micro-Fibrillated Cellulose in Lignin–Phenol–Formaldehyde Adhesives for Plywood Production

Sheikh Ali Ahmed
Linnaeus University, Växjö

Reza Hosseinpourpia
Michigan Technological University, hosseinp@mtu.edu

Stergios Adamopoulos
Sveriges lantbruksuniversitet

Follow this and additional works at: <https://digitalcommons.mtu.edu/michigantech-p2>


 Part of the [Forest Sciences Commons](#)

Recommended Citation

Ahmed, S., Hosseinpourpia, R., & Adamopoulos, S. (2023). Micro-Fibrillated Cellulose in Lignin–Phenol–Formaldehyde Adhesives for Plywood Production. *Forests*, 14(11). <http://doi.org/10.3390/f14112249>

Retrieved from: <https://digitalcommons.mtu.edu/michigantech-p2/316>

Follow this and additional works at: <https://digitalcommons.mtu.edu/michigantech-p2>

 Part of the [Forest Sciences Commons](#)

Article

Micro-Fibrillated Cellulose in Lignin–Phenol–Formaldehyde Adhesives for Plywood Production

Sheikh Ali Ahmed ^{1,*} , Reza Hosseinpourpia ^{1,2}  and Stergios Adamopoulos ³

¹ Department of Forestry and Wood Technology, Faculty of Technology, Linnaeus University, Georg Lückligs Plats 1, 351 95 Växjö, Sweden; reza.hosseinpourpia@lnu.se

² College of Forest Resources and Environmental Science, Michigan Technological University, Houghton, MI 49931, USA

³ Department of Forest Biomaterials and Technology, Division of Wood Science and Technology, Swedish University of Agricultural Sciences, Vallvägen 9C, 750 07 Uppsala, Sweden; stergios.adamopoulos@slu.se

* Correspondence: sheikh.ahmed@lnu.se; Tel.: +46-(0)470-76-7492

Abstract: Petrochemical-based phenol–formaldehyde (PF) adhesives are widely used in plywood production. To substitute phenol in the synthesis of PF adhesives, lignin can be added due to its structural similarity to phenol. Moreover, micro-fibrillated cellulose (MFC) can further enhance the bond performance, mechanical properties, and toughness of adhesive systems. Thus, the aim of this study was to evaluate the adhesion performance of lignin–PF (LPF) adhesives reinforced with MFC. In LPF formulations, three levels of MFC (0, 15, and 30 wt% based on the total solid content of adhesives) were added to the homogenous adhesive mixture. Three-layer plywood panels from birch (*Betula pendula* Roth.) veneers were assembled after hot pressing at 130 °C under two pressing durations, e.g., 60 and 75 s/mm. Tensile shear strength was measured at dry (20 °C and 65% RH) and wet conditions (water soaked at room temperature for 24 h). The results indicated that the addition of lignin reduced the strength of LPF adhesives in both dry and wet conditions compared to the control PF adhesive. However, MFC reinforcement enhanced the shear strength properties of the plywood. Furthermore, a longer pressing time of 75 s/mm slightly increased the shear strength.

Keywords: bio-based adhesives; tensile shear strength; viscosity; adhesive penetration; birch veneer



Citation: Ahmed, S.A.; Hosseinpourpia, R.; Adamopoulos, S. Micro-Fibrillated Cellulose in Lignin–Phenol–Formaldehyde Adhesives for Plywood Production. *Forests* **2023**, *14*, 2249. <https://doi.org/10.3390/f14112249>

Academic Editors: Angela Lo Monaco, Zeki Candan and Mehmet Hakki Alma

Received: 3 October 2023

Revised: 7 November 2023

Accepted: 11 November 2023

Published: 15 November 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Phenol–formaldehyde (PF) adhesives are widely used as adhesives for exterior-grade plywood panels, oriented strand board, and particleboards due to their high moisture resistance, improved mechanical strength, and chemical stability that prevent wood panels from delamination [1–3]. These features provide the wood panel products with improved stability for exterior applications. PF adhesives are generally synthesized using the petrochemicals phenol and formaldehyde with alkaline catalysts [4]. Concerns about environmental and health issues on formaldehyde-based adhesives, including PF, have promoted research efforts on bio-based adhesives from natural and renewable resources, such as cellulose, lignin, tannin, proteins, starch, and other bio-based adhesives [5]. Lignin is an abundant highly branched and three-dimensional polymer with a great variety of functional groups that provide numerous active sites for chemical interactions [6,7]. It is available inexpensively as a by-product of pulping processes. Extensive research work has been conducted to use lignin of different origins as a bio-based component in various adhesives, such as kraft lignin [8], lignosulfonates [9] or organosolv lignin [10]. Lignin has been used as a phenol substitute for the synthesis of PF adhesives due to its similar structure to phenol [11]. The bond quality of lignin–phenol–formaldehyde (LPF) is comparable or even better than that of commercial PF adhesives depending on the molar ratio of formaldehyde to lignin [8]. This is due to the higher degree of cross-linking formed with the phenolic component of lignin structures. In addition, LPF adhesives spread much

better than commercial PF adhesives, which ensures both cost and quality benefits [12]. Use of furfural as a cross-linking agent in LPF adhesives has been reported to increase water resistance and induce high bond strength and good thermal stability [13].

Adhesive properties can be optimized in different ways depending on the application. One of the obvious ways is the modification of their chemistry. However, another alternative approach is the introduction of filler materials to the adhesive systems. Usually, fillers are either organic or inorganic in nature [14]. The common properties of filler materials are that they are non-volatile, non-gluing substances and insoluble in the adhesive. The purpose of adding filler materials is to adjust the adhesives' viscosity, improve bond strength, reduce adhesive adsorption, limit formaldehyde emission, and lower the material costs [15]. Commonly used organic fillers are bark, wood, walnut, coconut, pecan shell, wheat and soya bean flour, rice husk, tannin, etc., whereas inorganic fillers are in various form such as powder (aluminum oxide and silica), fiber (glass fiber, mica), sheet-like materials (talc), and cubic materials (chalk, barytes) [16–18]. Lignocellulosic/bio-based fillers can be used as formaldehyde scavengers in wood panels' production [17,18]. According to Liu et al. [14], fillers play a crucial role in reducing formaldehyde emissions in wood adhesives, primarily through two mechanisms. Firstly, they decrease the amount of free formaldehyde in the adhesive by adding fillers. Secondly, these fillers can engage in chemical reactions or physical absorption processes with formaldehyde. For instance, substances such as proteins in wheat flour, or lignin and tannin in wood bark, may interact with formaldehyde via various functional groups, ultimately leading to a reduction in formaldehyde emissions. However, the type and the amount of filler greatly affect the performance of adhesives for the manufacturing of wood panel products. The addition of fillers with a suitable particle size has the potential to improve the bond strength of the adhesive. Moreover, the active surface of these filler particles can serve as sites for cross-linking multiple long molecular chains, thereby forming a network structure [19]. Fillers with relatively large particle sizes make it difficult to obtain homogenous adhesive mixtures and hinder an even spreading of the modified adhesive. On the other hand, nanoparticles or nanofibers from high-strength materials can lead to high-performance adhesives [20,21]. The choice of the filler material depends on the specific properties that the manufacturer is trying to achieve in the wood adhesive.

Cellulose is the most abundant, inexpensive, and readily available biopolymer found in nature and the main constituent of wood. Micro-fibrillated cellulose (MFC) and cellulose nanocrystals (CNC) produced thereof have been added to various adhesives to improve bond performance and the mechanical properties of wood products [15,20]. In MFC, cellulosic objects are usually obtained by purely mechanical pulp processing, while CNC production involves an additional acid hydrolysis step. MFC is characterized by its extended surface area with an increased number of functional hydroxyl (-OH) groups. Several studies showed the mechanical improvement offered by MFC [22–25]. Therefore, it showed great potential to reinforce synthetic, petrochemical-based adhesives, such as urea–formaldehyde (UF), melamine–urea–formaldehyde (MUF), polyvinyl acetate (PVAc), and PF, for subsequent improvement in the mechanical properties of the wood composites [20,26,27]. However, the effect of MFC in an LPF adhesive system has not yet been explored. This study was conducted with the aim of increasing the content of bio-polymers in the adhesive formula for manufacturing three-layer birch plywood panels by reinforcing the LPF adhesives with MFC. Therefore, the current study hypothesizes that the new LPF formulation containing MFC will provide good water resistance and a more stable multi-dimensional network structure for plywood production.

2. Materials and Methods

2.1. Adhesives, Hardeners, and MFC

Commercial Bakelite® phenol–formaldehyde (PF) 128 and lignin–phenol–formaldehyde (LPF) 1135 adhesives, and their respective hardeners Bakelite® PFH 676 and Bakelite® PFH 6055 were kindly provided by Hexion Oy, Puhos, Finland. The technical characteristics of

PF128 and LPF 1135 adhesives are given in Table 1. Micro-fibrillated cellulose (MFC) with a pH value of 8.0, fibre length of 311 μm , and solid content of 1.9% was kindly provided by FiberLean MFC® (Par Moor Center, Par, UK).

Table 1. Properties of phenolic adhesives.

| Adhesive | Solid Content (%) | Viscosity (mPa·s) | Free Formaldehyde (%) | Free Phenol (%) | Specific Gravity |
|----------|-------------------|-------------------|-----------------------|-----------------|------------------|
| PF 128 | 47.0–49.0 | 250–320 | <0.1 | <0.1 | 1.18 |
| LPF 1135 | 42.5–43.5 | 300–350 | <0.1 | <0.1 | 1.21–1.22 |

PF: Phenol–formaldehyde; LPF: lignin–phenol–formaldehyde.

2.2. Adhesive Formulations

For lignin–phenol-based adhesives, the required amount of adhesive was mechanically stirred for 5 min at 100 rpm, respective hardener was added and mixed at 800 rpm for 10 min, then 25–27 °C of water was added, and the adhesive was stirred for a further 5 min at 800 rpm and then 2 h at 250 rpm until a homogenous mixture was achieved. Three levels of MFC (0, 15%, and 30 wt% based on the total solid content of adhesives) was added to the homogenous adhesive mixture and stirred for an additional 10 min. The solid content of adhesive formulations was adjusted to 67.3% by regulating the water content. PF adhesive with 0% MFC was used as a control or reference sample. Details on all experimental adhesive formulations are given in Table 2.

Table 2. Experimental adhesives for plywood.

| Adhesive Type | Hardener | Adhesive (%) | Hardener (%) | MFC (%) |
|---------------|----------|--------------|--------------|---------|
| PF 0% | PFH 676 | 67.3% | 14.7% | 0% |
| PF 15% | PFH 676 | 67.3% | 14.7% | 15% |
| PF 30% | PFH 676 | 67.3% | 14.7% | 30% |
| LPF 0% | PFH 6055 | 67.3% | 10.7% | 0% |
| LPF 15% | PFH 6055 | 67.3% | 10.7% | 15% |
| LPF 30% | PFH 6055 | 67.3% | 10.7% | 30% |

PF: Phenol–formaldehyde; LPF: lignin–phenol–formaldehyde; PFH: hardener; MFC: micro-fibrillated cellulose. MFC was added based on the total solid content of adhesives.

2.3. Plywood Manufacturing

Defect- and knot-free commercial birch (*Betula pendula* Roth.) veneers from a tangential surface measuring 400 × 400 × 1.5 mm³ were purchased from a local producer (DecorPanel AB, Landsbro, Sweden). The veneers were conditioned at room temperature and were used for manufacturing 3-layer plywood. Adhesives were spread evenly on the veneer with an amount of 150 g/m². Assemblies were cold pressed first with a hydraulic press (AKE, Mariannelund, Sweden) for 5 min at 8 bar/cm² and then directly hot pressed at 17 bar/cm² with platens temperature of 130 °C for two different press factors, i.e., 60 and 75 s/mm. After pressing, the plywood panels were stored in a climate chamber for mass constancy under a climate of 20 °C and 65% RH. Two plywood assemblies were prepared for each adhesive formulation (PF and LPF) and pressing parameters ($n = 24$).

2.4. Adhesive Evaluation and Plywood Testing

Adhesive formulations were analyzed by means of their pH, viscosity, and gelation time. The pH value of the adhesives was measured using a VWR pH Enomenal IS21001 (Stockholm, Sweden). The viscosity was measured at room temperature using a TQC rotational portable viscometer (DV1400, Capelle aan den IJssel, The Netherlands) with a spindle SC3-5. The gelation time of the adhesives was determined by IMAL gel timer (IMALPAL Group, San Damaso, MO, Italy).

The plywood samples were evaluated at tensile shear mode according to the standard EN 314-1 [28], under dry and wet state conditions. For wet state, plywood samples

were water soaked at room temperature for 24 h and then wiped with a paper cloth to remove excess water from the surfaces. Then, tensile shear strength was measured using a universal testing machine (MTS 810, MTS System Corporation, Eden Prairie, MN, USA) with a constant load where the rupture occurred within 30 ± 10 s. Dry state samples were tested after acclimatization in a climate chamber at 20°C and 65% RH for three weeks. A total of ten (10) replicates were used for every adhesive system, pressing time, and test condition.

2.5. Adhesive Penetration

Cross-sections $15\ \mu\text{m}$ thick from plywood samples were prepared using a sledge microtome (WSL, Birmensdorf, Switzerland). Samples were fixed on glass slides with a few drops of glycerin, covered with cover slips, and then observed under a motorized Olympus BX63F light microscope (Olympus, Tokyo, Japan) equipped with the DP73 color CCD cooled camera (max. 17.28 megapixel) using the software program OLYMPUS cellSens Dimension, version 1.18 (Olympus, Tokyo, Japan). The maximum penetration of the adhesive was measured according to the equation below [29]:

$$MP = \frac{\sum_i^5 (y_i + r_i - y_0)}{5} \quad (1)$$

where MP = maximum depth of penetration (μm), y_i = centroid of adhesive object with i representing the deepest penetration (μm), r_i = mean radius of adhesive object i (μm), and y_0 = reference y-coordinate of the adhesive line interface (μm).

In total, 25 measurements were performed for each adhesive type on a randomly selected projection area of $1100 \times 600\ \mu\text{m}^2$. To gain a better understanding of adhesive flow, the penetration and localization of adhesives into the wood structure was performed on optical microscopic photographs for each case.

2.6. Statistical Analysis

For statistical evaluation, the IBM SPSS Statistics software package, version 29.0.1.0 (IBM Corporation, Armonk, NY, USA) was used to determine differences of tensile shear strength affected by different parameters, i.e., adhesive type, level of MFC reinforcement, pressing time, and test conditions. Univariate analysis of variance at a 0.05 significance level was applied to tests of treatment effects.

3. Results and Discussion

3.1. Adhesive Properties

Viscosity and gel time of adhesives are two important properties that can significantly affect their performance. Both viscosity and gel time can be influenced by factors such as temperature, pressure, and the chemical composition of the adhesive [30,31]. Table 3 shows some physical properties of the experimental adhesives.

Table 3. Physical properties of the experimental adhesives.

| Adhesive Type | Viscosity (mPa·s) | Gel Time at 120°C (s) | pH |
|---------------|-------------------|-------------------------------------|------|
| PF 0% | 940 | 361 | 11.9 |
| PF 15% | 2530 | 708 | 11.8 |
| PF 30% | 2040 | 309 | 11.8 |
| LPF 0% | 470 | 1898 | 13.2 |
| LPF 15% | 620 | 514 | 13.2 |
| LPF 30% | 1010 | 238 | 13.2 |

PF: Phenol–formaldehyde; LPF: lignin–phenol–formaldehyde.

The introduction of MFC into the adhesive mixture brought about a notable change in physical characteristics. One of the most prominent changes was the increase in viscosity, accompanied by a decrease in gel time. This trend was consistent across various adhesive

mixtures except for PF 15% (Table 3). The exact cause behind this anomaly remains somewhat unclear and warrants further exploration. Moreover, a change in viscosity was noted when lignin was introduced as a partial substitute for phenol. This substitution resulted in a significant 50% reduction in viscosity. This finding bears particular significance, particularly in its potential influence on the depth of adhesive penetration. Section 3.3 provides a more in-depth exploration of the implications of this lowered viscosity on adhesive penetration in wood substrate.

Viscosity, which is one of the adhesive parameters, depends on the size and shape of the adhesive prepolymer, the solid content of the adhesive solution, and the quantity of additives, such as fillers or extenders [32]. The viscosity of an adhesive mixture is a crucial parameter that plays a pivotal role in determining the applicability of the substance as a filler or modifier in plywood production. Recent studies by Kawalerczyk et al. [15] demonstrated that the addition of nanocrystalline cellulose to the adhesive mixture leads to a significant increase in viscosity compared to the mixtures containing only PF adhesive. The rise in viscosity values can be attributed to the progressive polycondensation reactions of PF and LPF adhesives, which generate temporary bonds between the fibrils due to the presence of hydroxyl groups on the surface of the MFC [33]. However, the viscosity of the MFC-modified mixtures remained at a level that allowed an even distribution of the adhesives on the surface of veneers without causing difficulties during application. Excessively low viscosity can lead to problems during both the application and pressing processes, such as excessive penetration into the veneer surface, resulting in an inadequate layer that does not ensure good properties of the adhesive joint. Adjusting the viscosity level is crucial, as Younesi-Kordkheili and Pizzi [34] confirm in their research, where they found that it significantly affects the strength properties of the bond. Furthermore, the surface of cellulose nanoparticles is rich in hydroxyl groups, and their location on the equatorial positions of glucopyranose rings makes them highly hydrophilic [35]. Interfacial bonding of nanocellulose with a phenolic adhesive can be attributed to the reaction between hydroxyl groups of cellulose and the methylol groups of the adhesive [36]. Thus, the hydrophilic nature of the cellulose nanoparticles' surface and the presence of hydroxyl groups play a crucial role in enhancing the adhesion properties of the adhesive mixture, making them suitable for use in plywood production as fillers or modifiers.

A comparison between the reference PF adhesive with the MFC-reinforced ones, showed a shorter gel time for the former, indicating higher reactivity. However, this increased reactivity could lead to premature adhesive curing reactions, causing complications during application. Conversely, the MFC-reinforced PF adhesives exhibited higher viscosity due to MFC's ability to act as a thickener, which can prevent the overpenetration of the adhesive into the wood substrate [26]. Moreover, the reference PF adhesive had a shorter gel time, indicating higher reactivity that could cause premature adhesive curing reactions. Comparing the reference PF adhesive with the LPF ones showed a notably shorter gel time (higher reactivity) for the reference adhesive, indicating an increase in cross-linking density upon incorporating lignin. Pizzi and Stephanou [37] showed that gel time is inversely proportional to the rate of polycondensation and cross-linking of the adhesive. MFC reinforcement reduced the gel time considerably for both PF and LPF adhesives. These findings highlight the crucial role of MFC in enhancing the adhesive properties of PF and LPF adhesives, making them suitable for use in plywood production as fillers or modifiers.

3.2. Shear Strength

The tensile shear strength test is a widely used method for evaluating adhesive behavior in plywood [38]. Figure 1 shows the shear strength of plywood samples both after conditioning at 20 °C and 65% RH and soaking in water for 24 h. The addition of MFC to the PF adhesive at elevated levels resulted in an improved shear strength, while the water resistance of the boards did not appear to be considerably affected. In terms of relative differences, the control PF adhesive showed higher strength values than the lignin-based

adhesives LPF: 16% higher at a 60 s/mm pressing time and 6% higher when pressing time was increased to 75 s/mm. The measured time-dependent shear strength provides insights regarding the cohesive bonding strength of thermosetting adhesives. Conversely, the addition of MFC at 30 wt% to LPF adhesives resulted in a significant increase in the shear strength of the plywood samples, especially under dry conditions. Adding 15 wt% of MFC to the PF and LPF adhesives increased the bonding strength by 10% for both blends at a pressing time of 60 s/mm. When the MFC addition was further increased to 30 wt%, these strength values were found to be 11% and 16% higher, respectively. Tests in wet conditions showed that adding MFC to the PF adhesive reduced shear strength, while it increased in LPF blends. Even though there was an improvement in water resistance (shear strength in wet condition) with a higher MFC content, the difference between 15 and 30 wt% MFC addition was found to be statistically similar. Increasing the pressing time from 60 to 75 s/mm increased the shear strength (tested in both dry and wet conditions) in some formulations, but these differences were insignificant.

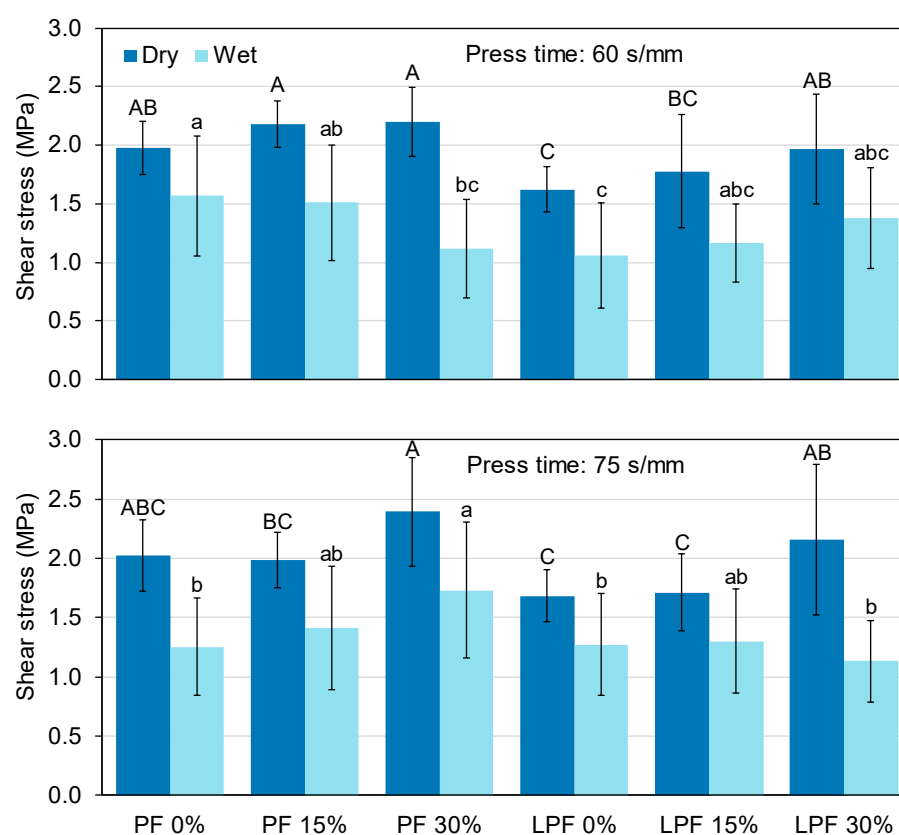


Figure 1. Tensile shear strength of 3-layer plywood in dry and wet conditions with pressing time of 60 s/mm (**above**) and 75 s/mm (**below**). PF and LPF denote phenol–formaldehyde and lignin–PF adhesives, respectively. Reinforcements are indicated by 0, 15, and 30 wt% of MFC based on the total solid content of adhesives. Mean values followed by different letters within bars (capital letter for dry and small letter for wet conditions comparison) indicate that there is a significant difference ($p \leq 0.05$) as determined by ANOVA and Duncan’s multiple range test. The error bars indicate the standard deviations.

Findings from Solt et al. [39] indicate that PF adhesives with additions of lignin require a higher press temperature or a longer pressing time in order to develop full adhesive joint strength. However, in this study, it was not obvious that the tensile shear strength increased for all adhesives both in dry and wet conditions when the pressing time was extended. Even though an expected increase in bond strength was observed with longer pressing times, these differences were not found to be notable. A previous study showed that nanocellulose enforcement can reduce the pressing time and maintain the same bonding

quality with the reference plywood panels [40]. Overall, the current experiment proved that when MFC is admixed with phenolic adhesives up to a specific level (15 wt%), it allows plywood properties to be equal to or even slightly better than those obtained with the reference PF formulation.

The quality of the adhesive and bonding are directly related to the shear strength, including factors such as homogeneity and fluidity [41]. LPF adhesives appeared to be homogeneous and exhibited excellent fluidity, which allowed them to be spread well on the wood surface. Good spreading of the adhesive on the wood surface is a critical factor in achieving good adhesion [42]. Therefore, the comparable dry bond strength of the plywood panels bonded with LPF adhesives can be related to the reactivity of the lignin and the level of cross-linking between different components (phenol, lignin, and formaldehyde). When MFC was added to the PF and LPF adhesive at 15 and 30 wt%, it helped to improve or retain the shear strength compared to the reference plywood panels with PF adhesive only. Lower adhesive reactivity and higher viscosity may have contributed to the improved shear strength of the panels with the MFC-reinforced formulations. Similar results were observed by Karagiannidis et al. [26], where MFC addition improved the rheology of adhesive mixtures allowing for a smoother and more even spreading than the reference and preventing early penetration of the adhesive mixtures into the wood substrate.

The tensile shear strength in plywood samples varied greatly, and therefore, an ANOVA was carried out to evaluate the interaction of different variables (Table 4). The results indicated that MFC reinforcement had a significant positive impact on the strength. However, the introduction of lignin to the PF adhesive resulted in a significant decrease in the strength values of the plywood samples. Additionally, the strength values of the wet samples showed an obvious reduction. Table 4 also suggests that there is no specific combination of parameters that could produce a significant difference in the subject group, which affects the strength values.

Table 4. Analysis of variance (ANOVA) for tensile shear strength of plywood.

| Source | SS | df | MS | F-Value | Sig. |
|---|--------|----|--------|---------|--------|
| Adhesive (PF, LPF) | 3.959 | 1 | 3.959 | 23.322 | <0.001 |
| MFC | 1.646 | 2 | 0.823 | 4.850 | 0.009 |
| Pressing time | 0.104 | 1 | 0.104 | 0.613 | 0.434 |
| Condition (dry, wet) | 24.692 | 1 | 24.692 | 145.466 | <0.001 |
| Adhesive (PF, LPF) × MFC | 0.100 | 2 | 0.050 | 0.296 | 0.744 |
| Adhesive (PF, LPF) × Pressing time | 0.001 | 1 | 0.001 | 0.004 | 0.947 |
| Adhesive (PF, LPF) × Condition (dry, wet) | 0.125 | 1 | 0.125 | 0.735 | 0.392 |
| MFC × Pressing time | 0.644 | 2 | 0.322 | 1.897 | 0.152 |
| MFC × Condition (dry, wet) | 1.088 | 2 | 0.544 | 3.206 | 0.043 |
| Pressing time × Condition (dry, wet) | 0.001 | 1 | 0.001 | 0.007 | 0.932 |
| Adhesive (PF, LPF) × MFC × Pressing time | 1.453 | 2 | 0.726 | 4.280 | 0.015 |
| Adhesive (PF, LPF) × MFC × Condition (dry, wet) | 0.006 | 2 | 0.003 | 0.019 | 0.981 |
| Adhesive (PF, LPF) × Pressing time × Condition (dry, wet) | 0.024 | 1 | 0.024 | 0.142 | 0.707 |
| MFC × Pressing time × Condition (dry, wet) | 0.162 | 2 | 0.081 | 0.478 | 0.621 |
| Adhesive (PF, LPF) × MFC × Pressing time × Condition (dry, wet) | 1.212 | 2 | 0.606 | 3.570 | 0.030 |

SS: sum of squares; df: degrees of freedom; MS: mean of the squares; Sig.: at 5% level of significance; PF: phenol–formaldehyde; LPF: lignin–phenol–formaldehyde; and MFC: micro-fibrillated cellulose.

The wet shear strength of plywood panels is an important factor to consider when evaluating their quality and durability. This particular strength is affected by a number of factors, including the addition of lignin to the adhesive used in the panels. It was observed that the wet strength of the panels decreased compared to their dry strength, which can be attributed to the amphiphilic structure of lignin. Lignin contains both polar and non-polar parts, and some of the free parts of lignin that do not contribute to cross-linking with phenol and formaldehyde can be degraded by water absorption, thus leading to a decreased wet strength [41]. However, the addition of lignin to a PF adhesive, which is commonly used as

the adhesive in plywood panels, does not necessarily result in a decrease in wet strength. In fact, the findings of this research work indicate that the plywood panels with added lignin still exhibit approximately equal wet strength compared to standard panels, regardless of the pressing times used during manufacturing. This suggests that lignin can be a viable option for improving the strength of plywood panels, even in wet conditions.

3.3. Adhesive Penetration

The process of adhesive application to wood products involves a complex interplay between the adhesive and the cellular structure of the wood. As the adhesive flows into the wood, it infiltrates the cell walls and creates what is known as the wood adhesive interphase, as shown in Figure 2. This interphase is the region where the wood and adhesive materials are combined, forming a zone of penetration. Adhesive penetration was observed in all cells near the bondline, including vessels, fibers, and ray parenchyma. Without the addition of MFC, deeper penetration was observed in the PF compared to the LPF adhesive; however, this difference was found to be statistically similar. The addition of MFC to the adhesive blend decreased penetration depth. All LPF blends exhibited lower viscosity than PF blends, resulting in better penetrability into the wood substrate. The addition of MFC increased viscosity, thereby restricting penetration depth. This effect was also observed for PF adhesives with 15 wt% MFC compared to those with 0 and 30 wt% MFC (Figure 3).

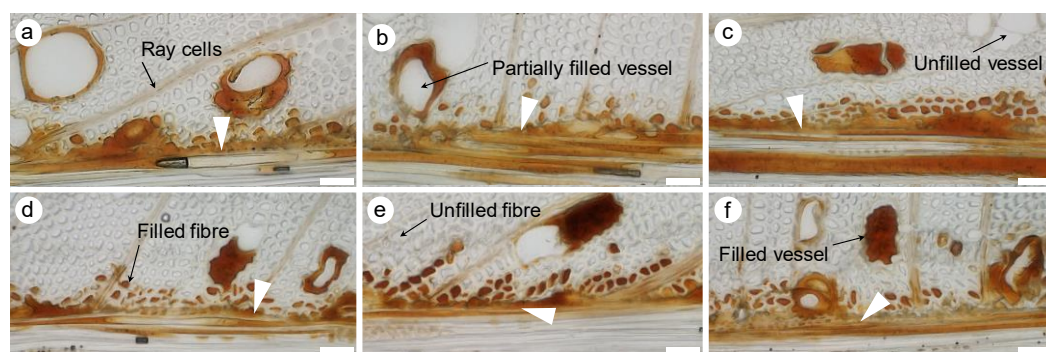


Figure 2. Adhesive penetration in plywood samples as observed under optical microscope. PF adhesive with MFC at 0 (a), 15 (b), and 30 (c) wt%, LPF adhesive with MFC at 0 (d), 15 (e), and 30 (f) wt%. Arrow heads indicate bondlines. Scale bar = 50 µm.

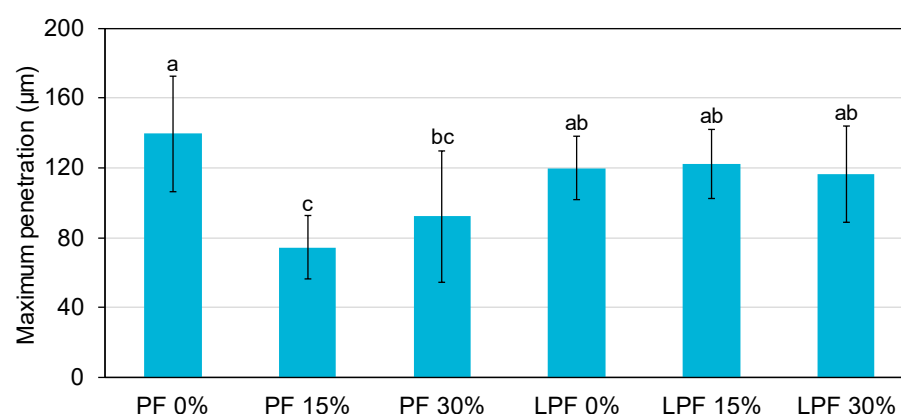


Figure 3. Maximum penetration of the different adhesive types in plywood samples. PF and LPF denote phenol formaldehyde and lignin–PF adhesive, respectively. Reinforcements are indicated by 0, 15, and 30 wt% of MFC based on the total solid content of adhesives. Pressing time 60 s/mm. Mean values followed by different letters within bars indicate that there is a significant difference ($p \leq 0.05$) as determined by ANOVA and Duncan's multiple range test. The error bars within the columns indicate the standard deviations.

The introduction of lignin into the adhesive mixture, substituting a fraction of the phenol content, could have the effect of lowering viscosity and enhancing penetration depth. This outcome is clearly depicted in Figure 3. Adhesive penetration is a crucial factor in bond performance, but it can be challenging to evaluate bond performance based solely on penetration depth. Other factors, such as cohesive strength, covalent bonding, and secondary chemical bonding, which can vary depending on the formulation, may have a more significant impact. Greater penetration results in increased surface contact between the adhesive and the wood, which raises the potential for secondary bonding forces and covalent bonding and ultimately strengthens the bond by increasing the surface area of contact between the adhesive and the wood fibers. However, excessive penetration can result in weakened bonds due to inadequate adhesive coverage, leaving insufficient adhesive at the interface, known as a ‘starved’ bondline [43]. In addition, the degree of penetration is influenced by various factors, including wood species, anatomical orientation, surface roughness, adhesive type, viscosity, applied pressure, and temperature [44]. Optical micrographs illustrate the varying degrees of penetration achieved by the different experimental adhesives (Figure 2). A higher viscosity corresponds to a narrower interphase represented by the brown-colored adhesive. Therefore, while increased penetration depth can result in stronger bonds by increasing the surface area of contact between the adhesive and wood fibers, other factors such as adhesive coverage and chemistry must also be taken into account to achieve optimal bond performance. As long as the adhesive fills out the topmost surface forming a cell layer, there is no correlation between the bonding quality and the penetration depth [45].

The replacement of lignin with phenol in the LPF adhesive showed similar water resistance compared to the conventional PF adhesive. Other studies showed even better moisture resistance [46,47]. The addition of MFC further increased the bonding strength for the dry conditioned samples; however, such an effect was not evident for all types of wet plywood samples (Figure 1). This could be related to the increase in viscosity and less penetration into the wood substrate. There was no significant positive effect on the shear strength of plywood panels when the MFC addition levels increased from 15 to 30 wt%. It was observed that the addition of 15 wt% MFC was enough to increase the shear strength both in dry and wet conditions. This effect was clear from the increase in viscosity and the penetration depth of adhesives (Table 3 and Figure 3). The tensile shear strength is related to both the viscosity and penetration depth of the adhesive. An optimal balance between viscosity and penetration depth is necessary to achieve strong adhesive bonds. Therefore, it is important to carefully consider the specific adhesive system being used and the potential benefits and drawbacks of applying MFC reinforcement. Overall, these findings highlight the complexity of factors that can affect the strength and durability of plywood panels, and the importance of carefully selecting and evaluating the materials and methods used in their manufacture.

The quality of the bond between the wood and adhesive is crucial for the overall strength of the final product. However, the variation in tensile strength cannot be solely explained by the depth of adhesive penetration, as the interactions between the wood and adhesive are complex and influenced by processing parameters, adhesive formulation, and the characteristics of the wood itself. Even though a higher amount of MFC reinforcement resulted in thin interphases that prevented overpenetration, it still enabled a comparable shear strength of the plywood panels to be maintained.

4. Conclusions

Petrochemical PF adhesives could partially incorporate lignin and the performance of plywood panels could be enhanced by the introduction of MFC in the adhesive mixture. The viscosity of adhesive mixtures is a critical factor in plywood production. Adding MFC to the mixture generally increased viscosity without causing difficulties during application or pressing. Except for the adhesive 15%, the MFC reinforcement reduced the gel time for PF and LPF adhesives and improved their properties for plywood production. PF had

higher strength than LPF adhesives, but LPF had better fluidity and homogeneity, leading to good penetration and adhesion. The wet strength of PF plywood decreased with the substitution of phenol with lignin. A longer press time of 75 s/mm had no significant effect on shear strength but adding MFC to plywood adhesives improved bonding strength without affecting water resistance. Increasing the addition levels of MFC at 30 wt% in LPF did not significantly improve shear strength compared to the lower level of 15 wt%. Nevertheless, MFC can be added as a thickener in LPF adhesive mixtures for plywood production while maintaining the panel performance. Overall, these findings emphasize the potential of replacing phenol with lignin and incorporating it in adhesives for the manufacture of high-quality and durable plywood panels. Further research on the curing mechanism of LPF-MFC adhesives and the biological resistance of final products needs to be conducted.

Author Contributions: Conceptualization, R.H. and S.A.; methodology, R.H., S.A.A. and S.A.; software, S.A.A.; validation, S.A.A., R.H. and S.A.; formal analysis, S.A.A.; investigation, S.A.A. and R.H.; visualization, S.A.A. and R.H.; data curation, S.A.A. and R.H.; writing—original draft preparation, S.A.A.; writing—review and editing, S.A.A., S.A. and R.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Öncel, M.; Vurdu, H.; Aydoğan, H. The tensile shear strength of outdoor type plywood produced from fir, alnus, pine and poplar wood. *Wood Res.* **2019**, *64*, 913–920.
- Moubarik, A.; Pizzi, A.; Allal, A.; Charrier, F.; Charrier, B. Cornstarch and tannin in phenol–formaldehyde resins for plywood production. *Ind. Crops Prod.* **2009**, *30*, 188–193. [\[CrossRef\]](#)
- Pizzi, A. *Wood Adhesives: Chemistry and Technology*; Marcel Dekker: New York, NY, USA, 1983; Volume 1.
- Zhao, M.; Jing, J.; Zhu, Y.; Yang, X.; Wang, X.; Wang, Z. Preparation and performance of lignin-phenol-formaldehyde adhesives. *Int. J. Adhes. Adhes.* **2016**, *64*, 163–167. [\[CrossRef\]](#)
- Ma, Y.; Kou, Z.; Hu, Y.; Zhou, J.; Bei, Y.; Hu, L.; Huang, Q.; Jia, P.; Zhou, Y. Research advances in bio-based adhesives. *Int. J. Adhes. Adhes.* **2023**, *126*, 103444. [\[CrossRef\]](#)
- Mariana, M.; Alfatah, T.; Abdul Khalil, H.P.S.; Yahya, E.B.; Olaiya, N.G.; Nuryawan, A.; Mistar, E.M.; Abdullah, C.K.; Abdulmajid, S.N.; Ismail, H. A current advancement on the role of lignin as sustainable reinforcement material in biopolymeric blends. *J. Mater. Res. Technol.* **2021**, *15*, 2287–2316. [\[CrossRef\]](#)
- Matsushita, Y. Conversion of technical lignins to functional materials with retained polymeric properties. *J. Wood Sci.* **2015**, *61*, 230–250. [\[CrossRef\]](#)
- Chen, C.M. Glueability of kraft lignin copolymer resins on bonding southern pine plywood. *Holzforschung* **1995**, *49*, 153–157. [\[CrossRef\]](#)
- Hemmilä, V.; Adamopoulos, S.; Hosseinpourpia, R.; Ahmed, S.A. Ammonium lignosulfonate adhesives for particleboards with pMDI and furfuryl alcohol as crosslinkers. *Polymers* **2019**, *11*, 1633. [\[CrossRef\]](#)
- Senyo, W.C.; Creamer, A.W.; Wu, C.F.; Lora, J.H. The use of organosolv lignin to reduce press vent formaldehyde emissions in the manufacture of wood composites. *Forest Prod. J.* **1996**, *46*, 73–77.
- Turunen, M.; Alvilä, L.; Pakkanen, T.T.; Rainio, J. Modification of phenol-formaldehyde resin resins by lignin, starch, urea. *J. Appl. Polym. Sci.* **2003**, *88*, 582–588. [\[CrossRef\]](#)
- Vázquez, G.; Antorrena, G.; González, J.; Mayor, J. Lignin-phenol-formaldehyde adhesives for exterior grade plywoods. *Bioresour. Technol.* **1995**, *51*, 187–192. [\[CrossRef\]](#)
- Zhang, Y.; Li, N.; Chen, Z.; Ding, C.; Zheng, Q.; Xu, J.; Meng, Q. Synthesis of high-water-resistance lignin-phenol resin adhesive with furfural as a crosslinking agent. *Polymers* **2020**, *12*, 2805. [\[CrossRef\]](#) [\[PubMed\]](#)
- Liu, J.; Li, Y.; Mo, H.; Xie, E.; Fang, J.; Gan, W. Current utilization of waste biomass as filler for wood adhesives: A review. *J. Ind. Eng. Chem.* **2022**, *115*, 48–61. [\[CrossRef\]](#)
- Kawalerczyk, J.; Dziurka, D.; Mirski, R.; Siuda, J.; Szentner, K. The effect of nanocellulose addition to phenol formaldehyde adhesive in water-resistant plywood manufacturing. *BioResources* **2020**, *15*, 5388–5401. [\[CrossRef\]](#)
- Zeppenfeld, G.; Grunwald, D. *Klebstoffe in der Holz- und Möbelindustrie*; DRW-Verlag: Leinfelden-Echterdingen, Germany, 2005.
- Aydin, I.; Demirkir, C.; Colak, S.; Colakoglu, G. Utilization of bark flours as additive in plywood manufacturing. *Eur. J. Wood Prod.* **2017**, *75*, 63–69. [\[CrossRef\]](#)

18. Kim, J.-S.; Eom, Y.G.; Kim, S.M.; Kim, H.-J. Effects of natural-resource-based scavengers on the adhesion properties and formaldehyde emission of engineered flooring. *J. Adhes. Sci. Technol.* **2007**, *21*, 211–225. [[CrossRef](#)]
19. Cao, L.; Zhou, X.; Du, G. Wood adhesive fillers used during the manufacture of wood panel products. In *Filler*; Huicochea, E.F., Ed.; Intech Open: London, UK, 2021.
20. Ayrlmis, N.; Lee, Y.-K.; Kwon, J.H.; Han, T.-H.; Kim, H.-J. Formaldehyde emission and VOCs from LVLs produced with three grades of urea-formaldehyde resin modified with nanocellulose. *Build. Environ.* **2016**, *97*, 82–87. [[CrossRef](#)]
21. Dorieh, A.; Selakjani, P.P.; Shahavi, M.H.; Pizzi, A.; Movahed, S.G.; Pour, M.F.; Aghaei, R. Recent developments in the performance of micro/nanoparticle-modified urea-formaldehyde resins used as wood-based composite binders: A review. *Int. J. Adhes. Adhes.* **2022**, *114*, 103106. [[CrossRef](#)]
22. Mahrtdt, E.; Pinkl, S.; Schmidberger, C.; van Herwijnen, H.W.G.; Veigel, S.; Gindl-Altmutter, W. Effect of addition of microfibrillated cellulose to ureaformaldehyde on selected adhesive characteristics and distribution in particle board. *Cellulose* **2016**, *23*, 571–580. [[CrossRef](#)]
23. Kamboj, G.; Gaff, M.; Smardzewski, J.; Haviarová, E.; Hui, D.; Rezaei, F.; Sethy, A.K. Effect of cellulose nanofiber and cellulose nanocrystals reinforcement on the strength and stiffness of PVAc bonded joints. *Compos. Struct.* **2022**, *295*, 115821. [[CrossRef](#)]
24. Lavoine, N.; Desloges, I.; Dufresne, A.; Bras, J. Microfibrillated cellulose—Its barrier properties and applications in cellulosic materials: A review. *Carbohydr. Polym.* **2012**, *90*, 735–764. [[CrossRef](#)] [[PubMed](#)]
25. Nakagaito, A.N.; Yano, H. The effect of fiber content on the mechanical and thermal expansion properties of biocomposites based on microfibrillated cellulose. *Cellulose* **2008**, *15*, 555–559. [[CrossRef](#)]
26. Karagiannidis, E.; Markessini, C.; Athanassiadou, E. Micro-fibrillated cellulose in adhesive systems for the production of wood-based panels. *Molecules* **2020**, *25*, 4846. [[CrossRef](#)] [[PubMed](#)]
27. Kaboorani, A.; Riedl, B.; Blanchet, P.; Fellin, M.; Hosseinaei, O.; Wang, S. Nanocrystalline cellulose (NCC): A renewable nano-material for polyvinyl acetate (PVA) adhesive. *Eur. Polym. J.* **2012**, *48*, 1829–1837. [[CrossRef](#)]
28. EN 314-1; Plywood-Bonding Quality-Part 1: Test Methods. European Committee for Standardization: Brussels, Belgium, 2005.
29. Sernek, M.; Resnik, J.; Kamke, F.A. Penetration of liquid urea-formaldehyde adhesive into beech wood. *Wood Fiber Sci.* **1999**, *33*, 41–48.
30. Cheng, E.; Sun, X. Effects of wood-surface roughness, adhesive viscosity and processing pressure on adhesion strength of protein adhesive. *J. Adhes. Sci. Technol.* **2006**, *20*, 997–1017. [[CrossRef](#)]
31. Jeong, B.; Park, B.-D. Practical relationship between apparent viscosity and molecular weight of urea-formaldehyde resin adhesives. *J. Adhes. Sci. Technol.* **2019**, *33*, 209–216. [[CrossRef](#)]
32. Gavrilovic-Grmusca, I.; Dunky, M.; Miljkovic, J.; Djiporovic-Momcilovic, M. Influence of the viscosity of UF resins on the radial and tangential penetration into poplar wood and on the shear strength of adhesive joints. *Holzforschung* **2012**, *66*, 849–856. [[CrossRef](#)]
33. Iotti, M.; Gregersen, Ø.W.; Moe, S.; Lenes, M. Rheological studies of microfibrillar cellulose water dispersions. *J. Polym. Environ.* **2011**, *19*, 137–145. [[CrossRef](#)]
34. Younesi-Kordkheili, H.; Pizzi, A. Improving the properties of phenol-lignin-glyoxal as a wood adhesive by lignin nanoparticles. *Eur. J. Wood Prod.* **2023**, *81*, 507–512. [[CrossRef](#)]
35. Yamane, C.; Aoyagi, T.; Ago, M.; Sato, K.; Okajima, K.; Takahashi, T. Two different surface properties of regenerated cellulose due to structural anisotropy. *Polym. J.* **2006**, *38*, 819–826. [[CrossRef](#)]
36. Singha, A.S.; Thakur, V.K. Fabrication and study of lignocellulosic Hibiscus sabdariffa fiber reinforced polymer composites. *BioResources* **2008**, *3*, 1173–1186. [[CrossRef](#)]
37. Pizzi, A.; Stephanou, A. Completion of alkaline cure acceleration of phenol-formaldehyde resins: Acceleration by organic anhydrides. *J. Appl. Polym. Sci.* **1993**, *51*, 1351–1352. [[CrossRef](#)]
38. Mirski, R.; Kawalerczyk, J.; Dziurka, D.; Wieruszewski, M.; Trociński, A. Effects of using bark particles with various dimensions as a filler for urea formaldehyde resin in plywood. *BioResources* **2020**, *15*, 1692–1701. [[CrossRef](#)]
39. Solt, P.; van Herwijnen, H.W.G.; Konnerth, J. Thermoplastic and moisture-dependent behavior of lignin phenol formaldehyde resins. *J. Appl. Polym. Sci.* **2019**, *136*, 48011. [[CrossRef](#)]
40. Kawalerczyk, J.; Dziurka, D.; Mirski, R. The effect of a phenol-formaldehyde adhesive reinforcement with nanocellulose on the pressing parameters of plywood. *Wood Res.* **2022**, *67*, 796–808. [[CrossRef](#)]
41. Younesi-Kordkheili, H.; Pizzi, A. Properties of plywood panels bonded with ionic liquid-modified lignin-phenol-formaldehyde resin. *J. Adhes.* **2018**, *94*, 143–154. [[CrossRef](#)]
42. Li, R.; Guo, X.; Ekevad, M.; Marklund, B.; Cao, P. Investigation of glue line shear strength of pine wood bonded with PVAc by response surface methodology. *Bioresources* **2015**, *10*, 3831–3838. [[CrossRef](#)]
43. Hass, P.; Müller, C.; Clauss, S.; Niemz, P. Influence of growth ring angle, adhesive system and viscosity on the shear strength of adhesive bonds. *Wood Mater. Sci. Eng.* **2009**, *4*, 140–146. [[CrossRef](#)]
44. Kamke, F.A.; Lee, J.N. Adhesive penetration in wood—A review. *Wood Fiber Sci.* **2007**, *39*, 205–220.
45. Suchsland, O. On the penetration of glue in wood gluing and the significance of the penetration depth for the strength of glue joints. *Holz. Roh Werkst.* **1958**, *16*, 101–108. [[CrossRef](#)]

-
46. Cavdar, A.D.; Kalaycioglu, H.; Hiziroglu, S. Some of the properties of oriented strandboard manufactured using kraft lignin phenolic resin. *J. Mater. Process. Technol.* **2008**, *202*, 559–563. [[CrossRef](#)]
 47. Park, Y.; Doherty, W.O.S.; Halley, P.J. Developing lignin-based resin coatings and composites. *Ind. Crops Prod.* **2008**, *27*, 163–167. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.