

Nanocellulose-Phenol Formaldehyde Adhesive System for Engineered Wood Products: Review

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Abstract

Incorporating cellulose nanomaterials into wood adhesives has recently been considered for improving sustainability within wood composite panels. The role of nanocellulose in such an application is mainly determined by nanocellulose dimension, form, morphological and physicochemical properties, characteristics of an adhesive system, and chemical interaction of nanocellulose and adhesive, as well as the dispersion and the orientation of nanomaterials in the polymeric matrix of adhesive. Phenol formaldehyde (PF) adhesives have been extensively used in engineered wood products for decades, and concerns about their brittleness led to continued research efforts for modifying the resin. Recently, the developments in the bio-economy and the nanocellulose industry provided new possibilities for PF adhesive modification and its structural reinforcement with a renewable, biodegradable, abundant, and mechanically strengthened resource. This paper aims to review and demonstrate the available research on the development of nanocellulose-reinforced PF as an adhesive matrix for engineered wood products, in particular, plywood, particleboard, and oriented strand board.

Engineered wood products are sustainable materials created from the adhesive bonding of wooden elements where the adhesive properties and its chemistry and physics play important roles in the performance control of the products and govern the transfer of mechanical loads across the adhesive bonds (Konnerth et al. 2007; Kurt et al. 2012; Barbu et al. 2014; Divekar 2016; Hemmilä et al. 2017; Alawode et al. 2019, 2020; Musah et al. 2021). An adhesive bond in engineered wood products consists of three zones: pure adhesive, wood, and interface. An interface is where the adhesive penetrates wood microstructure, as well as the boundary between wood and adhesive (Konnerth et al. 2006b). The penetration of an adhesive into wood structure significantly affects the distribution of strain across the wood bond lines (Gindl et al. 2004). Recent advances and innovations in wood adhesives technologies have allowed their utilization even in load-bearing applications (Klemm et al. 2005, Pröller et al. 2018, Dugmore et al. 2019, Wessels et al. 2020). Study of a wide variety of wood adhesives theoretically and experimentally indicated a strong correlation between the toughness of an adhesive, and the mechanical strength of corresponding wood adhesive bonds and the final wood product (Serrano 2004; Konnerth et al. 2006a, 2006b). Phenol formaldehyde (PF) is one of the common adhesives used in the wood industry, especially for

structural-based applications. It is made by reacting phenol and formaldehyde to yield a strong three-dimensional cross-linked network that is resistant to moisture and high temperature exposure while providing superior bond strength and dimensional stability (Joseph et al. 2002, Hunt et al. 2010, Liu et al. 2014, Wang and Xing 2016). PF is, however, reported to be a brittle resin, and its brittleness increases

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when it cures at the surface of wood because the curing chemistry of PF resin is affected by its interactions with wood (Li et al. 2021).

To address this issue, performance improvement of the PF resin has been mostly implemented by either modifying the resin chemistry (Dunky et al. 2002, Mirski et al. 2011, Tabarsa et al. 2011, Bekhta et al. 2014), or adding fillers in the form of fiber, particle, or elastomer to decrease its brittleness and cure shrinkage (Achary and Ramaswamy 1998). Cellulose nanomaterials are one of the most important bio-based and environmentally safe fillers and reinforcements for wood adhesives (Vineeth et al. 2019) with which the phenolic resins can chemically bond (Zheng et al. 2007). Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs), shown in Figure 1, are two of the most produced types of cellulosic nanomaterials (Somvanshi and Gope 2021, Bello and Chimphango 2022). CNCs are small, rigid cellulose crystal whiskers, with a diameter of 3–35 nm and a length of 200–500 nm, produced through acid treatment (Nechyporchuk et al. 2016). CNFs are tubular cellulose aggregates with amorphous regions, produced mainly by mechanical disintegration (Faria et al. 2020). Having great mechanical properties, modulus of elasticity (MOE), tensile strength, specific rigidity, and aspect ratio, CNFs are highly effective at transferring the mechanical load from polymer matrix to the fiber phase (Eichhorn et al. 2010, Dufresne 2012, Kim et al. 2015). Based on reports in the literature, using CNFs to modify

wood adhesives such as urea-formaldehyde (Veigel et al. 2011, 2012; Moslemi et al. 2020; Wibowo et al. 2021; Pinkl et al. 2022), melamine-urea-formaldehyde (Veigel et al. 2012), and poly diphenylmethane diisocyanate (Chen et al. 2020, Hornus et al. 2021) significantly improved the bonding strength in wood composite products. However, the improvements greatly depend on the individual operational conditions. Similarly, CNCs, which have a modulus of elasticity of ~138 GPa and a tensile strength of ~10 GPa, can have stronger action than Kevlar fibers, and are another biodegradable reinforcement resource for polymeric matrices (Zimmermann et al. 2004, Lahiji et al. 2008, Kim et al. 2015). In addition, CNCs have a high aspect ratio, low density, and a reactive surface which is favorable for chemical interactions with other materials. This reactive surface helps CNCs to tune the surface properties (Orts et al. 2005, Lahiji et al. 2010) to the desired application. According to the research by Zhang et al. (2013), Mesquita et al. (2018), and Kawalerczyk et al. (2020b, 2021a, 2021b, 2022b), CNC proved to have a positive impact on the bonding quality, mechanical properties, and formaldehyde emission of formaldehyde-based wood products.

Therefore, both CNC and CNF are promising reinforcements to adjust the properties of polymers and wood adhesives and improve their performance (Saïd Azizi Samir et al. 2004, Dalmas et al. 2006, Noorani et al. 2007, Petersson et al. 2007, Cui et al. 2015, Moslemi et al. 2020). This

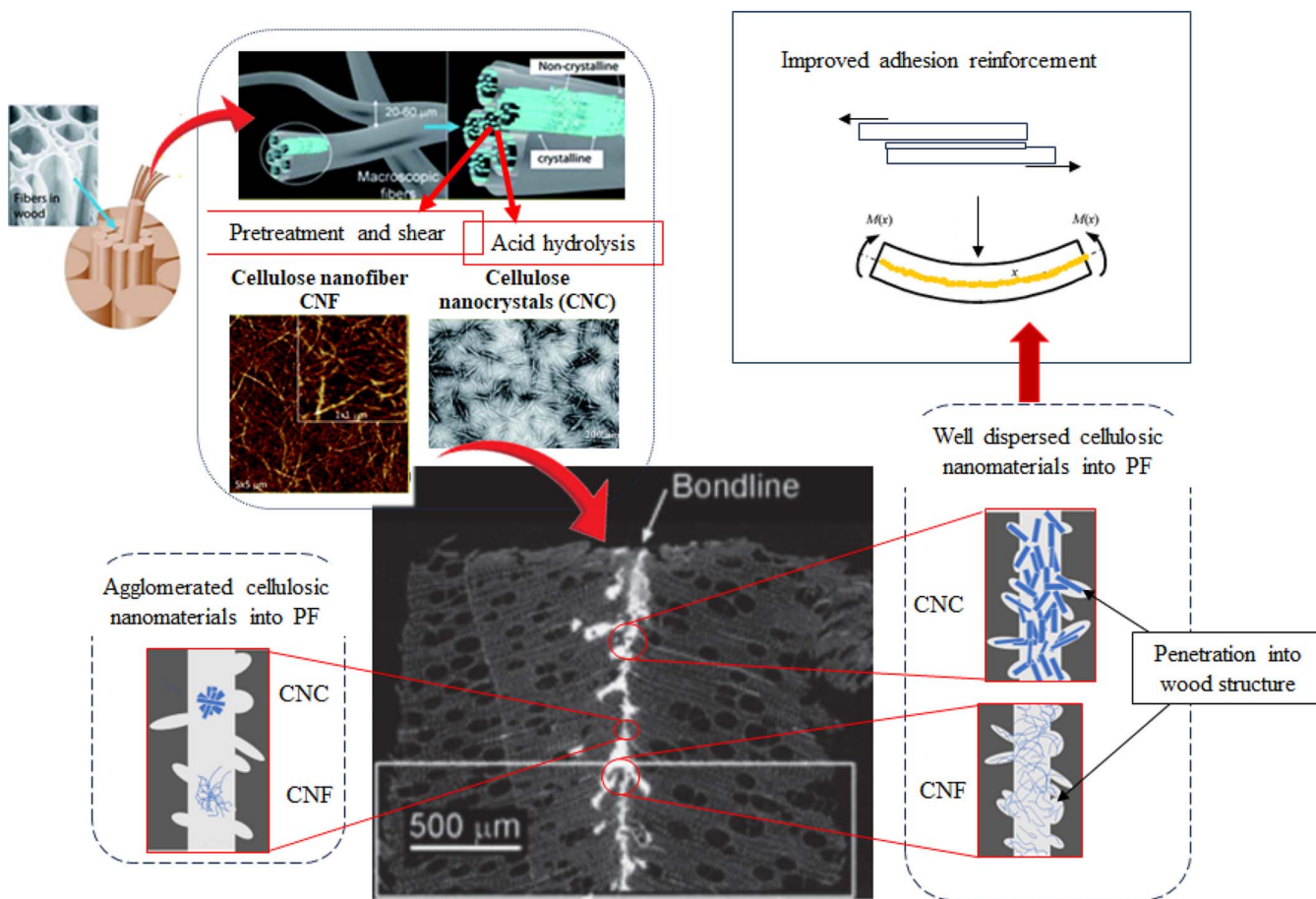


Figure 1.—Schematic of cellulose nanofiber (CNF) and cellulose nanocrystal (CNC) production from fiber cell walls and penetration of phenol formaldehyde (PF) resin into wood microstructure. Redrawn from the works of Salas et al. (2014) and Shirmohammadi and Leggate (2021).

paper reviews the current developments in the modification of PF adhesive with CNFs and CNCs, and the effect it has on the performance of plywood, oriented strand board (OSB), and particleboard.

Nanocellulose-Reinforced Phenolic Adhesive: The Effect of Shear Rate and Concentration

The biphasic CNC aqueous suspension mostly exhibits a behavior intermediate between those shown by the isotropic (Newtonian) and chiral-nematic (shear-thinning) materials (Hong 2009). Based on the research by Orts et al. (1995, 1998) and de Souza Lima and Borsali (2004), a softwood-derived CNC aqueous suspension of 280 nm length at a concentration of 5 percent by weight, and a cotton-derived CNC suspension at a concentration of 2.7 percent by weight exhibited shear-thinning behavior at low and high shear rates, meaning that their viscosity decreased with increasing shear rate. At intermediate shear rates, the suspension exhibited a Newtonian plateau where the viscosity was independent of shear rate.

However, PF resins are typically Newtonian liquids, meaning that their viscosity is independent of the applied shear rate (Hong 2009). The addition of nanocellulose to PF adhesive can change its viscosity and rheological properties, which limits its application for some engineered wood products. Hong (2009) investigated four CNC–PF resin mixtures with CNC contents of up to 3 percent by weight. The results showed that the neat resin exhibited Newtonian behavior over the entire range of shear rates. In contrast, the resin mixtures containing CNCs exhibited a shear-thinning region at low shear rates, and at this shear rate range the viscosity of the resin is considerably increased by incorporating CNCs, shown in Figure 2. At a higher shear rate, the CNC-reinforced PF indicated a Newtonian region the same as neat PF resin (Hong 2009). At very high shear rates, the shear-thinning behavior is, however, commonly reported for CNCs due to the alignment of the rod-like CNC particles with the shear direction. The shear-thinning at a low shear rate, is the least understood (Habibi et al. 2010, Lahiji et al. 2010). It is commonly believed to occur due to a complex supramolecular microstructure which is disrupted by shear forces. The viscoelastic behavior at low shear rates has been

reported to strongly depend on the shear history of the sample, possibly explaining why it is only observed in some studies and not in others.

Apart from the shear rate, the concentration of nanomaterial in an adhesive matrix is another key parameter for the performance control of the adhesive. It has been found that the flow index decreased with increasing CNC content, indicating a more pronounced deviation from Newtonian behavior at higher CNC contents. At a shear rate of 0.01 per second, the viscosity of 3 percent CNC–PF exceeded that of neat PF by almost two orders of magnitude (Hong 2009). However, sometimes higher CNC concentrations result in lower viscosity. For example, the viscosity of 1 percent CNC–PF is higher than that of the 10 percent by weight CNC at a low shear rate (Hong 2009). Therefore, there is the possibility of using the shear rate and nanomaterial concentration information to obtain a suitable viscosity for the adhesive mixture for engineered wood products. It is well understood that the CNCs aggregate in resin mixtures at higher concentrations, shown in Figure 1. The CNC aggregates manifested themselves in the form of gel beads, which are visible in thin layers of the resin under low-shear conditions. A short ultrasonic pulse can disaggregate the beads (Hong 2009). However, there are some cases where high CNC concentrations in PF resin do not show any aggregations (Hong 2009).

Application of Nanocellulose-Reinforced PF in Wood Composite

In the production process of wood-based composites, covalent bonding between PF resins and wood is negligible because covalent bonding occurs at significantly higher temperatures and longer cure times than generally used in wood-based composites manufacturing (Pizzi et al. 1994). The bonding is believed to be in the forms of the hydrogen bonds, van der Waals forces, and secondary intermolecular interactions (Pizzi and Eaton 1987, He and Riedl 2004). By penetrating the cell wall, PF resin develops primary bonds with cell wall polymers (Gindl et al. 2004, Liang et al. 2011, Jakes et al. 2015), degrades some of them, and at the same time bonds with some polymers, especially the guaiacyl units of lignin. These chemical reactions result in a high number of

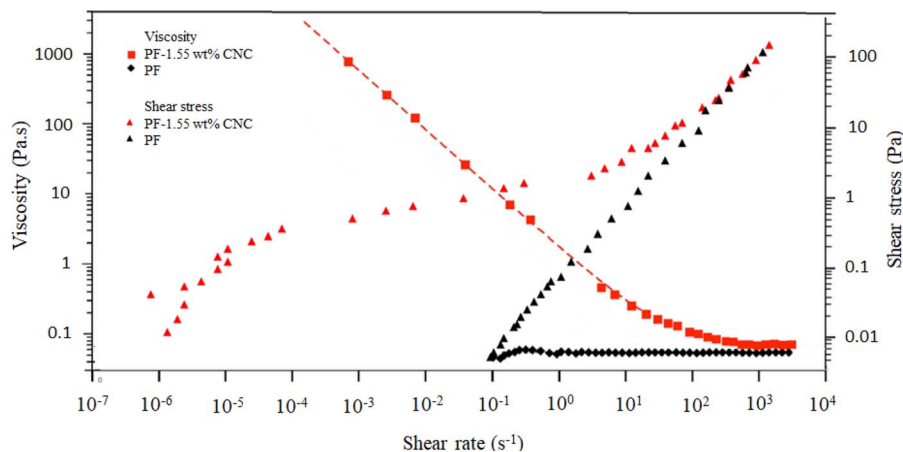


Figure 2.—Viscosity and shear stress of phenol formaldehyde (PF): 0% and 1.55 percent by weight cellulose nanocrystal (CNC)-reinforced PF, as a function of shear rate. This figure was redrawn from Hong (2009).

ortho–para and para–para bonds in latewood and ortho–para bonds in the earlywood cell wall (Yelle and Ralph 2016).

Other studies have indicated that wood carbohydrates, such as cellulose and hemicellulose, are responsible for the decrease in activation energy caused by wood, provided that the resin has molecular contact with the wood substrate (Pizzi et al. 1994). Hydrogen bonding and van der Waals forces have been proposed to be responsible for the catalytic activity of wood in contact with PF resin; therefore, the number of hydroxyl groups on the surface of the wood is an important parameter for its adhesion with PF resin. As such, cellulosic nanomaterials having high surface area followed by a large number of the hydroxyl groups can react with methylol groups of PF resin and change its curing behavior extensively (Singha and Thakur 2008, Hong 2009). In addition, the materials with phenolic end-groups can also react with other phenols and hydroxy methylated phenols (Ekman 1965) present in phenolic adhesives. Unbleached CNF can be one of these materials; however, there is no literature available about its application in a mixture with PF adhesive. In the following, the effect of nanocellulose-reinforced PF resin on different properties of wood engineered panel products (plywood, OSB, and particleboard) is reviewed briefly. While a considerable amount of research can be found regarding the reinforcement of urea–formaldehyde resins with nanocellulose, publications on PF-reinforced nanocellulose are scarce.

Plywood

Plywood is a laminated engineered wood product whose structural application has considerably increased in recent years. PF adhesive, mostly resole (which has more formaldehyde than phenol), is one of the resins that has been used for exterior-grade plywood (Moubarik et al. 2009). The viscosity of the adhesive mixture plays an important role in the performance of this engineered wood product. Suitable resin viscosity helps achieve optimal spreading of the resin, desired penetration depth, and improved mechanical and physical performances of the bond line (Hong and Park 2017). According to the GB/T2794-1995 standard, the allowable viscosity range for plywood adhesives can vary from 5 to 25 Pa·s (Zhang et al. 2019). If its viscosity is more than the allowable range, it is difficult to spread the adhesive uniformly on the veneer surface and it also does not wet and penetrate the veneer structure to create physical interlocking. Therefore, the resulting thick glue line lowers the mechanical strength of the plywood (Kurt and Cil 2012). However, if the viscosity of the adhesive mixture is lower than the permissible range, it may lead to difficulties for the application of the adhesive and pressing of the plywood. The overpenetration of the low viscosity adhesive into the wood structure results in a starved bond line and a thin layer of adhesive with low adhesion strength (Frihart 2005). In the manufacture of plywood, organic (walnut shell flour, wood flour, bark powder, soybean powder, and corn cob residue) or inorganic (calcium carbonate, clay, talcum powder) fillers are usually used to adjust the resin viscosity, prevent excessive penetration of adhesive into the veneer, reduce the adhesive consumption, shorten the assembly time, and increase the bond-line strength (Najafi and Doosthoseini 2000, Yang and Frazier 2016, Cao et al. 2020, Benhamou et al. 2021). Nanocellulose is another bio-based

filler that has been considered for this application recently and research has shown that incorporating nanocellulose into PF is beneficial for various aspects of plywood production such as increasing the resin viscosity, lowering the pressing time and temperature, lowering resin spread rate, and improving the mechanical performance of the panels, which means promoting a more efficient use of phenolic resins (Liu et al. 2015, 2018; Kawalerczyk et al. 2020a, 2020c, 2022a; Lengowski et al. 2021). Table 1 summarizes the available research articles on the application of nanocellulose in plywood panel production with PF resin.

According to Kawalerczyk et al. (2020c), incorporating 3, 5, and 7 percent by weight of CNC powder increases the viscosity of PF resin by 9, 10, and 14 percent immediately after mixing and by 18, 20, and 23 percent after 1 hour, respectively. Adding 3–5 percent CNC to PF resin improves the MOE and shear and bending strengths of plywood, while 7 percent CNC addition results in agglomeration of the nanoparticles and consequently, deteriorates the mechanical properties (Kawalerczyk et al. 2020c). Three percent by weight CNC improved the shear strength, both after 24 hours soaking in water and after 4 hours boiling, by 19 and 16 percent, respectively. Despite a great number of hydroxyl groups and interaction sites, CNC did not show any chemical interactions with PF resin; however, introducing it into PF resin improved the fracture mechanism and plasticity of the glue line in plywood, and produced a glue line with lower porosity, which limits the occurrence of microcracks in the glue line. As shown in Figure 1, it is believed that PF resin can penetrate the wood cell wall along with CNC particles and develop a strong mechanical interlocking with the wood which can improve the mechanical properties of a glue joint (Liu et al. 2014). In a different study, Liu et al. (2015) found that CNC did not change the activation energy of the curing reaction of the lignin-based phenol-formaldehyde (LPF) resin as the differential scanning calorimetry curves of the resins, with and without CNC, were the same, which may indicate no reaction between CNC and LPF resin. However, in other research with the same experiments on PF resin, higher condensation rates for methylolureas in the presence of CNCs were reported, which led to a greater number of thermally labile methylene ether linkages (Hong 2009). This translates to the significant effect of CNC on accelerating the first stage of PF resin curing, yet a very small or no effect on the second stage of the resin curing. Liu et al. (2015) also found that using CNC in the range of up to 1.0 percent based on the liquid weight of the resin increases the viscosity of lignin-based PF slightly. At higher percentages of CNC addition, the viscosity increases excessively. For 1.5 percent CNC-reinforced phenolic resin, the viscosity increased 10 times compared to the neat resin. Based on their results, adding 0.25 percent CNC content was suitable for inducing a good wet shear strength in plywood, both after 48 hours of soaking and 1 hour of boiling, and with further increase of CNC content, the strength decreased. The wet shear strength for a 1.5 percent addition of CNC was still a bit higher than that of the pure resin. Samples with higher CNC content showed a higher wood failure percentage, which is not in agreement with the shear test data (Liu et al. 2015). When mixing CNC with PF resin, because of the high surface area of CNC, the resin cannot cover the whole surface area of the nanoparticles, especially in high CNC concentration ($\geq 0.5\%$).

Table 1.—Production parameters of plywood with nanocellulose-reinforced phenol formaldehyde resin.

Reference	Phenol formaldehyde resin										Production parameters				Veneer	
	Density (g/cm ²)	Viscosity (Pa·s)	Solid content (%)	pH	Gel time (s)	Additive	Nanocellulose	Press parameters		Time (min)	Adhesive spread rate (g/m ²)	Wood species	Veneer thickness (mm)	Moisture content (%)		
								Pressure (MPa)	Temperature (°C)							
Kawalerczyk et al. (2020c)	1.2	0.55	47	12.5	192 (130°C)	Tannic	CNC ^a powder	1.4	140	4	160	Birch	1.5	6 ± 1		
Lengowski et al. (2021)	—	—	52.4	12	480 (121°C)	Wheat flour	Bleached CNF	1.08	140	12	380	<i>Pinus taeda</i>	2.8	8–12		
Liu et al. 2018	—	0.04–0.09	45	—	—	—	Freeze-dried CNC and CNF	—	—	—	—	—	—	—		
Liu et al. 2015	—	0.15–0.2	45	—	—	—	CNC	2.3	150	5	178	Yellow birch	1.5	—		
Kawalerczyk et al. (2020a)	1.2	0.55	48	12.5	192 (130°C)	Tannic	CNC powder	1.4	140	4	120–170	Birch	1.5	6 ± 1		
Kawalerczyk et al. (2022)	1.2	0.933	52	—	192 (130°C)	Tannic	CNC powder	1.4	115–140	2.5–4	160	Birch	1.3 ± 0.2	5		

^a CNC = cellulose nanocrystal; CNF = cellulose nanofiber.

Therefore, there is a possibility of interaction between CNCs followed by their agglomeration. Due to their shape, CNCs can transfer the loads in the polymeric matrix of adhesive. Pressing may cause partial alignment of the CNC, resulting in better load transfer along the CNC long axis direction, and improving the compression and tension stress response during bending. Therefore, in the case of CNC agglomerations, the stress accumulates in specific points, which deteriorates the mechanical performance of the plywood. This could explain why the strength improved with a certain percentage of CNC addition but worsened with increasing CNC content.

The adhesive spread rate is another parameter that affects the production cost and strength properties of plywood by controlling the glue-line thickness. If the glue-line is too thin, it cannot withstand the stresses induced by either the mechanical loads or dimensional changes. By further increasing the glue-line thickness, the plywood performance improves to a certain point, then deteriorates after that point (Bekhta and Marutzky 2007). Kawalerczyk et al. (2020a) studied the possible reduction of resin spread rate of PF reinforced with CNCs. They measured bond quality in birch-veneer plywood manufactured with PF with 3 percent by weight CNC and spread rates ranging from 170 to 120 g/m². The results showed that the plywood produced with 170, 160, and 150 g/m² of CNC-reinforced PF resin showed higher shear and bending properties compared to the reference plywood with PF consumption of 170 g/m². Surprisingly, even the 140 g/m² variant had equal glue joint properties to the reference plywood (Kawalerczyk et al. 2020a). This 30-g reduction of glue per square meter of veneer is profitable and economically beneficial for plywood production.

In the plywood industry, pressing time and temperature are two influential parameters due to their influence on the properties and manufacturing cost of plywood panels (Hong and Park 2017). Pressing is considered one of the most energy-consuming stages in the plywood production process (Bekhta et al. 2020). Accordingly, Kawalerczyk et al. (2022a) studied the possible reduction of plywood pressing parameters by reinforcing PF resin with 3 and 5 percent by weight of CNC. This 3 and 5 percent by weight CNC reinforcement decreased the curing time of the PF resin, and based on the results from the shear and bending tests, there is a possibility of reducing pressing time by 25 and 38 percent and pressing temperature by 7 and 14 percent due to incorporation of CNC into PF resin, respectively. Shear strength is a more reliable indicator of adhesive bond-line performance in plywood, so even if the bending test results proved the ability to decrease the pressing time further, the shear strength is a limiting factor. Pressed for 180 seconds, CNC-containing plywood showed the same shear strength as the panels with neat PF resin pressed for 240 seconds, both after soaking and after boiling. Additionally, adding CNC decreased the pressing temperature by 10°C (to 130°C). It should be noted that the temperature required to complete the polycondensation of phenolic resins is 135°C to 150°C (Mirski et al. 2011), therefore pressing below 130°C will weaken the bonding quality of both nonreinforced and CNC-reinforced plywood.

CNF is another cellulosic nanomaterial that has been recently considered for plywood improvement research. According to Lengowski et al. (2021), by adding small

amounts of CNFs, 0.026, 0.038, and 0.064 percent by weight, to the PF resin mixture, the viscosity of PF resin increased by 45, 50, and 58 percent, and gel time decreased by 26, 32, and 33 percent, respectively. Decrease in the gel time can translate to shorter working and pressing times. From that, 0.038 percent CNF-reinforced plywood showed the best mechanical properties. However, incorporating 0.064 percent CNF deteriorated the properties of the plywood. The authors used the adhesive spread rate of 380 g/cm² in this research, which is quite high and according to Vick (1999), PF resin is not capable of forming strong bonds in the thick and variable thickness of the adhesive layers.

Both CNF and CNC are proven to remarkably improve the viscoelasticity and creep properties of the wood–PF resin interface. They have synergistic effects on PF resin and act as a foundation for the PF particles. As pointed out by Liu et al. (2018), CNF-reinforced PF resin deforms less than the CNC-incorporated one at the same loading condition, and its permanent deformation after unloading is also lower (Liu et al. 2018). This could be attributed to the different strengthening effects of the nanoparticles. PF resin can probably penetrate the wood microstructure with accompanied CNF fibrils. The high aspect ratio of CNFs enhanced the stiffness of the bonding interface as a load carrier (Liu et al. 2018). PF resin can also penetrate the CNF's structure, then the nanofibrils entangle and form an interconnected and strong network (Xing et al. 2016) which can significantly improve the viscoelastic properties of a wooden joint. CNCs are smaller than CNFs, and they can be transferred with the PF resin into the wood microstructure. However, the CNC particles have a limited reinforcement effect (Liu et al. 2018). Accordingly, the deformation-resistance capability of CNC is lower than that of CNF and microfibrillated cellulose (MFC) on the wood–resin interface (Liu et al. 2018). Adding nanocellulose particles to PF resin reduced its brittleness and improved the wood sample flexibility, promising vast potential in many applications (Liu et al. 2018).

In CNF, molecules regularly arrange along the cellulose chain, giving rise to amorphous and crystalline regions. The amorphous regions buffer against stress-reduced deformation on the wood–resin interface. CNC is a crystalline material with no amorphous regions. Therefore, in viscoelastic deformation, the cellulose chain of CNC has a poor curling and stretching performance compared with CNF. CNF is a single fibril with a higher permanent deformation due to lower elasticity. The CNC-incorporated PF has the lowest deformation tendency, while the CNF-incorporated PF has a slightly higher deformation tendency. In addition, MFC-reinforced PF showed lower initial deformation, while CNC- and CNF-reinforced PF resins perform better with time (Liu et al. 2018). In contrast, Fu et al. (2016) pointed out that the CNF–PF morphology showed very high deformability (up to 85%–90% strain) but failed to recover their shape after being highly compressed.

OSB and particleboard

Particleboard and OSB are engineered wood products manufactured utilizing wood particles or strands bonded together with different wood resins. PF is one of the resins that has been used for these applications and the amount of its consumption is 5–15 percent wt/wt in typical commercial

applications. Cellulose nanomaterials proved to be promising resources for partially replacement of synthetic resins in the wood industry to increase the adhesive viscosity, shorten the assembly time, reduce adhesive consumption, and increase the panels' performance while making it lighter in weight. For particleboard or OSB production, the adhesive is converted into small resin drops (40–60 μm in diameter) and sprayed onto the wood particles or strands. In this case, the amount of resin used is small compared to plywood, and a continuous glue line is not formed. The bigger the grain size of the fillers, the larger resin droplets that will be produced. This results in poor distribution of the resin on the surface of wood particles or strands. Table 2 lists the available literature on the application of nanocellulose in PF resin as a bonding agent in either particleboard, OSB, or two wood flakes.

Research by Kojima et al. (2018) showed that particleboard bonded with 20 percent CNF develops the same properties as particleboard with 1 percent by weight neat PF resin. CNF can attach to the surface of wood particles and creates hydrogen bonding between them.

It is reported that adding 3 percent MFC (based on the dry weight of resin) significantly improved the elastic modulus and strength of PF resin by 31.6 and 24.1 percent, respectively (Wang and Xing 2016). The mechanical properties of OSB panels produced with this reinforced resin also significantly increased. The flexural MOE increased by ~22.5 percent and the flexural modulus of rupture (MOR) increased by ~18–23.5 percent compared to the panels containing neat PF resin and similar density. Internal bond (IB) strength was found to increase and the thickness swelling decreased. More significantly, adding a 3 percent mixture of microcellulose and nanocellulose fibers (which was blended with nano-clay) to the PF resin increases the MOE, MOR, and IB of OSB panels by 23, 29.1, and 23.2 percent, respectively. The thickness swelling was also reduced by 9.9 percent. The blend of micro- and nanocellulose with nano-clay easily was dispersed into PF resin via a simple mechanical mixer and improved the performance of OSB panels (Wang and Xing 2016). Due to the small size of cellulosic nanomaterials, better interlocking and bonding between the web-like structure of nanocellulose and PF resin can occur. The hydrophilicity of CNF and PF increases their compatibility, making CNF swell prior to PF polymerization. This generates a molecular cell wall–PF composite in the outer layer of CNFs, creating a robust fiber-matrix interface (Neelamana et al. 2013). Although it is believed that a chemical interaction is another cause for the improvement of the mechanical performance of PF resin with the addition of nanocellulose, there are conflicting data available in this regard. For example, CH₂ and CH groups are produced during the curing process of the PF resin as well as from the interaction between PF and nanocellulose. As the two phenomena occur simultaneously, there is a doubt whether these two products are due to the chemical interaction between nanocellulose and PF resin or due to the standard curing of PF resin (He and Riedl 2004, Poljansek and Krajnc 2005). Joseph (2006) reported that the cellulosic hydroxyl groups could easily create hydrogen bonds with phenolic hydroxyl groups of the resole at 50°C. These groups can experience cross-condensation reactions at higher temperatures to form the cellulosic fiber–PF three-dimensional network, increasing

Table 2.—Production parameters of particle board or oriented strand board with nanocellulose and/or phenol formaldehyde resin.

Reference	Phenol formaldehyde				Production parameters			Wood species	
	Viscosity (Pa·s)	Solid content (%)	pH	Nanocellulose	Press parameters		Adhesive spread rate (g/m ²)		
					Pressure (MPa)	Temperature (°C)			Time (min)
Liu et al. (2014)	0.04–0.09	45	10.3–10.7	CNF and CNC ^a	—	160	30	160	Red oak (<i>Quercus rubra</i>)
Hong (2009)	—	50	—	CNC	—	—	—	22.5	Yellow pine
Kojima et al. (2018)	1.1	40	11.8	Freeze dried CNF	2.4	180	1.5	—	—
Wang and Xing (2016)	—	—	—	CNF	—	204.4	4–5	—	Southern pine

^a CNC = cellulose nanocrystal; CNF = cellulose nanofiber.

the chemical interlocking strength at the hydrophilic centers of the PF resin.

When CNF or CNC is added to the PF resin and the mixture is used as a joint for two pieces of wood flakes, the mechanical properties at different distances from the bond line change (Liu et al. 2014). For instance, the bond line shows a higher elastic modulus than the locations close and far from the bond line. This is because PF resin can penetrate the wood microstructure (Gindl et al. 2004, Liu et al. 2018). It is highly probable that the filling of pores with PF resin would increase the shear rigidity of the cell wall, which should, in turn, reduce shear deformation during loading. Nevertheless, Liu et al. (2018) reported no increase in indentation modulus in PF-infiltrated wood cell walls. During PF penetration, the CNF or CNC can also partly penetrate the wood microstructure. However, accumulates in the glue line. In the case of being exposed to a mechanical load, CNF or CNC uniformly disperses the stress into the adhesive matrix and increases the load-bearing capacity of engineered wood products. Liu et al. (2014) found that in the samples containing CNF, the modulus at 0.4 mm away from the bond line was 76 percent lower than the one at the bond line. Apart from the distance from the bond line, different parts of the wood cell wall (middle lamella, secondary cell wall S2 layer, and lumen) can also be affected differently by the addition of nanocellulose to the PF resin (Liu et al. 2014). This can be attributed to the partial penetration of nanocellulose in the wood microstructure. The CNF and CNC significantly increase the indentation modulus of the S2 layer, followed by the lumen and middle lamella. Close to the glue line, the modulus of the S2 layer increased by 67.1 and 79.0 percent for CNC and CNF, respectively. Cellulose nanomaterials mostly accumulate at the bond line and have a positive impact on interlocking formation between the wood substrates. Additionally, close and far from the glue line, the hardness of the S2 layer increased by 8.92 and 49.6 percent for CNC, and by 47.7 and 70.3 percent for CNF. The cellulose nanomaterial-reinforced PF resin improves the modulus but not the hardness in the compound corner-middle lamellae (Liu et al. 2014).

However, there is contradictory information regarding the effect of nanocellulose on mechanical properties of the bond line in wood products; some results showed that by increasing the CNC content in PF resin, a weak boundary layer is created, and the fracture energy of the composite decreases drastically (Hong 2009). The curing process of resin and more cross-linking with CNC can cause shrinkage and internal stress in the bond line, which can be a reason for the lower fracture energy of PF resins with higher levels of CNC. Additionally, the higher the degree of resin vitrification, the higher the number of voids that appeared in the bond line, and the less symmetric resin penetration into the wood in CNC-containing PF adhesive. A higher number of voids can result from the substantial increase in resin viscosity at low shear rates after adding CNC, leading to difficulty in spreading the adhesive on the wood particles and trapping air bubbles inside the adhesive which further act as glue-line defects and stress points (Fig. 3). It should be noted that at low and high shear rates, CNC suspensions show shear thinning behavior, and at the intermediate shear rates, they behave as Newtonian suspensions (Orts et al. 1995).

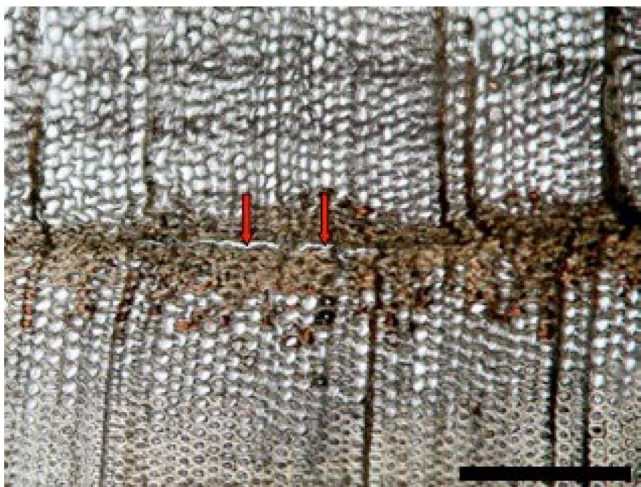


Figure 3.—Transverse image of the glue line for a mixture of 1.55 percent by weight cellulose nanocrystal and phenol formaldehyde resin with the red arrows showing voids. (Scale bar: 0.5 mm). This figure was adapted from Hong (2009).

Conclusion

Nanocellulose (CNC and CNF) performance as a reinforcement for PF adhesive is primarily dependent on the morphology and chemistry of nano-cellulosic materials, the adhesive properties, and the extent of dispersion and orientation of nanocellulose in the adhesive matrix, as well as the extent of penetration of the PF resin and nanocellulose into the wood structure. Although research on the applications of nanocellulose for the reinforcement of PF wood adhesive is scarce, the information presented in this paper is promising for the engineered wood panels industry in terms of advancing the physical and mechanical properties of wooden products, adjusting the resin viscosity, and reducing the adhesive spread rate, curing time, and hot press time and temperature. Nevertheless, more research is still needed to answer the questions regarding (1) the chemical interaction between PF resin and different cellulosic nanomaterials such as bleached and unbleached materials, (2) the penetration mechanism of nanocellulose into the wood cell wall and the distribution of the nanomaterials in the bond line and adjacent wood, (3) the effect of nanocellulose on water resistance of PF-glued wood panels, and (4) the failure mechanisms and microscopy of the wood bond line with nanocellulose-reinforced PF resin.

Literature Cited

Achary, P. S. and R. Ramaswamy. 1998. Reactive compatibilization of a nitrile rubber/phenolic resin blend: Effect on adhesive and composite properties. *J. Appl. Polym. Sci.* 69(6):1187–1201.

Alawode, A. O., P. E. Bungu, S. O. Amiandamhen, M. Meincken, and L. Tyhoda. 2019. Properties and characteristics of novel formaldehyde-free wood adhesives prepared from *Irvingia gabonensis* and *Irvingia wombolu* seed kernel extracts. *Int. J. Adhes. Adhes.* 95:102423.

Alawode, A. O., P. S. Eselem-Bungu, S. O. Amiandamhen, M. Meincken, and L. Tyhoda. 2020. Evaluation of *Irvingia* kernels extract as biobased wood adhesive. *J. Wood Sci.* 66:1–13.

Barbu, M. C., R. Reh, and M. Irl. 2014. Wood-based composites. In: *Research Developments in Wood Engineering and Technology*. A. Aguilera and J. P. Davim (Eds.) IGI Global, Hershey, Pennsylvania. pp. 1–45.

Bekhta, P., and R. Marutzky. 2007. Reduction of glue consumption in the plywood production by using previously compressed veneer. *Holz als Roh-und Werkstoff*. 65(1):87–88.

Bekhta, P., G. Ortyńska, and J. Sedliacik. 2014. Properties of modified phenol-formaldehyde adhesive for plywood panels manufactured from high moisture content veneer. *Drvna Industrija* 65(4):293–301.

Bekhta, P., J. Sedliacik, and N. Bekhta. 2020. Effects of selected parameters on the bonding quality and temperature evolution inside plywood during pressing. *Polymers* 12(5):1035.

Bello, F. and A. Chimpango. 2022. Non-catalyzed formic acid based process for preparing thermally stable spherical cellulose nanocrystals from mango seed husk. *Biomass Conversion Biorefinery* 14: 1133–1148. <https://doi.org/10.1007/s13399-022-03245-y>

Benhamou, A. A., A. Boussetta, Z. Kassab, M. Nadifyine, M. H. Salim, N. Grimi, M.E. Achaby, and A. Moubarik. 2021. Investigating the characteristics of cactus seeds by-product and their use as a new filler in phenol formaldehyde wood adhesive. *Int. J. Adhes. Adhes.* 110:102940.

Chen, H., P. Gnanasekar, S. S. Nair, W. Xu, P. Chauhan, and N. Yan. 2020. Lignin as a key component in lignin-containing cellulose nanofibrils for enhancing the performance of polymeric diphenylmethane diisocyanate wood adhesives. *ACS Sustain. Chem. Eng.* 8(46):17165–17176.

Cao, L., X. Zhou, and G. Du. 2020. Wood adhesive fillers used during the manufacture of wood panel products. E.F Huicochea (ed.) In: *Fillers*. IntechOpen. London, United Kingdom. pp. 1–9.

Chinese standard, GB/T 2794 (1995). *Determination Methods For Viscosity Of Adhesives*.

Cui, J., X. Lu, X. Zhou, L. Chrusciel, Y. Deng, H. Zhou, ... and N. Brosse. 2015. Enhancement of mechanical strength of particleboard using environmentally friendly pine (*Pinus pinaster* L.) tannin adhesives with cellulose nanofibers. *Ann. Forest Sci.* 72:27–32.

Dalmas, F., L. Chazeau, C. Gauthier, J. Y. Cavallé, and R. Dendievel. 2006. Large deformation mechanical behavior of flexible nanofiber filled polymer nanocomposites. *Polymer* 47(8):2802–2812.

de Souza Lima, M. M. and R. Borsali. 2004. Rodlike cellulose microcrystals: Structure, properties, and applications. *Macromol. Rapid Comm.* 25(7):771–787.

Divekar, N. 2016. Introduction to new material—Cross laminated timber. *Int. J. Eng. Res.* 5(3):675–679.

Duffresne, A. 2012. Potential of nanocellulose as a reinforcing phase for polymers. *J. Sci. Technol. Forest Prod. Process.* 2(6):6–16.

Dugmore, M., M. Nocetti, M. Brunetti, Z. Naghizadeh, and C. B. Wessels. 2019. Bonding quality of cross-laminated timber: Evaluation of test methods on *Eucalyptus grandis* panels. *Construct. Build. Mater.* 211:217–227.

Dunky, M., T. Pizzi, and M. V. Leemput. 2002. Wood adhesion and glued products. Report on the state of the art. COST Action E13 - WG 2. COST Association (European Cooperation in Science and Technology), Brussels, Belgium.

Eichhorn, S. J., A. Duffresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A. N. Nakagaito, A. Mangalam, J. Simonsen, A. S. Benight, A. Bismarck, L. A. Berglund, and T. Peijs. 2010. Current international research into cellulose nanofibres and nanocomposites. *J. Mater. Sci.* 45:1–33.

Ekman, K. H. 1965. Formaldehyde obtained by alkaline hydrolysis of wood and lignin. *TAPPI*. 48(7): 398–402.

Faria, L. U. S., B. J. S. Pacheco, G. C. Oliveira, and J. L. Silva. 2020. Production of cellulose nanocrystals from pineapple crown fibers through alkaline pretreatment and acid hydrolysis under different conditions. *J. Mater. Res. Technol.* 9(6):12346–12353.

Frihart, C. R. 2005. Adhesive bonding and performance testing of bonded wood products. *Journal of ASTM International*. 2(7). <https://doi.org/10.1520/JAI12952>.

Fu, J., S. Wang, C. He, Z. Lu, J. Huang, and Z. Chen. 2016. Facilitated fabrication of high strength silica aerogels using cellulose nanofibrils as scaffold. *Carbohydr. Polym.* 147:89–96.

Gindl, W., T. Schöberl, and G. Jeronimidis. 2004. The interphase in phenol-formaldehyde and polymeric methylene di-phenyl-di-isocyanate glue lines in wood. *Int. J. Adhes. Adhes.* 24(4):279–286.

Habibi, Y., L. A. Lucia, and O. J. Rojas. 2010. Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chem. Rev.* 110(6):3479–3500.

He, G. and B. Riedl. 2004. Curing kinetics of phenol formaldehyde resin and wood-resin interactions in the presence of wood substrates. *Wood Sci. Technol.* 38:69–81.

- Hemmilä, V., S. Adamopoulos, O. Karlsson, and A. Kumar. 2017. Development of sustainable bio-adhesives for engineered wood panels—A review. *RSC Adv.* 7(61):38604–38630.
- Hong, J. K. 2009. Effect of cellulose nanocrystals on the rheology, curing behavior, and fracture performance of phenol-formaldehyde resin. Doctoral dissertation. Virginia Tech, Blacksburg.
- Hong, M. K. and B. D. Park. 2017. Effect of urea-formaldehyde resin adhesive viscosity on plywood adhesion. *J. Korean Wood Sci. Technol.* 45(2):223–231.
- Hornus, M., B. K. Via, T. Gallagher, and M. S. Peresin. 2021. Partial substitution of pMDI with lignin containing cellulose nanofibrils: Low density oriented strand board. *Wood Mater. Sci. Eng.* 16(6):391–396.
- Hunt, C. G., J. E. Jakes, and W. Grigsby. 2010. Evaluation of adhesive penetration of wood fibre by nanoindentation and microscopy. In: *BIOCOMP 2010: 10th Pacific Rim Bio-based Composites Symposium*. Banff, Alberta, Canada on October 5-8, 2010. pp. 216–226.
- Jakes, J. E., C. G. Hunt, D. J. Yelle, L. Lorenz, K. Hirth, S. C. Gleber, ... and C. R. Frihart. 2015. Synchrotron-based x-ray fluorescence microscopy in conjunction with nanoindentation to study molecular-scale interactions of phenol-formaldehyde in wood cell walls. *ACS Appl. Mater. Interface.* 7(12):6584–6589.
- Joseph, S. 2006. PhD thesis. Banana fibre: A potential reinforcement in Phenol Formaldehyde resin. Mahatma Gandhi University, Kottayam, Kerala, India.
- Joseph, S., M. S. Sreekala, Z. Oommen, P. Koshy, and S. Thomas. 2002. A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibres and glass fibres. *Compos. Sci. Technol.* 62(14):1857–1868.
- Kawalerczyk, J., D. Dziurka, and R. Mirski. 2020a. The possible reduction of phenol-formaldehyde resin spread rate by its nanocellulose-reinforcement in plywood manufacturing process. *Ann. Warsaw Univ. Life Sci. SGGW Forestry Wood Technol.* 111:21–26.
- Kawalerczyk, J., D. Dziurka, R. Mirski, and J. Siuda. 2021a. The reduction of adhesive application in plywood manufacturing by using nanocellulose-reinforced urea-formaldehyde resin. *J. Appl. Polym. Sci.* 138(7):49834.
- Kawalerczyk, J., D. Dziurka, R. Mirski, J. Siuda, and M. Babicka. 2021b. Possibility of use of NCC-reinforced melamine-urea-formaldehyde adhesive in plywood manufacturing. *Drvna Industrija* 72(3): 279–289.
- Kawalerczyk, J., D. Dziurka, R. Mirski, and K. Szentner. 2020b. Properties of plywood produced with urea-formaldehyde adhesive modified with nanocellulose and microcellulose. *Drvna Industrija* 71(1):61–67.
- Kawalerczyk, J., D. Dziurka, R. Mirski, J. Siuda, and K. Szentner. 2020c. The effect of nanocellulose addition to phenol-formaldehyde adhesive in water-resistant plywood manufacturing. *BioResources.* 15(3):5388–5401.
- Kawalerczyk, J., D. Dziurka, and R. M. Poland. 2022a. The effect of a phenol formaldehyde adhesive reinforcement with nanocellulose on the pressing parameters of plywood. *Wood Res.* 67(5):796–808.
- Kawalerczyk, J., J. Walkiewicz, D. Dziurka, R. Mirski, and J. Brózdowski. 2022b. APTES-modified nanocellulose as the formaldehyde scavenger for UF adhesive-bonded particleboard and strawboard. *Polymers* 14(22):5037.
- Kim, J. H., B. S. Shim, H. S. Kim, Y. J. Lee, S. K. Min, D. Jang, ... and J. Kim. 2015. Review of nanocellulose for sustainable future materials. *Int. J. Precis. Eng. Manuf. Green Technol.* 2:197–213.
- Klemm, D., B. Heublein, H. Fink, and A. Bohn. 2005. Fascinating biopolymer and sustainable raw material angewandte. *Polym. Sci. Cell.* 44:3358–3393.
- Kojima, Y., N. Kato, K. Ota, H. Kobori, S. Suzuki, K. Aoki, and H. Ito. 2018. Cellulose nanofiber as complete natural binder for particleboard. *Forest Prod. J.* 68(3):203–210.
- Konnerth, J., W. Gindl, M. Harm, and U. Müller. 2006a. Comparing dry bond strength of spruce and beech wood glued with different adhesives by means of scarf-and lap joint testing method. *Eur. J. Wood Wood Prod.* 64(4):269–271.
- Konnerth, J., W. Gindl, and U. Müller. 2007. Elastic properties of adhesive polymers. I. Polymer films by means of electronic speckle pattern interferometry. *J. Appl. Polym. Sci.* 103(6):3936–3939.
- Konnerth, J., A. Jäger, J. Eberhardsteiner, U. Müller, and W. Gindl. 2006b. Elastic properties of adhesive polymers. II. Polymer films and bond lines by means of nanoindentation. *J. Appl. Polym. Sci.* 102(2):1234–1239.
- Kurt, R. and M. Cil. 2012. Effects of press pressures on glue line thickness and properties of laminated veneer lumber glued with phenol formaldehyde adhesive. *BioResources* 7(4):5346–5354.
- Kurt, R., H. Meriç, K. Aslan, and M. Cil. 2012. Laminated veneer lumber (LVL) manufacturing using three hybrid poplar clones. *Turk. J. Agric. Forestry* 36(2):237–245.
- Lahiji, R. R., R. Reifenger, A. Raman, A. Rudie, and R. J. Moon. 2008. Characterization of cellulose nanocrystal surfaces by SPM. In: *Technical Proceedings of the 2008 NSTI Nanotechnology Conference and Trade Show*. June 1-5, Boston, Massachusetts, USA. Boca Raton, FL: CRC Press. 2: 704–707.
- Lahiji, R. R., X. Xu, R. Reifenger, A. Raman, A. Rudie, and R. J. Moon. 2010. Atomic force microscopy characterization of cellulose nanocrystals. *Langmuir* 26(6):4480–4488.
- Lengowski, E. C., E. A. Bonfatti Jr., R. Dallo, S. Nisgoski, J. L. M. D. Mattos, and J. G. Prata. 2021. Nanocellulose-reinforced phenol-formaldehyde resin for plywood panel production. *Maderas. Ciencia Tecnología* 23. <http://dx.doi.org/10.4067/s0718-221x2021000100405>.
- Li, F., C. Ye, Y. Huang, X. Liu, and B. Fei. 2021. Incorporation of in situ synthesized nano-copper modified phenol-formaldehyde resin to improve the mechanical properties of Chinese fir: A preliminary study. *Polymers* 13(6):876.
- Liang, K., G. B. Du, O. Hosseinaei, S. Q. Wang, and H. Wang. 2011. Mechanical properties of secondary wall and compound corner middle lamella near the phenol-formaldehyde (PF) adhesive bond line measured by nanoindentation. *Adv. Mater. Res.* 236:1746–1751.
- Liu, C., Z. Cheng, S. Wang, Y. Zhang, and O. Hosseinaei. 2018. Effects of nanocrystalline cellulose on the micro-creep properties of phenol formaldehyde resin. *Mater. Res. Expr.* 5(12):125019.
- Liu, C., Y. Zhang, S. Wang, Y. Meng, and O. Hosseinaei. 2014. Micromechanical properties of the interphase in cellulose nanofiber-reinforced phenol formaldehyde bondlines. *BioResources* 9(3):5529–5541.
- Liu, Z., Y. Zhang, X. Wang, and D. Rodrigue. 2015. Reinforcement of lignin-based phenol-formaldehyde adhesive with nano-crystalline cellulose (NCC): Curing behavior and bonding property of plywood. *Mater. Sci. Appl.* 6(06):567.
- Mesquita, R. G. D. A., L. M. Mendes, A. R. Sanadi, A. R. de Sena Neto, P. I. C. Claro, A. C. Corrêa, and J. M. Marconcini. 2018. Urea formaldehyde and cellulose nanocrystals adhesive: studies applied to sugarcane bagasse particleboards. *J. Polym. Environ.* 26:3040–3050.
- Mirski, R., D. Dziurka, and J. Łęcka. 2011. Potential of shortening pressing time or reducing pressing temperature for plywood resinated with PF resin modified using alcohols and esters. *Eur. J. Wood Wood Prod.* 69(2):317–323.
- Moslemi, A., T. Behzad, and A. Pizzi. 2020. Addition of cellulose nanofibers extracted from rice straw to urea formaldehyde resin; effect on the adhesive characteristics and medium density fiberboard properties. *Int. J. Adhes. Adhes.* 99:102582.
- Moubarik, A., A. Pizzi, A. Allal, F. Charrier, and B. Charrier. 2009. Cornstarch and tannin in phenol-formaldehyde resins for plywood production. *Ind. Crops Prod.* 30(2):188–193.
- Musah, M., X. Wang, Y. Dickinson, R. J. Ross, M. Rudnicki, and X. Xie. 2021. Durability of the adhesive bond in cross-laminated northern hardwoods and softwoods. *Construct. Build. Mater.* 307:124267.
- Najafi, S. K. and K. Doosthoseini. 2000. The use of gall flour as the filler of phenol-formaldehyde resin in plywood manufacturing. *Iran. J. Nat. Res.* 53(2):155–164.
- Nechyporchuk, O., M. N. Belgacem, and J. Bras. 2016. Production of cellulose nanofibrils: A review of recent advances. *Ind. Crops Prod.* 93:2–25.
- Neelamana, I. K., S. Thomas, and J. Parameswaranpillai. 2013. Characteristics of banana fibers and banana fiber reinforced phenol formaldehyde composites—Macroscale to nanoscale. *J. Appl. Polym. Sci.* 130(2):1239–1246.
- Noorani, S., J. Simonsen, and S. Atre. 2007. Nano-enabled microtechnology: Polysulfone nanocomposites incorporating cellulose nanocrystals. *Cellulose* 14:577–584.
- Orts, W. J., L. Godbout, R. H. Marchessault, and J. F. Revol. 1995. Shear-induced alignment of liquid-crystalline suspensions of cellulose

- microfibrils. Flow-Induced Structure in Polymers-Chapter 23. pp 335–348. <http://dx.doi.org/10.1021/bk-1995-0597.ch023>.
- Orts, W. J., L. Godbout, R. H. Marchessault, and J. F. Revol. 1998. Enhanced ordering of liquid crystalline suspensions of cellulose microfibrils: A small angle neutron scattering study. *Macromolecules* 31(17):5717–5725.
- Orts, W. J., J. Shey, S. H. Imam, G. M. Glenn, M. E. Guttman, and J. F. Revol. 2005. Application of cellulose microfibrils in polymer nanocomposites. *J. Polym. Environ.* 13:301–306.
- Petersson, L., I. Kvien, and K. Oksman. 2007. Structure and thermal properties of poly (lactic acid)/cellulose whiskers nanocomposite materials. *Compos. Sci. Technol.* 67(11–12):2535–2544.
- Pinkl, S., S. Veigel, W. Gindl-Altmutter, H. van Herwijnen, and M. Riegler. 2022. Effects of fibrillar cellulosic additives on particleboard production and properties. *Wood Mater. Sci. Eng.* 17(2):106–112.
- Pizzi, A. and N. J. Eaton. 1987. A conformational analysis approach to phenol-formaldehyde resins adhesion to wood cellulose. *J. Adhes. Sci. Technol.* 1(1):191–200.
- Pizzi, A., B. Mtsweni, and W. Parsons. 1994. Wood-induced catalytic activation of PF adhesives autopolymerization vs. PF/wood covalent bonding. *J. Appl. Polym. Sci.* 52(13):1847–1856.
- Poljansek, I. and M. Krajnc. 2005. Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. *Acta Chimica Slovenica* 52(3):238.
- Pröllner, M., M. Nocetti, M. Brunetti, M. C., Barbu, M. Blumentritt, and C. B. Wessels. 2018. Influence of processing parameters and wood properties on the edge gluing of green Eucalyptus grandis with a one-component PUR adhesive. *Eur. J. Wood Wood Prod.* 76:1195–1204.
- Azizi Samir, M. A., F. Alloin, M. Paillet, and A. Dufresne. 2004. Tangling effect in fibrillated cellulose reinforced nanocomposites. *Macromolecules* 37(11):4313–4316.
- Salas, C., T. Nypelö, C. R. Abreu, C. Carrillo, and R. Rojas. 2014. Nanocellulose properties and applications in colloids and interfaces. *Curr. Opin. Colloid Interface Sci.*, 19:383–396
- Serrano, E. 2004. A numerical study of the shear-strength-predicting capabilities of test specimens for wood–adhesive bonds. *Int. J. Adhes. Adhes.* 24(1):23–35.
- Shirmohammadi, M. and W. Leggate. 2021. Review of existing methods for evaluating adhesive bonds in timber products. *Eng. Wood Prod. Construct.* 30. <https://doi.org/10.5772/intechopen.99237>
- Singha, A. S. and V. K. Thakur. 2008. Fabrication and study of lignocellulosic hibiscus sabdariffa fiber reinforced polymer composites. *Bio-Resources* 3(4):1173–1186.
- Somvanshi, K. S., P. C. Gope, and S. Tiwari. A review on properties of nano biocomposite film for packaging applications from cellulose nano fiber. *International Journal of Engineering Research and Applications.* 11(1):29–39.
- Tabarsa, T., S. Jahanshahi, and A. Ashori. 2011. Mechanical and physical properties of wheat straw boards bonded with a tannin modified phenol–formaldehyde adhesive. *Compos. B Eng.* 42(2):176–180.
- Veigel, S., U. Müller, J. Keckes, M. Obersriebnig, and W. Gindl-Altmutter. 2011. Cellulose nanofibrils as filler for adhesives: effect on specific fracture energy of solid wood-adhesive bonds. *Cellulose* 18:1227–1237.
- Veigel, S., J. Rathke, M. Weigl, and W. Gindl-Altmutter. 2012. Particle board and oriented strand board prepared with nanocellulose-reinforced adhesive. *J. Nanomater.* 2012:1–8.
- Vick, C. B. 1999. Adhesive bonding of wood materials. *In: Wood-Hand Book—Wood As An Engineering Material.* Forest Prod. Lab. Rep. GTR-113. USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin. pp. 9.1–9.24.
- Vineeth, S. K., R. V. Gadhave, and P. T. Gadekar. 2019. Nanocellulose applications in wood adhesives. *Open J. Polym. Chem.* 9(4):63–75.
- Wang, S. and C. Xing, inventors; University of Tennessee Research Foundation, assignee. 2016. Wood adhesives containing reinforced additives for structural engineering products. U.S. Patent 9,284,474.
- Wessels, C. B., M. Nocetti, M. Brunetti, P. L. Crafford, M. Pröllner, M. K. Dugmore, ... and Z. Naghizadeh. 2020. Green-glued engineered products from fast growing Eucalyptus trees: A review. *Eur. J. Wood Wood Prod.* 78:933–940.
- Wibowo, E. S., M. A. R. Lubis, and B. D. Park. 2021. In-situ modification of low molar ratio urea–formaldehyde resins with cellulose nanofibrils for plywood. *J. Adhes. Sci. Technol.* 35(22):2452–2465.
- Xing, D., J. Li, X. Wang, and S. Wang. 2016. In situ measurement of heat-treated wood cell wall at elevated temperature by nanoindentation. *Ind. Crops Prod.* 87:142–149.
- Yang, X. and C. E. Frazier. 2016. Influence of organic fillers on surface tension of phenol-formaldehyde adhesives. *Int. J. Adhes. Adhes.* 66:160–166.
- Yelle, D. J. and J. Ralph. 2016. Characterizing phenol–formaldehyde adhesive cure chemistry within the wood cell wall. *Int. J. Adhes. Adhes.* 70:26–36.
- Zhang, H., Y. She, S. Song, Q. Lang, and J. Pu. 2013. Particulate reinforcement and formaldehyde adsorption of modified nanocrystalline cellulose in urea-formaldehyde resin adhesive. *J. Adhes. Sci. Technol.* 27(9):1023–1031.
- Zhang, J., Y. Zhang, J. Li, and Q. Gao. 2019. Development of a high-performance adhesive with a microphase, separation crosslinking structure using wheat flour and a hydroxymethyl melamine prepolymer. *Polymers* 11(5):893.
- Zheng, Z. F., J. C. Zou, H. J. Zhang, and M. Ling, M. 2007. Study on liquefaction of walnut shell in phenol and application of its resinification product as wood adhesives. *Chem. Ind. Forest Prod.* 27(4):31–36.
- Zimmermann, T., E. Pöhler, and T. Geiger. 2004. Cellulose fibrils for polymer reinforcement. *Adv. Eng. Mater.* 6(9):754–761.