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Review

Nanocellulose in Heterogeneous Water-Based Polymerization for Wood Adhesives

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Abstract: The interest in the development of biobased adhesives has increased due to environmental concerns. Moreover, as the production of engineered wood products (EWPs) is expected to grow, the wood adhesives market needs to transit toward formaldehyde-free products. Cellulose nanoparticles (CNPs) are a material with unique properties and advantages for producing hybrid materials as biobased wood adhesives. Besides their traditional use as reinforcing additives, CNPs can be incorporated at the beginning of the polymerization reaction to form in situ polymerized hybrid adhesives with better mechanical and physicochemical properties than the neat adhesive. Despite their outstanding characteristics, CNPs are still an emerging nanomaterial in the wood adhesive field, and the studies are incipient. This review explores the utilization of CNPs in heterogeneous polymerization for the production of polyvinyl acetate, polymeric isocyanates, waterborne polyurethane systems, and other waterborne polymer latexes. The main challenges are discussed, and some recommendations are set down for the manufacture of these novel hybrid nanocomposites.

Keywords: cellulose nanoparticles; emulsion polymerization; wood adhesives; waterborne adhesives; engineered wood products; nanocomposites; biobased adhesives

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1. Introduction

Adhesives are a preferred choice for binding solid wood and wood composites based on wood strips, chips, fibers, strands, and veneer for manufacturing engineered wood products (EWPs), such as laminated veneer lumber (LVL), laminated strand lumber (LSL), oriented strand board (OSB), cross-laminated timber (CLT), plywood, particle board, medium density fiberboard (MDF), and high-density fiberboard. An increasing population and the awareness of emitting fewer greenhouse gasses and pollutants have led to innovative programs to use wood in buildings to reduce the carbon footprint. As a result, the demand for wood-based panels in furniture and building construction is driving the market to grow. Governments such as Canada's, for example, are developing programs that encourage the use of wood in construction project thus supporting the country's transition to a low-carbon economy [1]. In addition, solid wood possesses some disadvantages that limit its application, thus EWPs appear as an alternative to solid wood, providing improvement to the characteristics of the raw material [2].

Most adhesives for manufacturing EWPs are based on formaldehyde resins, which have adverse effects on human health and the environment. The International Agency for Research on Cancer (IARC) has classified formaldehyde as a substance carcinogenic to humans [3]. Therefore, alternative adhesives must be produced by using renewable feedstocks and novel greener processing methods, not only to reduce fossil resources but also to offer adhesives that comply with industry standards with adequate technical and mechanical properties. In the rigorous sense of the definition, biobased adhesives correspond to those adhesives produced from sources of natural, nonmineral origin that can be used as such or after small modifications [4]. Following this definition, the renewable raw materials that have been used to synthesize biobased adhesives are lignin [5,6], tannin [7,8], carbohydrates as starch [9,10], and proteins [11,12]. Moreover, the market is driven to the development of different products, more competitive and sustainable. In these efforts, nanotechnology offers opportunities for the reinforcement of adhesives using nanocellulose mainly in the form of microfibrillated cellulose (MFC), cellulose nanofibrils (CNFs), or cellulose nanocrystals (CNCs). The unique properties of this nanomaterial, such as a high aspect ratio, crystallinity and surface area, excellent mechanical properties combined with less weight and biodegradability [13,14], nontoxicity, and sustainability [15] have highlighted the benefits for the development of hybrid nanomaterials. Moreover, cellulose nanoparticles (CNPs) are recognized as reinforcing nanofillers with great potential for more sustainable polymer composite production [16,17]. Among the benefits of using nanocellulose as reinforcements in adhesives are the modification of the viscosity of adhesives, improvement in mechanical, physical, and thermal properties, and a reduction in formaldehyde emissions. Most of the work done in the field of CNP-based adhesives involves the mixing of polymeric matrices.

The manufacture of particleboard panels using CNFs as a sole binder met the industry requirements in terms of mechanical properties only for low-density grades [18]. Phenol–formaldehyde (PF), urea–formaldehyde (UF) and melamine–urea–formaldehyde (MUF) adhesives are extensively used on different wood panels (laminated panels, particleboard panels, OSB, plywood panels, agglomerated panels, and so on). For example, Veigel et al. [19] prepared particleboards and OSBs with UF and MUF in combination with CNF, resulting in a reduced thickness swelling and an improvement in the internal bond and bending strength. Bacterial cellulose (BC), untreated CNFs, and tempo-oxidized CNFs were studied by Veigel et al. [17]. They added these biopolymers to UF adhesives showing an increase in the bond line thickness due to the high viscosity of the filled adhesive, whereas the specific fracture energy of UF-wood adhesive was improved in the case of BC and CNFs but not for modified CNFs. Zhang et al. [20] studied modified CNCs in combination with UF resin to increase the bonding strength and reduce formaldehyde emissions. Ayrilmis et al. [21] found that the total organic volatile compounds (TVOC) from LVLs decreased with increasing MFC on UF resin at 25 °C, which can be an environmentally friendly solution for reducing the TVOC from wood-based panels. More recently, Kawalerczyk et al. [22] added MFC and CNCs as fillers to a UF adhesive and used it for plywood manufacturing, where they found an increase in viscosity and extension of the gel time of the adhesive and also an improvement of the mechanical properties with a slight reduction in formaldehyde emissions.

Poly(vinyl acetate) (PVA) is an alternative “green” adhesive due to its water-solubility, low toxicity, high-quality chemical resistance and biodegradability [23]. The addition of MFC and CNFs into PVA increased thermal stability and improved shear strength on the adhesive line in tropical wood samples tested by Rigg-Aguilar et al. [24]. Jiang et al. [25] mixed dicarboxylic acid CNFs with commercial PVA and found an increase in the joint strength of wood joints. Moreover, Chaabouni et al. [26] also found an increase in adhesive viscosity, the shear strength of wood joints, water resistance, and an improvement in mechanical properties when they used CNFs. In addition, Lopez-Suevos et al. [27] mixed chemically modified CNFs with PVA to produce boards with superior heat. Kaboorani et al. [28] have also mixed CNCs with PVA to increase the thermal stability, hardness, modulus of elasticity and creep of PVA films.

In all these examples, the CNPs were first carefully dispersed in water and then mixed with the polymers under continuous stirring, and then the mixture was cast onto the surfaces. Nevertheless, several drawbacks have been identified: (i) the process is difficult to scale-up at industrial levels; (ii) when CNPs concentration is below 1% (*w*/*w*) the time to achieve film formation is longer; (iii) the distribution of these nanoparticles is not homogeneous through the resulting film; and (iv) no covalent linkages are formed between the CNPs and the polymers [29]. The nanocellulose content increases the viscosity [22,30,31] and the solid content of the adhesive, limits the penetration of the adhesive, representing an obstacle for spraying and impregnation in the wood [32], and it affects the gel time thus delaying curing [22,31]. New approaches should be implemented that permit nanocellulose to extend its application in wood adhesives, improving its dispersion and redistribution inside the polymer matrix, thus enhancing the interaction among nanocellulose, adhesive, and substrate [23].

Within the constant search for better performance of adhesives, the use of nanocelluloses appears a viable option, specially by using novel techniques to polymerize in situ the resins with this biopolymer. The development of nanocellulose hybrid nanocomposites exhibits superior properties for adhesives due to the structure and surface chemistry of nanocellulose, where this solid "particle" acts as a stabilizer in heterogeneous water-based polymer systems. The ability of nanocellulose to assemble at oil–water interfaces is particularly useful and has led to hundreds of recent articles and several patents in this area [33]. Heterogeneous (or particle forming) polymerization is an inventive technology to successfully synthetize nanocellulose-based adhesives. It consists of the combination of two (or more) immiscible liquids in which one liquid is the starting monomer that is later polymerized. Three free-radical heterogeneous polymerization categories are dispersion, suspension, and emulsion polymerization. Extensive and dedicated reviews about these types of heterogeneous polymerization systems have been done by Arshady [34], Fritz and Olivera [34], and Kedzior et al. [33] and the reader is encouraged to study these publications for further investigation. The intrinsic properties of nanocellulose such as aspect ratio, surface charge density, and particle flexibility influence directly how this biopolymer stabilizes emulsion and heterogeneous water-based polymer systems [35]. It is also critical to know the morphology of the starting nanocellulose since this can help to predict emulsion or heterogeneous water-based polymers' stabilization mechanism [33,36].

Emulsion polymerization is considered as a sustainable technique to produce hybrid polymeric materials because of its use of water as the polymerization medium, it is a biobased feedstock, it prevents waste and pollution, reduces the emissions of volatile organic compounds, maximizes energy efficiency, and minimizes the potential for accidents [37].

This review aims to highlight the advantages CNPs can provide to the development of wood adhesives via heterogeneous polymerization, focusing on the type, size, and modification of nanocellulose particle, as well as the barriers that these new hybrid nanocomposites need to overcome to be used in the production of wood adhesives. Thus, this review covers briefly the basics of adhesion mechanism, water-based emulsions and the evolution of the nanocellulose-based heterogeneous polymerization preparation strategies.

2. Overview of Adhesives and Adhesion Mechanism

Wood adhesives can be divided in two categories depending on their origin, natural or synthetic. Natural adhesives can be proteins of animal or vegetable origin, while synthetic ones are petroleum-based materials. At the same time, the synthetic adhesives can be separated in two types: thermoplastic adhesives and thermoset adhesives. These two types differ in their performance. The specific information about chemical structure, characteristics and implementation of these adhesives is beyond the scope of this review and the reader can find more information in several scientific reviews done by Stoeckel et al. [38], Lengowski et al. [2], Pizzi et al. [4], and Forest Product Laboratory [39]. Thermoplastic adhesives are liquid adhesives that, in general, are not as strong and stiff as wood [39]. Thermoplastics are long-chain polymers that soften when the temperature is increased and then harden again upon cooling. Their resistance to heat, moisture, and long-term static loading is less than that of thermosetting adhesives. Common thermoplastic adhesives for wood include poly(vinyl acetate) emulsions, elastomerics, contacts, and hot-melts. In contrast, thermosetting adhesives are excellent structural adhesives that undergo irreversible chemical change when cured, forming cross-linked polymers that have high resistance to heat, moisture, and other chemicals, and can support high long-term static loads without deforming. Phenol–formaldehyde, resorcinol–formaldehyde, melamine– and melamine–urea–formaldehyde, urea–formaldehyde, isocyanate, and epoxy adhesives are examples of thermosetting polymers. Notwithstanding the large number of adhesives available for EWPs, the most used are phenol–formaldehyde, urea–formaldehyde, resorcinol–formaldehyde, and melamine–formaldehyde [40]. Table 1 shows the adhesives used to produce EWPs, their application area, and typical uses.

Table 1. Classification of adhesives used in EWPs and their general application area (adapted from [2,39,41,42]).

Type of Adhesive	Adhesive	Application Area/Typical Uses
Thermoplastic	Cross-linked poly(vinyl acetate) emulsion	Nonstructural Interior and exterior doors; molding and architectural woodwork; cellulosic overlays
	Polyvinyl/acrylate Polyethylene Polystyrene Synthetic rubber	
Thermoset	Urea–formaldehyde	Structural Hardwood plywood; furniture; medium density fiberboard; particleboard; underlayment; flush doors; furniture cores
	Melamine and melamine–urea–formaldehyde	Structural Melamine–urea–formaldehyde primary adhesive for durable bonds in hardwood plywood; end-jointing and edge-gluing of lumber; and scarf joining softwood plywood, ultra-low emitting formaldehyde adhesive for particleboard and fiberboard
	Phenol–formaldehyde	Structural Primary adhesive for exterior softwood plywood, flakeboard, hardboard, pressed laminated wood, glued laminated wood, waferboard and OSB and low emission particleboard
	Tannin–formaldehyde Tannin–phenol–formaldehyde Tannin–urea–formaldehyde	Nonstructural Plywood (interior and exterior)
	Resorcinol– and phenol–resorcinol–formaldehyde	Structural/ Primary adhesives for laminated timbers and assembly joints that must withstand severe service conditions
	Isocyanate-based adhesives	Structural Laminated strand lumber, OSB, I-beams

The most used thermosetting wood adhesive worldwide is UF with approximately 11 million tons per year, which is mainly utilized for wood panel composites for the preparation of interior furniture and panels [4]. Although it lacks resistance to exterior weather conditions and formaldehyde emissions, its full substitution is difficult to achieve because of its low cost, low cure temperature, short pressing time, excellent adhesive performance, and ease of handling. MUF adhesives can be considered as an improved version of traditional melamine–formaldehyde ones, since the expensive melamine resin is partially replaced with urea. MUF adhesives exhibit an enhancement in water and weather resistance, mechanical strength, and a diminution of formaldehyde emission. MUFs exhibit a medium price, cure temperature and pressing time. PF adhesives are the second most important wood composite adhesive, with 3 million tons per year used worldwide [4]. PFs have a medium price, high cure temperature, medium pressing time, and very low formaldehyde emissions [43]. In contrast, phenol–resorcinol–formaldehyde adhesives are cold-setting adhesives. These adhesives are expensive due to the high cost of resorcinol; however, they are binders for fully exterior-grade and weather-resistant composites, with a low volume of around 30 thousand tons per year worldwide [4].

Understanding wood adhesion theories and mechanisms would enable the production of adhesive formulations suitable for a wide range of applications of EWPs and would encourage the development of novel biopolymers-based adhesives. The role of an adhesive for wood is to transfer and distribute loads between components, thereby increasing the strength and stiffness of wood products [42].

There is no universal theory of adhesion on which to accurately model all interactions that take place between the adhesive and the adherend; nor is there an agreement about the mechanisms involved. The existing theories of adhesion are generally useful in understanding why and how adhesives stick and why they fail. The adhesion theories provide methods to rationalize and to make predictions about the joint strength. Being familiar with these theories and mechanisms would allow the development of an understanding and awareness of adhesives' performance. An entirely satisfactory definition of adhesion has not been established yet; however, according to the American Society for Testing and Materials (ASTM) [44], adhesion corresponds to the state in which two surfaces are held together by interphase forces. Wu [45] defined that those forces arise from van der Waals forces, chemical bonding, or electrostatic attraction.

Traditionally, mechanical interlocking, adsorption/specific, electrostatic, and diffusion adhesion theories have been applied to define the mechanisms of adhesion. However, other theories have arisen to explain adhesive bonding mechanisms, such as wettability, covalent chemical bonding, acid–base, and weak boundary layers theories. A combination of different theories would explain the complex adhesive mechanism since it is often difficult to fully attribute it to one individual theory.

The mechanical theory proposes that mechanical, physical, and interlocking of an adhesive into the macro- and microirregularities of the substrate's surface is the major factor of adhesion. The adhesion occurs when an adhesive penetrates the porous wood surface, displacing the trapped air at the interface. If an adhesive flows deeply into cell cavities, the mechanical interlocking increases thus increasing the bonding [46].

The specific adhesion between the adhesive and the adherend involves the bond created because of molecular attraction between the surfaces in contact. This theory is the most widely accepted, and an applicable theory of adhesion. The intermolecular attractive forces that participate in the specific adhesion can be ionic, covalent, or induced by any other intermolecular forces. Therefore, ionic interactions or hydrogen bonds are due to strong dipole–dipole forces; van de Waals forces are due to a fixed dipole in one molecule that induces oscillating dipoles in another molecule. These electrodynamic forces can be divided as Keesom (permanent–permanent dipoles) interaction; Debye (permanent–induced dipoles) forces; and London dispersion forces (fluctuating dipole–induced dipole interaction). The strength of these van de Waals interactions is strongly dependent on distance, decreasing with the sixth power of the interatomic or molecular distance.

Kumar and Pizzi [42] explained the mechanism of adhesion for wood by adding another type of adhesion called effective adhesion, which combines the specific and mechanical adhesion explained above. They also established that the bonding effectiveness is a combination of adhesion and cohesive strength. Cohesion is defined as the internal strength of an adhesive because of a variety of interactions within the adhesive (Figure 1). In this way, an adhesive bond would fail if either an interfacial adhesion failure occurs (if the adhesive is separated from substrate) or if there is a cohesive failure.

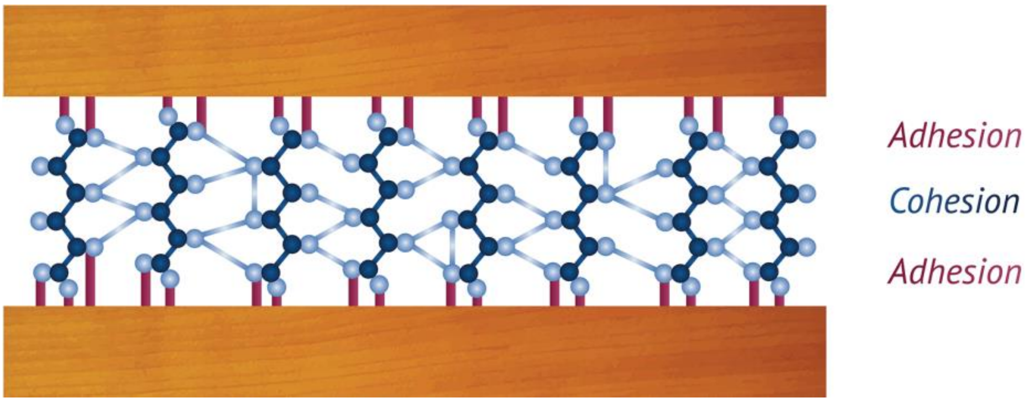

Figure 1. Adhesion and cohesion forces on wood surfaces explained by chemical bonds and intermolecular forces [47].

The formation of an electrical double layer at the adhesive–adherend interface is explained by the electrostatic theory. These forces are primarily dispersion forces and forces arising from the interaction of permanent dipoles. The electrostatic theory is often used to describe the adhesion behavior of powders to solid surfaces [48–50]. Practical applications of this theory to wood and EWPs is limited to coatings of furniture, sandpaper manufacture, inkjet printing, novel bioactive papers, and colloidal interactions in papermaking [51–54].

In the case of wood surfaces, the diffusion theory is unlikely to explain the adhesive mechanism since both the adhesive and adherends should be long-chain polymers capable of movement and exhibit similar values of solubility [42,55]. Wood is heterogeneous in composition, the basic three biopolymers, cellulose, lignin, and hemicellulose, exhibit different chain lengths, molecular weight, and crystallinity. However, in the case of wood adhesive bonding, this theory is applicable if the adhesive can diffuse or penetrate into the cell wall, which is not the case for thermosetting wood adhesives [56].

The wetting theory proposes that adhesion results from molecular contact between two materials and the surface forces that develop. For an adhesive to wet a solid surface, the adhesive should have a lower surface tension than the critical surface tension of the solid [55]. Incomplete wetting generates interfacial defects, thereby reducing the adhesive bond strength. Complete wetting achieves the highest bond strength. Hiziroglu et al. [57] demonstrated that roughness of wood surfaces affected their wettability, thus affecting the strength of bonding.

Covalent bonds occur in certain fields of adhesion; however, their existence was for a long time not believed to occur between wood and adhesives [58,59]. Zhou and Frazer [60] and Das et al. [61] studied phenyl isocyanate-based adhesives and determined that these adhesives are likely to form urethane (or carbamate) bonds with wood biopolymers, also showing these adhesives can penetrate the wood cell wall and intimately associate with wood biopolymers. Gardner et al. [62] concluded that it is very likely that covalent bonds between the wood and adhesive are not necessary for durable wood adhesive bonds. This is because the contribution of the formation of adhesive–substrate covalent bonds induced by lignin [63] is very small and often negligible under the conditions pertaining to thermosetting adhesive applications [63,64] and do not exist for MUF systems [65].

According to the acid–base theory, adhesion results from the polar attraction of Lewis acids and bases. It has been identified that hydrogen bonding is a special type of acid–base interaction. In addition, in chemically heterogeneous materials such as wood, the extractives are the dominant factor influencing the acid–base characteristic [66].

The weak boundary layer theory establishes that bond failure at the interface is caused by either a cohesive break or a weak boundary layer [67]. Weak boundary layers can originate from the adhesive, the adherend, the environment, or a combination of any of these three factors. Here, the wetting of surfaces is key, since if the adhesive does not wet the substrate, a weak boundary layer is formed at the interface, causing a reduction in joint strength.

3. Overview of Heterogeneous Polymerization

As mentioned previously, the typical three types of heterogeneous polymerization of hybrid particles are dispersion, suspension, and emulsion polymerization. These types are distinguished by the initial state of the polymerization mixture, kinetics of polymerization, mechanism of particle formation, and shape and size of the final polymer particles [34]. Heterogeneous polymerization consists of a two-phase system in which the starting monomer is later polymerized in the form of a fine dispersion in the immiscible liquid. Various combinations of monomers, initiator, polymerization medium, and additives or emulsifiers are employed to produce the polymer particles. Asua [68] concluded that the molecular and morphological characteristics of the polymer depend on the formulation, the polymerization process, and the process conditions. In terms of sustainability, using water as continuous phase instead of organic solvents is ideal. Waterborne latexes correspond to a colloidal dispersion of submicron polymer particles dispersed in aqueous media. They can be used in applications such as adhesives, paints, rubber products, paper coating, cement reinforcements, printing inks, and in the medical industry [69–71]. The process for producing these waterborne latexes meets the principles of green chemistry and green engineering [72,73] by using the greenest solvent of all, water, thus reducing the use of organic solvents and preventing the emissions of volatile organic compounds. Moreover, the use of a water-based medium would allow one to improve the heat transfer of this exothermic polymerization process, control temperature, facilitate polymer recover, and obtain a lower viscosity polymer.

In dispersion polymerization, the monomer and the initiator are both soluble in the polymerization medium, but the resulting polymer is not. Depending on the solvency of the medium, phase separation occurs at the beginning of the polymerization process, which leads to nucleation and the formation of primary particles. These particles are swollen by the polymerization medium and/or the monomer, resulting in the formation of spherical monodispersed particles in the range 0.1–15 μm [34,74], which are too large for emulsion polymerization and too small for suspension polymerization [75].

In suspension polymerization the initiator is soluble in the monomer, and these two are insoluble in the polymerization medium. The monomer is initially dispersed in the continuous phase (usually water) by a combined effect of constant stirring and surface-active agents (inorganic and/or water-soluble polymers), but no surfactants. Under these conditions, the monomer “microdroplets” are converted directly to the corresponding polymer “microbeads”. As a result, rigid and spherical polymer particles are formed in the range of 50–500 μm [76].

In classical emulsion polymerization, the emulsion polymerization system is formed by water, monomers of low water-solubility, usually a water-soluble initiator, and surfactant or nanoparticles. Contrary to suspension polymerization, the initiator is soluble in the medium, but not in the monomer. Although simple, the process involves many mechanistic steps, which dictate the rate of formation and growth of the composite particles. The process is complex because the nucleation, growth, and stabilization of composite particles are controlled by the free radical polymerization mechanism in combination with various colloidal phenomena. Monomers are in the form of relatively large droplets (1–10 μm) [34]. A typical emulsion polymerization reaction consists of three distinct intervals [77]. The first interval is associated with particle formation where monomer droplets, surfactant (with a concentration exceeding the critical micelle concentration), and precursor particles are present, which will eventually grow and form a colloidally stable mature particle by entry of radicals into the micelles. Interval II is where mature latex particles exist, the polymerization is carried out within the monomer-swollen particles, the particle number density stays constant, and the monomer droplets allow the propagation of new particles. In this interval, the diffusion of a monomer from a droplet to a particle is relatively fast, and the droplets act as monomer reservoirs, which ensures constant monomer concentration. Interval III begins once monomers contained within the particle are polymerized, there is a change in the polymerization rate, usually faster at the beginning of the reaction. The success of this polymerization is given by the diffusion of the monomer from the monomer droplets to the aqueous phase, which, in some cases, represents a severe limitation. The mass transfer of monomer from monomer droplets would be greatly effective if a large fraction of the monomer droplets were nucleated, which is achievable if the surface area of monomer droplets is large compared with that of the micelles, and this requires a submicron droplet size. The size of the monomer-swollen micelles is 10–20 nm, thus the surface area of micelles is orders of magnitude greater than that of the monomer droplets. The strategy of miniemulsion polymerization was first studied by Ugelstad et al. [78], and it describes submicron oil-in-water dispersions that are stable for a period ranging from hours to months. Miniemulsion polymerization systems involve the use of a costabilizer or hydrophobe to produce very small monomer droplets (10–500 nm). Because the polymerization reaction proceeds in these minireactors, no interval II is present. The combination of high shear to break up the emulsion and this costabilizer ensures submicron monomer droplets with decelerated droplet coalescence caused by Brownian motion, settling, and creaming, preventing Ostwald ripening, hence obtaining a kinetically stable miniemulsion.

Emulsion polymerization is a widely used strategy industrially to synthesize large quantities of latexes. Even though surfactants can improve properties such as shelf-life, freeze–thaw stability and mechanical stability, their addition can also have a negative effect on end-use properties, because they remain in the latex after polymerization. To overcome this drawback, surfactant-free emulsion polymerization has been investigated [79], and surfactants have been replaced with macromonomers or amphiphilic copolymers [80]. However, these techniques have certain limitations such as a low solid content and the high number of steps required for the synthesis.

Another emulsion system stabilized only by the use colloidal particles (solid particles) has been investigated to develop armored nanostructured composites, which is known as Pickering emulsion [81], and represents an alternative route to synthesize hybrid nanocomposites because it does not require the addition of surfactant molecules. The mechanism of particle formation occurs via the adsorption of the nanoparticle at the water–droplet interface. It is argued that modifying the shape from sphere to rod-like could allow emulsification above a critical aspect ratio threshold, leading to long-lasting emulsions [82]. The structural properties of nanocelluloses such as aspect ratio and surface properties are correlated with the high efficiency in forming colloidally stable multiphase systems [83]. For example, it has been shown that CNCs can stabilize oil–water interfaces by strong adsorption along the less polar crystalline plane [83–86]. However, it has been discussed whether nanocellulose without modification is a true emulsifier because it only has intermediate wettability, certain amphiphilic properties, and it does not form micelle-like aggregates [33].

4. Nanocellulose-Based Adhesives through Heterogenous Polymerization

The type of nanocellulose, aspect ratio, surface charge density and particle flexibility directly influence how nanocellulose stabilizes heterogenous polymerization processes. One of the most important characteristics of CNPs is their exceptional mechanical strength. A broad range of values has been reported; however, an average elastic modulus value of 130 GPa is established for cellulose nanocrystals. The Young's modulus of nanocellulose is much higher than that of glass fibres (70 GPa), similar to Kevlar (60–125 GPa), and possibly stronger than steel (200–220 GPa) [87]. Therefore, CNCs are an ideal candidate for enhancing the mechanical properties of a polymer matrix [88]. Emulsion polymers containing nanocellulose have been investigated by Chaabouni et al. [26], Dastjerdi et al. [89], Dastjerdi et al. [84], Ouzas et al. [90], and Yu et al. [91] to produce pressure-sensitive adhesives with properties such as permanent tack, adherence with no more than finger pressure, sufficient ability to hold onto an adherend, and sufficient cohesive strength to be removed cleanly from the adherend. However, there is scarce literature on the performance of nanocellulose polymerized in situ for the development of wood adhesives and their application to produce EWPs. Nevertheless, it is known that the interactions between cellulose particles and monomer droplets/polymer particles are governed by hydrogen bonding, van de Waals forces, surface activity, hydrophobic interactions (in the case of nanocellulose surface modification), and even the polymerization initiator could induce some free radical reactions sites onto nanocellulose.

Within the following subsections, the use of CNPs to produce adhesives for EWPs production is discussed. This discussion is based on the incorporation of CNPs at the beginning of the polymerization reaction, i.e., in situ incorporation. Specifically, this literature review is based on studies in heterogeneous polymerization for the production of polyvinyl acetate, polymeric isocyanates, waterborne polyurethane systems, and other waterborne polymer latexes.

4.1. Polyvinyl Acetate (PVA)

PVA is a linear and thermoplastic polymer, water-soluble, and biodegradable material with excellent chemical resistance. PVA is characterized by its strong hydrogen bonding between acetates groups, which leads to an adhesive interaction within wood cell wall with OH groups. Curing PVA does not require high temperatures. However, it has low resistance to water and heat.

Mabrouk et al. [92] prepared PVA dispersion by emulsion polymerization in the presence of negatively charged CNCs and without any added surfactant. For this, vinyl acetate was added to a CNCs dispersion, and a comonomer of polyethylene glycol methacrylate (MPEG) was used to study how its level affected the colloidal properties of the dispersion. The initiator of the polymerization was potassium persulfate (KPS), and this reaction was carried out for 2 h. It was found that CNCs partially contribute to the stabilization of the polymer particle dispersion due to the hydrophilic character of CNCs and the presence of sulfate-charged groups, indicating a Pickering effect. The authors concluded that the CNPs would accumulate within the continuous water phase and only a fraction of CNCs would likely adsorb on the polymer particle during their nucleation and growth, without being able to ensure a high coverage degree which is a prerequisite for an effective Pickering stabilization process. In contrast, when the authors added MPEG, the colloidal stability of the dispersion was improved and favored the binding of CNCs to the polymer particle, thus reducing the particle size from 300–500 nm to 200–300 nm. The bond strength of this novel adhesive was tested on wood joints, revealing an enhancement in reinforcement accounting for 195% of the strength compared to conventional PVA. The molecular weight of the PVA-nanocomposite was not determined in this study.

4.2. Polymeric Isocyanate Adhesives

Isocyanate resins for wood adhesives have grown significantly, since they are formaldehyde-free resins that offer not only a mechanical bond but also a tough, water-resistant chemical bond. Polymeric diphenyl methane diisocyanate (pMDI) adhesives are a complex mixture of diisocyanate monomer and complex oligomeric with different polymerization degree. They are composed of almost equal weight parts mixture of methylene-bridged polyphenyl polyisocyanates and of 4,4′-diphenylmethane diisocyanate (MDI), composed in great majority (>90–95%) of the 4,4′ isomer and in the minority of 2,4′ isomer [93]. pMDI can deeply penetrate into the wood cell walls, causing wood cell walls plasticization, and its mobility limits its application for the production of plywood, for example [93]. The main advantage of this adhesive is that it can be used at much lower adhesive loads for the same results, which compensate its higher price compared to PF adhesives. pMDI adhesives offer additional benefits, including a high reactivity, fast curing, excellent dry/wet bonding strengths, and good tolerance to substrate moisture content [94], decreasing thickness swelling, and providing high flexural strength to OSB, laminated strand-lumber, and exterior particleboard [95]. Most of the research done in this area has utilized the physical method for mixing CNPs and isocyanate adhesives. Chen et al. [96] studied the addition of lignin-containing cellulose nanofibrils (LCNFs) to pMDI with promising results for wood adhesives. They showed evidence of covalent interactions between LCNFs and pMDI due to the reaction of hydroxyl groups in lignin (at the γ position) and isocyanate. Moreover, they found that the presence of lignin influenced the curing behavior of pMDI by three orders of magnitude compared to CNFs, since lignin is amorphous, more accessible, and appeared to be more reactive to pMDI than CNFs. Of course, more research needs to be done related to the mixing with CNPs and CNP-containing lignin.

4.3. Waterborne Polyurethane (WBPU) Systems

The hydrophilic characteristic of CNPs converts them into suitable additive for polyurethane polymers. Polyurethane (PU) is the general name for a family of synthetic copolymers that contain the urethane moiety in their chemical repeat structure. PUs can also be divided into many different groups based on the desired properties: thermoplastic PU, flexible PU, rigid PU, PU ionomer, waterborne PU, and thermosetting PU [97]. The chemical composition of PUs can be tuned by choosing different raw materials and processing conditions to accommodate a specific requirement [97]. Basically, PU production involves the reaction between the polyol and the diisocyanate. The environmental problems and toxicity associated with diisocyanates have led researchers to minimize or eliminate their use. Biobased PU resins have been developed by Lima-García et al. [98] using lignin to overcome traditional PU problems such as high penetration of the adhesive into the wood, low resistance to delamination, and unsatisfactory gap filling properties. Moreover, Arias et al. [99] conducted an industrial-scale design and environmental evaluation through the life cycle assessment methodology concluding that organosolv lignin and soy could be used as renewable sources for producing nonisocyanate polyurethanes (NIPU). Soy-based tannin-modified adhesives have been developed by Ghahri et al. [100] and were successfully used to bond plywood. In that work, tannins reacted with proteins and formed cross-links between polypeptide chains, exhibiting good resistance to water thus passing delamination and shear strength tests.

Waterborne polyurethanes (WPUs) possess several of the attractive advantages associated with conventional organic solvent-borne PU such as low viscosity at high molecular weight, nontoxicity, and good applicability, without the problems associated to environmental pollution, health, and safety risks [101,102].

A series of WPU/CNC composites were synthesized via in situ polymerization by Cao et al. [101]. They demonstrated the formation of a cocontinuous phase between the matrix and filler, which significantly enhanced the interfacial adhesion and consequently contributed to an improvement in the thermal stability and mechanical strength of the nanocomposites. As a result, a good dispersion was achieved that improved the mechanical properties. However, this novel adhesive has not yet been tested on wood components.

More specifically, the addition of CNCs into WBPU nanocomposites was performed in three different ways [36]. The authors compared a physical method, a method where the CNCs dispersion was added in a prepolymer stage, and one where the nanoparticles were added at the beginning of the synthesis. These methods permitted the control of the degree of interaction between the CNCs and the WPU through hydrogen bonds. CNCs, as well as the step of the reaction in which they were added, influenced the morphology of the polyurethane. For example, they found an increase of 220% in tensile strength and 337% in Young's modulus by adding the CNCs at the beginning of the synthesis compared to neat WPU. These authors also showed that WPU/CNC nanocomposites fabricated in a traditional way, i.e., by a physical method, exhibited poor adhesion and a less efficient dispersion, which indicates that in situ polymerization is an approach to be considered for the development of wood adhesives.

Moreover, Choi et al. [103] developed a one-step process of regenerated cellulose nanoparticles/waterborne polyurethane nanocomposite for ecofriendly polyurethane polymers. After investigating which stage was optimal for the incorporation of regenerated cellulose nanoparticles, they could produce WPU nanocomposites by cross-linking between WPU and CNPs with a high biodegradability and improved mechanical and thermal properties compare to neat WPU. These researchers highlighted the environmentally friendly applications of the novel WPU nanocomposites. Their application as wood adhesives has not been tested, thus further analyses need to be done.

Furthermore, to overcome the disadvantages of nanocellulose materials, Zhang et al. [104] grafted octa(aminopropyl) polyhedral oligomeric silsesquioxane (POSS) onto TEMPO-oxidized cellulose microfibrils (TOCMF) to prepare oil-based waterborne polyurethane by in situ polymerization. It was believed that the filamentous structure of TOCMF could reduce the negative impact of the rigid structure of a single POSS particle. In addition, the "button" action of POSS combined the polyurethane matrix to TOCMF with chemical bonds. The test results showed that the mechanical properties, thermal stability, and water resistance of the modified WPU composite film were greatly improved by the synergistic effect of the nanomaterials.

Recently, PU/CNC nanocomposites were fabricated by Khadivi et al. [105] through in situ polymerization by using polydimethylsiloxane, methylene diphenyl diisocyanate, and 1,4-butanediol as polyol, aromatic diisocyanate, and chain extender, respectively. They found that the CNC content affected the microstructure and thermophysical properties of the nanocomposites. For example, it was found that CNCs decreased the crystallization of hard segment and glass transition temperatures of hard and soft segments were shifted to higher temperatures. Moreover, the cytocompatibility of CNC/PU nanocomposites was improved by the addition of CNCs. Even though these studies have shown promising results for wood adhesives, to date, none of them have been tested to evaluate the bond strength in wood specimens.

4.4. Other Waterborne Polymer Latexes

CNCs can be surface-modified such that they are incorporated into the core of the polymer latex particles. This novel investigation was by done by Kedzior et al. [106], who grafted both poly(methyl methacrylate) and poly(butyl acrylate) at varying graft lengths from CNCs with the goal of dispersing CNCs into the methyl methacrylate monomer droplets before polymerization. They found that unmodified CNCs cannot be incorporated inside the polymer particles, mainly due to their hydrophilic character. To overcome this issue, CNCs were grafted with short polymer chains, they were hydrophobic enough to be compatible with the monomer droplets but did not aggregate and subsequently, could be incorporated into the resulting polymer particles. It is worth mentioning that the performance of CNCs grafted with poly(methyl methacrylate) and poly(butyl acrylate) did not experience significant differences in the polymer latex, indicating that the degree of hydrophobic modification may be more important than matching the surface-grafted polymer to the bulk latex polymer. Moreover, more recently, Saelices et al. [86] studied the effect of unmodified CNCs to produce highly stable Pickering emulsions for nanocomposites latex particles development. They found that unmodified CNCs are efficient to produce both monomer-in-water Pickering emulsion and nanocomposite latex particles with controlled dimensions. Moreover, they demonstrated that the ability of the monomer to diffuse across the continuous phase was related to the solubility and was a key parameter to regulate the size distribution of the latex particles. These findings prove that the incorporation of CNCs can be tuned for use in commercial adhesives and coatings.

5. Challenges and Recommendations

It is expected that the global market for wood adhesives will grow at a compound annual growth rate (CAGR) of 3.4%, projecting a market size of USD 4.9 billion by 2026 [107] partly due to the manufacturing of wooden products used in furniture and engineering wood-based panels. Environmental and sustainability concerns are driving the market to pursue biobased alternatives, switching to low-VOC products. The use of less hazardous and renewable alternatives is an obvious strategy to achieve a greener emulsion polymerization. Although there are several studies using CNPs as a reinforcing filler for adhesives, the use of this nanomaterial in emulsion polymerization for producing wood adhesives is incipient and it has not been systematically studied. Undoubtedly, there are many challenges in this field to overcome and further investigations need to be done.

An important feature is the scalability, production, and commercialization of CNPs since all the advances indicated here would require a standard and reproducible process. Nowadays, the manufacture of CNCs and CNFs is attracting considerable commercial interest and there are pilot and commercial plants producing these renewable materials. Dispersion of CNPs into the polymer matrices is a relevant aspect to consider and at this time the industry has improved the drying process of this material by using spray-drying technique to form a powder. However, the commercialization configuration should be thinking accordingly; for example, for emulsion polymerization, it is challenging to use CNP powder because of the high energy required for redispersion. Therefore, a controlled solid content and uniform aqueous dispersion of CNPs is crucial for success and predictable properties in heterogeneous water-based polymer systems for wood adhesives.

Another main challenge of using CNPs in emulsion polymerization is that they tend to agglomerate mainly due to the high specific surface area and their hydrophilic character. In addition, the presence of sulfate-charged groups on the surface of CNCs, for example, will promote the accumulation within the continuous water phase and only a fraction of CNCs are likely to adsorb on the polymer particle during their nucleation and growth, without being able to ensure a high coverage degree, which is a prerequisite for an effective Pickering stabilization process [92]. These issues can be overcome by modifying the dispersion method to obtain a homogeneous nanoparticle dispersion. In the case of CNPs, this can be achieved by chemically modifying their surface. The surface modification of nanoparticles has been reported to improve their dispersion and interaction within the polymer matrix. This surface modification can be achieved by either a noncovalent modification or through the functionalization of the surface (covalent modification). Errezma et al. [108] prepared a stable nanocomposite dispersion based on CNFs via miniemulsion polymerization by adding a small amount of a cationic polyelectrolyte and an anionic surfactant to promote the binding of negatively charged CNFs onto the monomer/polymer particles. Through this strategy, they were able to enhance the colloidal stability of the nanocomposite dispersion. However, the trend is to avoid the use of surfactant, since it has been reported by Errezma et al. [109] that functionalized nanocellulose might contribute to the stabilization of the polymer dispersion through the Pickering effect, in which CNPs adsorbed on the surface of the polymer particle generate a physical barrier impeding the particle aggregation.

Even though nanocellulose-based emulsion for adhesives production can compete favorably with polymer synthetic adhesives for wood, considerable environmental concerns remain. Replacement of toxic and/or nonrenewable materials should further follow the 12 principles of green chemistry and engineering [72]; these include preventing waste, maximizing energy efficiency, minimizing byproduct formation, preventing pollution and accidents. In addition, other considerations and engineering tools must be adopted in the design process such as a life cycle assessment to evaluate the environmental impact of the entire process, thus providing a pathway to a more sustainable polymers and EWPs production.

Moreover, the physicochemical characteristics of the adhesive, such as viscosity, gel time, working time, content of solids, and pH are critical parameters that researchers must test to transit towards the development of nanocellulose-based adhesives for production of EWPs. In addition, the density and moisture content of wood are the most important physical properties in terms of bonding and adhesive performance. In low-density woods, there is a greater penetration of adhesive, resulting in greater adhesive consumption. The opposite occurs in high-density woods, where dimensional changes and moisture content would generate higher adhesive lines that would complicate the bonding process. In the case of moisture content, a low content is related to a high rate of absorption, cure rate, and solidification of adhesive.

The factors affecting wood adhesive performance must be considered to evaluate the effect of biobased adhesives, especially when CNPs are used to produce in situ emulsion polymerization of different adhesives, as those reviewed in this document. To date, comprehensive and applicable studies about those effects have not been reported; however, there are several studies related to the fundamental bases of the importance of adding CNPs to adhesives technologies, thus pursuing the replacement of traditional adhesives that are controversial because of their environmental and human impacts. In this way, Pizzi [110] identified four broad classes of challenges for introducing biobased adhesives: (1) challenges related to their performance and application in relation to synthetic and current adhesives, (2) challenges related to their cost in relation to the cost of current benchmark adhesives, (3) challenges related to the supply of raw materials, and last but not least, (4) challenges related to the resistance to their introduction. Therefore, many factors need to be considered when selecting the best adhesive for a particular application. The strength, durability, wetting, timing, consistency (to be compatible with the application equipment), mixing, pressure, temperature, moisture content, color and finishing properties, easy and simplicity, cost, and health and safety. Possibly the greater challenge to develop biobased adhesives is the availability and supply of raw materials. In the case of CNP-based adhesives, the nanocellulose commercial production has advanced during the last decades and currently there are several pilot plants around the world producing and commercializing nanocellulose. In fact, the revenue projected to be generated in the CNCs market is forecasted to surpass USD 1 billion by 2024 [111].

This review presented a variety of monomers and polymers that are compatible with CNPs and mentioned some ways to control the dispersion and final product performance of potential wood adhesives. In addition, it was shown how the synthetic surfactants may be replaced with renewable CNPs. In heterogeneous water-based polymerization, there is a tremendous potential to improve the stability and tunability of adhesive performance by using CNPs, which leads to products with longer shelf-lives and low VOC emissions. All the studies shown in this review utilized a low CNPs content (less than 5% relative to the monomer). Therefore, it would be worth using as much CNPs as possible to develop hybrid materials with biodegradable properties as well as introducing renewably sourced oils and monomers to fully produce biobased adhesives.

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