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Nanofluid thermosetting adhesives for bonding forest-based lignocellulosic materials: A Brief Review of Synthesis, characterization, and applications

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ABSTRACT

Nanofluids are heat transfer fluids invented in recent decades and are helpful in various industries, including electrical microchannels, engines, spacecraft, nuclear, and solar energy. Nanofluids are created by floating small nanoparticles in base fluids such as water or ethylene glycol, with or without stabilizing methods. The typical size of nanoparticles is less than 100 nm2. Nanofluid thermosetting adhesives have the advantages of enhanced bonding strength, improved thermal conductivity, and reduced curing time. These qualities might improve the performance of thermosetting adhesives, which harden or set when heated. However, the creation of such adhesives would necessitate various disadvantages, such as high cost of production and potential health and environmental risks. Understanding the physicochemical mechanism of using nanofluids in the adhesive would be critical. This would include examining the effects of particle size, shape, surfactant, temperature, etc. on thermal conductivity. While developing nanofluid thermosetting adhesives offers great opportunities, it also requires overcoming several technical hurdles. Further study in this area may lead to the creation of adhesives with improved thermal and adhesive qualities. Applications of nanofluid adhesives might cover a broad area of the wood industry, particularly furniture manufacturing and wooden flooring. This study reviewed possible methods of synthesizing, characterization, and applications of nanofluid thermosetting adhesives for wood-based composites.
Keyword: Adhesion, Cohesion, Nanoparticles, Nanofluid Adhesives, Thermosetting

1. Introduction

In recent years, with the advances in structural biomaterials and green adhesives, substantial improvements have been made in engineered wood products [1-3]. The popularization of engineered wood products such as laminated veneer lumber, oriented strand board, and plywood as a kind of construction material encourages the applications of engineered wood products. It has been widely accepted that using the right adhesive for the right applications is very important, and the desirable perspectives for engineered wood products result from green and sustainable resources. Consequently, lignin-based thermosetting adhesives are an exciting alternative to traditional petrochemical-based adhesives, and these have received great research interest [4-5].

With the advances in engineered wood products, lignin-based thermosetting adhesives are a compelling alternative to petrochemical-based adhesives. Adhesives are chemicals that create a robust and long-lasting bond between two or more materials [6]. Adhesives are widely utilized in several industries, such as wood-based panels and furniture industries [7]. Wood adhesives are compounds utilized to attach pieces of wood or lignocellulosic materials, commonly referred to as wood glues or wood bonding agents. Nanofluids are fluids that contain nanoparticles, usually particles of nanometer size, mixed into a base fluid [6, 8-9]. Nanometersized particles of various materials, such as metallic, oxide, or carbide, are scattered throughout the fluid [8]. Incorporating nanoparticles can greatly change the characteristics of the original fluid, resulting in improved thermal, electrical, or mechanical properties. Nanofluid research has shown that nanoparticles can improve thermal conductivity and heat transfer, promising as a heat transfer fluid due to their high thermal conductivity and rheological qualities [8], making them suitable for various applications such as adhesives [9].

Adding nanoparticles to adhesive compositions could enhance nanofluid adhesive characteristics and performance. Nanoparticles can enhance nanofluid adhesives' mechanical, thermal, and electrical properties because of their distinctive features. Nanoparticles can improve the strength, hardness, and durability of adhesives [6, 9]. This enhancement is particularly beneficial in applications where superior mechanical performance is essential, such as in the aerospace or automotive sectors. Nanofluids often have lower viscosity than conventional adhesives, allowing them to penetrate substrates more effectively and enhance bonding performance. Incorporating nanoparticles, such as metallic or carbon-based nanomaterials, can greatly enhance the thermal conductivity of adhesives. This feature is crucial when managing heat dispersion is a priority in adhesive applications [9].

One of the adhesive applications is for bonding lignocellulosic materials. Lignocellulosic materials are intricate natural materials consisting mostly of cellulose, hemicellulose, and lignin [10]. These compounds originate from plant cell walls and are plentifully present in different types of biomasses, such as wood, agricultural leftovers, and specific grasses. Lignocellulosic materials are highly valued for their potential as sustainable resources in various applications such as biocomposites. The production of biocomposites from lignocellulosic materials entails blending with a polymer adhesive to get materials with improved characteristics [11]. Biocomposites provide a sustainable option compared to conventional composites by using renewable resources and potentially reducing environmental effects [12]. Thermosetting adhesives such as urea-formaldehyde (UF), melamine-formaldehyde (MF), phenol-formaldehyde (PF), epoxy and polyurethane (PU) are commonly used to produce biocomposites from lignocellulosic materials [10-12].

In particular, thermosetting adhesives are cured by a chemical reaction that changes them from a liquid or pliable form to a solid, cross-linked state [13-14]. Heat plays a crucial role in starting and speeding up this curing process. The correlation between heat transfer and adhesive curing is important, as heat plays a vital role in both the application and curing stages [15]. When examining nanofluids thermosetting adhesives, adding nanoparticles may affect the adhesives' thermal characteristics and curing process. This improvement could lead to increased heat transfer efficiency during the curing process. Higher thermal conductivity of nanofluids can affect the cure temperature and duration of thermosetting adhesives, affecting the heat transport in the adhesive, which may result in quicker or more consistent curing. Furthermore, nanofluid thermosetting adhesives could impact the viscosity and dispersion properties. Ensuring the uniform distribution of nanoparticles is crucial to maintaining consistent characteristics and avoiding problems such as agglomeration, which can affect the application and curing procedures [16-17].

Nanofluid research has successfully transitioned from laboratory scale to industrial research. Yet, it is merely the initial stage in advancing commercial nanofluid technology in thermosetting adhesive applications. Nanofluid technology is currently limited in its development and demonstration for commercialization but is anticipated to expand quickly through close collaboration between nanofluid researchers in academia and industry [17]. A consumer must consider utility, strength, reactivity time, bonding strength, eco-friendliness, and price in the adhesives industry before purchasing the appropriate product. The adhesives market is expanding, and opportunities to develop and commercialize these new nanofluids are on the horizon, as indicated by the increasing number of publications in nanofluid adhesion. Market forecasts indicate that the global nanomaterial adhesion market is expected to grow rapidly in the coming years. Two particular fields of interest that are experiencing rapid growth at the moment and can quickly rise to prominence as key factors in the nanofluid sector in the next few years are renewable energy, such as solar and lithium-ion batteries that need improved materials with efficient heat exchange or electrical pathways and the advanced manufacturing sector including 3D printing, where heat dissipation is an artifact of the constituent material.

This review provides the latest developments in the last decade on nanofluid-based Maillard thermosetting adhesives and the correlation of applied post conditions and bonding performance. It also represents the use of the Maillard reaction in adhesive application and its contributions to the field of engineered wood products. Future trends, premium properties, and application insufficiency are further discussed and proposed to guide researchers toward further development. The valuable summary in this review is beneficial for those who are interested in this field.

2. Synthesis of Nanofluids Thermosetting Adhesives

The concept of using nanofluids as adhesives or adhesion enhancers for bonding lignocellulosic materials, such as wood, for both construction and building applications has recently been introduced and is still in the infancy stage [9, 18]. In general, an adhesively bonded assembly is fabricated based on the adhesive nature, such as thermosetting or thermoplastic adhesives, which, regardless of the micro, meso, and/or macrostructures of the surfaces of the bonded materials, flow and interact with the materials, thus establishing strong and rigid bonds upon curing [19-20]. For wood or wood products, the bonding technique using adhesives can be considered "tuning" the chemical functionality of surfaces and allowing the adhesive system to couple with the inherent chemical functionality of natural wood cell walls and wood cell wall surfaces. Although many factors need to be considered, in general, the success of the adhesively bonded assembly relies on the interactions established between each wood substrate and each adhesive.

It has been demonstrated that adhesive pH, surface energy, solid content, and, more importantly, adhesive phase thermomechanical properties are the crucial factors that affect adhesive performance, mainly the strength of the bonded assembly [9, 21]. Meanwhile, the properties of the adhesive itself are determined by molecular and supramolecular chemistry and microstructure. Surprisingly, within the existing limits of manufacturability, much less attention has been paid to the adhesive phase design strategy to fit an adhesive protocol to wood materials, wood repair, and wood build systems. These considerations are important for wood bonding and applicable when other natural materials derived from plant- or animal-based polymers are used as composite materials, conservation substances, reinforcement materials, packaging additives, and even paper-based products.

Nanofluids are commonly prepared in one or two steps (Fig. 1). The one-step process is based on producing nanoparticles in situ in the solvent phase from precursors. In other words, nanoparticles are synthesized and dispersed concurrently in the solvent phase [22]. As a result, the nanoparticles created in situ have a lower inclination to agglomerate. The one-step process can be done via physical or chemical techniques, such as direct evaporation, condensation, or chemical breakdown. Controlling particle morphology is challenging as small changes in synthesis conditions, such as temperature, time, and feeding rate, can significantly impact the properties of nanofluids due to differences in size distribution and stability [23]. Understanding and optimizing synthesis conditions is crucial for better control over transport mechanisms, including homogeneous or heterogeneous nucleation of nanoparticles from precursors and growth and agglomeration in situ.

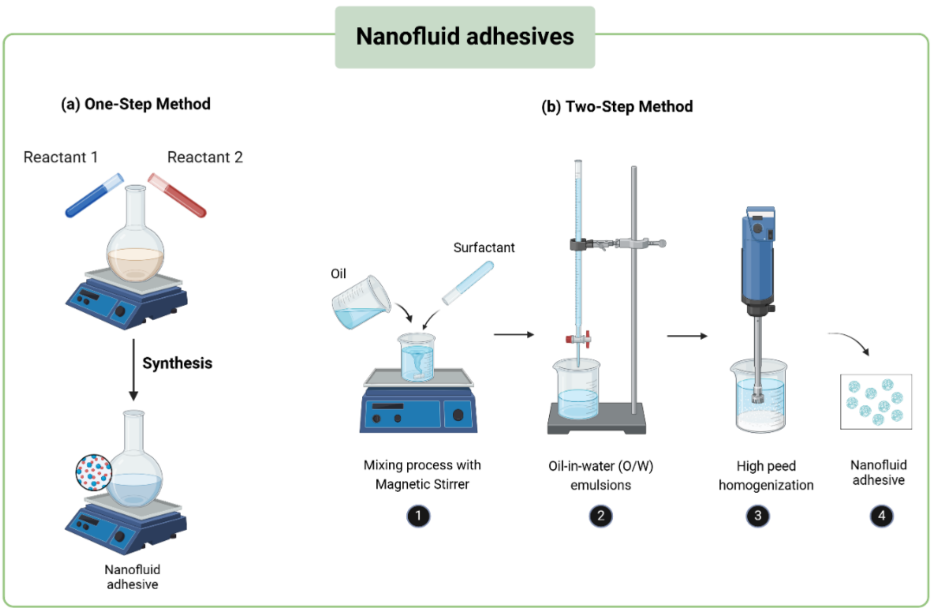

Figure 1. Illustration of nanofluid adhesives preparation. (a) one-step method, (b) two-step method

2.1. One-step Method of Nanofluids Thermosetting Adhesives

The term "nanofluid" describes suspension fluids containing nano-sized particles, typically those with sizes of 1–100 nm [9, 18]. The solids in nanofluids are often composed of pure metals, oxides, nitrides, or carbides. They are mainly used as heat transfer fluids for high-performance and thermal control of electronic cooling devices. Nanofluids have proved to possess outstanding thermal properties. They can be used in various engineering applications, such as automobile engines, microelectronics, and marine engines, including nuclear, space, and cryogenic applications. These exceptional properties of nanofluids include extremely high thermal conductivity, enhanced cooling performance of heat exchangers, and substantial enhancement of boiling heat transfer. The primary preparation methods of nanofluids include the one-step and two-step methods [24-25]. Furthermore, additional aspects of nanofluids are beginning to be considered to enhance their practical applications in an increasingly broad range of fields. In summary, nanofluids are an innovative family of fluids that have caught the interest of both academics and industry experts for the past several decades.

To address agglomeration in mixed nanofluids, researchers are exploring a one-step technique that combines nanoparticle production and dispersion [9, 26]. Synthesis methods can be characterized as physical or chemical. Physical synthesis methods have an advantage over chemical approaches because there is no solvent contamination during nanoparticle formation. Evaporation-condensation is a common method for creating nanofluids in a single step, but additional options are also available [27]. It can be performed by changing the tightness of the network and the regular arrangement of the adhesive molecules, which will further change the molecular energy or reduce the viscosity, affecting their wetting ability and dispersion in water and leading to reduced activity. This can significantly change the curing degree, lead to adhesive fracture, and improve mechanical performance [9, 18]. Furthermore, it should be noted that hydroxyl-functionalized melamine, Mannich base-type melamine, and melamine-modified isocyanate trimethylolmelamine used in modification should have good dispersion in water to avoid the precipitation of nano-microscale modification agents, adversely affecting the mechanical properties [28-30].

Studies have demonstrated the importance of the thermal and mechanical properties for modifying nanofluid adhesive admixtures [28-30]. Hence, how to help modify nanofluid thermosetting adhesives to form finer, more stable network structures are worthy of further implementation. It should be noted that melamine could undergo a series of paraformaldehyde and acid catalysts under alkaline conditions. Under normal conditions, active methylene and methylene of the formaldehyde condensation reaction with melamine, an intermediate, substituted product Mannich base, and finally to form a methylolmelamine were formed. In addition to methacryl-formylmelamine obtained by a methacrylation reaction from the amino group of formaldehyde, the chlorine-substituted melamine modified isocyanate trimethylolmelamine method produced through the chlorine substitution reaction of the amino groups on the melamine and the isocyanate hydroxyl. This method can prepare the active modification agents that can disperse well in water to avoid the modification agents' influence on the final product's structure and properties. These three types of hydroxyl-monas-acrylate monomers and nano-modification agents undergo the hydrolysis and condensation of tetraethoxysilane to synthesize the sols [31-32]. Then, the sols were added to the internal thermosetting adhesives or to the melamine-formaldehyde resins according to the use order. The silicon-organic-modified melamine-formaldehyde adhesives with 1-5% mass contents showed good performance for bonding Chinese fir.

2.2. Two-step Method of Nanofluids Thermosetting Adhesives

The two-step procedure involves manufacturing nanoparticles and distributing them into a base fluid [22], [24]. These approaches are widely utilized in nanofluid research because of their simplicity. Choosing the right synthesis technique improves the stability and accuracy of nanoparticles in suspension. This approach typically uses commercially available nanomaterials in the form of dry powders [33]. Because of advancements in synthesis processes, such as combustion synthesis, Commercial producers can now produce nanoparticles with high accuracy in size and form. Nanoparticles can be created via mechanical means (e.g., milling, grinding), physical methods (e.g., physical vapor deposition, inert gas condensation), or chemical synthesis (e.g., sol-gel process, solution combustion, electrolysis, combustion synthesis).

A new two-step method is suitable for preparing nanofluids and thermosetting adhesives that have commercial potential. In this method, different from traditional approaches, the first step involves the preparation of a stable dispersion of various nanoparticles. Afterward, modified aminosilane was combined with epoxy resin to generate adhesives [34-35]. This two-step method greatly enhanced nanoparticles in the matrix, which meant improving the interface compatibility [36]. The outcome is confirmed by experiments that detected better dispersion and more surface interaction between the nanoparticles and the adhesive matrix. Also, they found that the nanoparticles do not agglomerate and are homogeneously dispersed with this method. The rheological properties of epoxy adhesives loaded with nanofluids were improved. Nanofluids epoxy adhesives have great potential in practical applications where nano-adhesives are technologically crucial [37].

Nano-enthalpies can solve the technical challenge of low surfaces, organic materials, and strong interfaces [38]. However, nanofluids prepared using different approaches affect the properties of nanofluid adhesives. A precursor aminosilane before adding the nanoparticles has been adopted in some studies to improve the dispersion and properties of the nanofluid adhesives. Moreover, the two-step method of nanofluid preparation was provided in an adhesive. The nanoparticles were added to the solution at room temperature during the first step. Then, the prepared nanoparticles loaded with aminosilane were mixed with epoxy. Overall, the two-step method is suitable for the preparation of the nanoparticles-loaded thermosetting adhesives, which may outperform long-term storage [34, 35, 37].

For the successful application of nanofluids in the advanced two-step method, good dispersion of nanoparticles in the base fluid is essential, and it is important to prepare a stable dispersion of nanoparticles in the chosen base fluid [19, 39]. The first step is to disperse nanoparticles in a stable condition. The second step is to disperse the stable dispersion into the base fluid, such as disulfide, thiol, epoxy functional resin, etc. Preparing a stable dispersion of nanoparticles or nanofluids in each base fluid is a considerable challenge. Successful nanofluids are strongly dependent on factors such as particle concentration, particle size, and surface forces working on nanoparticles and the base fluid [40-41]. Many parameters, such as the type of solvent, solubility, solvation, temperature, and the surfactant or stabilizer, are also important for the dispersion of nanoparticles. The right kind of surface modification, particle size reduction, and further surface modification, mentioned as the basic synthesis of useful nano macromolecules, is required.

The effect of using surfactants and stabilizers is to increase the stability of the epoxy resin system and the dispersion of nanoparticles. The approach to preparing a stable dispersion of nanoparticles is to control the nanoparticles' characteristics. Characteristics such as particle size, shape, size distribution, effective density, and other differences may need to be controlled before the dispersion process to achieve optimum final performance [21]. As for the dispersion operation, various manufacturing methods should be explored to identify the type of manufacturing that produces the desired dispersion. The production process used for the dispersion operation also influences the characteristics and performance of the product and, therefore, should be studied. Currently, there are many methods used to mix particles and components in liquids that have the potential to produce well-dispersed dispersions. The best technique varies depending on the type of dispersion to be produced. Mechanical agitation or sonication is a common way to disperse particles in liquids. However, there are advantages and disadvantages to both methods. Sonication should be conducted with care and attention to prevent cavitation.

2.3. Solvothermal and Hydrothermal Synthesis of Nanofluid Adhesives

Solvothermal and hydrothermal techniques have several benefits, such as reducing agglomeration and stabilizing these particles within a solution [42-43]. As pressure increases, the tendency for the nucleation process increases, and crystal growth becomes more substantial. Heat dissipation during the process can be difficult, particularly in solvothermal systems, as the dissolution of the solvent decreases. Here, solvent selection and control of reaction conditions are also significant. Various reaction times, temperatures, pressures, and catalyst concentrations can strongly impact nanofluid epoxies' adhesive strength and shear modulus. Additionally, crystallinity is generally boosted in a hydrothermal system. The synthesis process is more straightforward, safer, effective, and efficient than other processes. Moreover, the process is easy to implement and crucial for mass production. Hydrothermal processes are suitable for real industrial applications and vital to the niche filler wire bonding nanofluid adhesive market.

Solvothermal and hydrothermal synthesis are widely utilized in preparing different nanoparticles and inorganic materials at a commercial level. The significant difference between the physical and chemical properties of the synthesized materials lies in solvothermal and hydrothermal temperatures and pressures that exist in both solvothermal and dry-synthesis processes. In solvothermal and hydrothermal processes, nanoparticle nucleation is a significant process that largely occurs at a higher temperature of 200 °C or higher, and particle growth happens at specific superheated conditions [42-44]. According to the simulation and calculation, formed nuclei may have different particle size profiles, even in a high-temperature range.

Hydrothermally synthesized nanoparticles typically possess non-porous single crystals of well-crystallized material with a slight distortion of lattice parameters because of the influence of fluid-solid interface properties, which act as a limiting factor for crystallization.

In solvothermal and hydrothermal processes, the synthesis reaction of nanoparticles is dissolved in a solvent, and the autoclave provides both thermal and mechanical energy to the solution to facilitate the formation of nanoparticles in the solvent [44-45]. In a high-temperature solution, the crystalline precursors, if added, get dissolved to form an unlimited amount of free cations and anions available for forming ions and ion-bound clusters through the nucleation process. These freshly formed nanoparticle nuclei will start aggregating and growing along different pathways to form the nanocrystals. The growth pathways into the solution for particle aggregation of individual layers and compact 3D structures may be responsible for whether nanocrystals are formed based on detailed aspects like the pressure of the autoclave, the capping agents used, and stirring scenarios. Conditions like the amount of surfactant, concentration of the precursor salt, type, and volume of the solvent used can predefine the size of the particle. The solvent used interacts with the freshly formed nuclei through solvent-solute interactions and stabilizes them by maintaining the thickness of the double layer [42-43]. Though the method is always time-consuming on a lab scale, scaling up this procedure may be feasible on a large scale if the production is from bulk solvents, which gives a constant concentration of solute in a large volume of solvent.

3. Characterization of Nanofluids Thermosetting Adhesives

3.1. Physical Properties

The physical state of nanofluid thermosetting adhesives comes under physical characterization methods [9]. These physical techniques include measuring thermal properties, mesoscale agglomeration, surface activity, specific surface area, core-shell nature of nanofluid adhesives, and tensile strength, each briefly explained here. Techniques that include light scattering, dynamic light scattering, atomic force microscopy, and scanning electron microscopy are used to understand the agglomeration pattern. The zeta potential measurement can identify the surface-active nature of the nanofillers. This surface-active character improves the particles' dispersion within the fluid material. The core-shell type allows adhesive preparation with a uniform nanofiller concentration. The specific surface area is the area per unit mass, and mass-based properties such as catalysis and nanofluids have been seen in this context. These techniques help to understand the handling and end-use performance more, thus identifying the variables involved in the end-use process.

The synthesis of hydrophilic Ag-nanoparticles (NPs) in water and toluene and performed the size analysis by counting 330 particles from Transmission Electron Microscope (TEM) micrographs [22]. The results showed that the synthesis of Ag-NPs in water gave roughly spherical (first eccentricity is 0.46) particles in the range of 3 nm to 17 nm with a size distribution of 7.3 ± 2.5 nm, displaying good colloidal properties in water (Fig. 2A). The hydrophobic particles obtained were also roughly spherical (first eccentricity is 0.43) with sizes in the range of 4 and 17 nm, with a size distribution of 8.4 ± 2.0 nm, as shown in Fig. 2B.

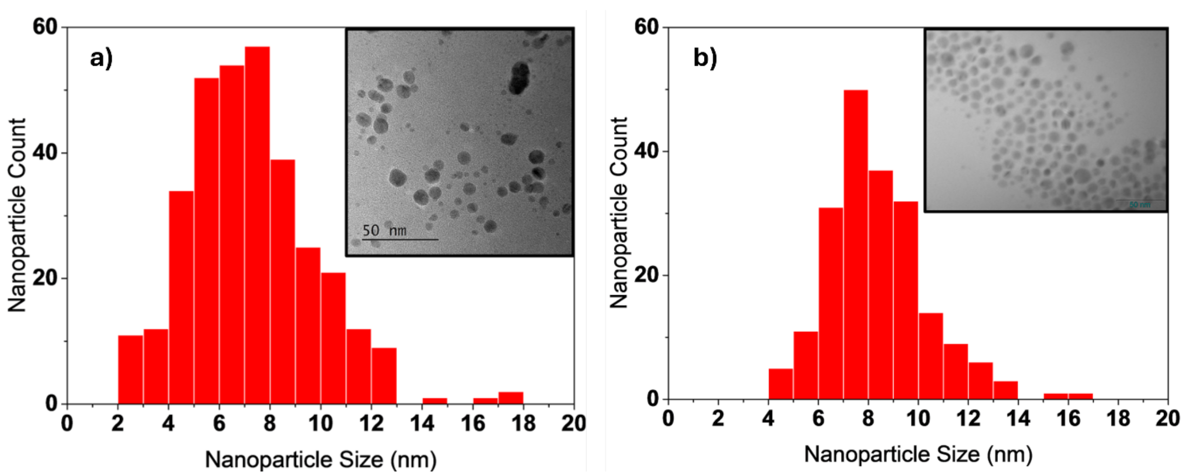

Figure 2. TEM images and size distribution of Ag/w NPs synthesized in water (a), and in toluene (b) [22]. Open Access CC BY-NC-ND 4.0.

Optimum dispersing can give good properties to nanofluid adhesives. Several methods can be used, namely mechanical stirring, sonication, ultrasonication, and grinding, to disperse nanoparticles in the base fluid [39, 46]. The use of surfactant agents can also help to stabilize the nanofluids due to their ability to adsorb on the surface of nanoparticles to provide an electrosteric stabilizing effect, and the surfactant on the surface of nanoparticles decreases the inter-particle van der Waals forces, leading to the stability of nanofluids [24, 46]. This work investigates the ability of surfactant only and surfactant followed by ultrasonication to facilitate nanoparticle dispersion in distilled water as the base fluid for a stable suspension. The effect of surfactant volume was given in 0.1, 0.5, 1.0, and 2.0%, and ultrasonication times were 30, 45, 60, and 70 minutes, which were also observed [22, 47]. The stability state of the nanofluids was observed through aggregate samples for 21 days.

The stability of the suspension and good physical properties are the main bases of a good nanofluid. The dispersion of nanoparticles in water can be influenced by their physical properties and the effect of ultrasonic cavitation. The use of surfactant agents may also help to stabilize the nanofluid due to their ability to adsorb on the surface of nanoparticles and provide an electrostatic stabilizing effect [24, 48]. Other mechanisms that help stabilize the suspension are the adsorbed surfactants on the surface of nanoparticles, which decrease the interparticle van der Waals forces and lead to agglomeration. However, too many surfactant agents can deteriorate the physical properties of the base fluid and/or nanofluid and affect heat transfer. Therefore, choosing the right type and amount of surfactant agent is essential.

3.2. Mechanical Properties

The viscoelastic behaviour of wood or any lignocellulosic-based materials differs considerably from organic polymers or traditional materials such as metals [49]. This occurs due to their special three-dimensional porous structure composed of elastic cellulose fibrils, microfibrillated fibrils, hemicellulose, and lignin [50, 51]. Although there are several ways to determine the bond strength of adhesively bonded wood, determining the bond strength of wood bonded with polymer adhesives is still the most important method to evaluate the efficiency of adhesives used in heavy flakeboards. The mechanical properties of an adhesive or bonding performance are classified in terms of shear, tensile, and peel strengths for assessing the longitudinal, transverse, and perpendicular bonding performance, respectively.

An ideal wood adhesive should possess moderate thermal stability and viscosity, a long, convenient open time, good shelf life, and excellent bonding strength. The choice of adhesive should effectively result in high strength and an adhesive bond line that causes weaker wood bond separations. The selected UV-curable thermosetting-based nanofluid adhesives produced even higher bond strength than those using the Polyvinyl Alcohol (PVA) adhesive. It was stated that the bonding strength of the epoxy and urea-formaldehyde (UF) adhesives improved if a combination of nanoparticles was employed. They demonstrate that the UV-curable lignin-epoxy adhesive and the soiligo-epoxy adhesive are particularly suitable for bonding wood containing formaldehyde. This review points out that nanofluid adhesives generally provide improved penetration and surface structure, better performance, and less harmful impact. The assessment of various effects, mechanisms, curing conditions, structures, and variations that influence key adhesive properties and bonding performance has not yet been done for these adhesives.

A study briefly reported that styrene (St), methyl methacrylate (MMA), and a crosslinker divinyl benzene (DVB) were injected in a mixture of water and ethanol containing an initiator, 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA), at 70 °C [48]. Scanning electron microscopy (SEM) analysis confirmed that each particle has multiple and significantly large bumps on its surface, imitating raspberry, and has a diameter of about 310 nm, as shown in Fig. 3a. Zetasizer found that the hydrodynamic diameter (Dh) of these particles is ≈330 nm. Polydispersity index (PDI) is 3.7% (Fig. 3b), whereas the sur- face charge, a Zeta potential is +39.0 (±3.57) mV. The initiator, AIBA, imparts the positive surface charge on the nanoparticles. The synthesized raspberry-like colloidal (RC) particles in a colloidal solution were present at a 4.06% volume fraction (or 3.7 wt%). It was confirmed that polymerized MMA (PMMA), used with styrene and DVB during synthesis, contributes mainly to these particles' surface roughness. SEM analysis confirmed that PMMA particles are smooth-surfaced colloids (SC) of ≈290 nm diameter, as shown in Fig. 3c. Their hydrodynamic diameter (Dh) is ≈315 nm (Figure 1d), PDI is 5.8% (Fig. 3d), and the Zeta potential is +38.0 (±4.81) mV. PMMA or SC nanoparticles in a colloidal solution were present at a 4.01% volume fraction (or 3.8 wt%).

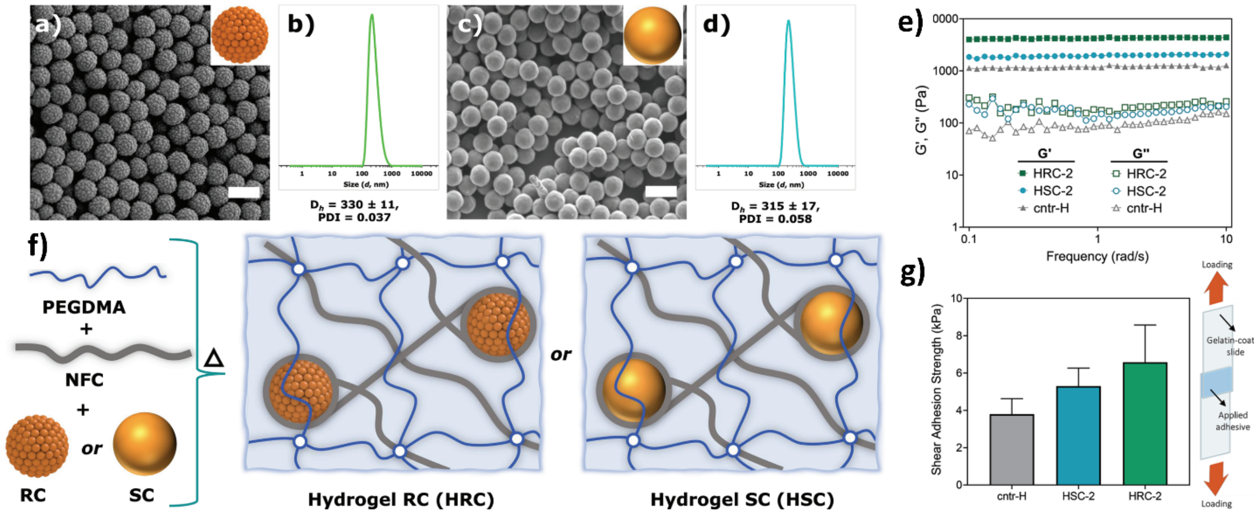

Figure 3. Morphological and mechanical properties of hydrogel-NPs-based adhesive. (a) Scanning electron microscopy (SEM) images, (b) the number averaged dynamic light scattering (DLS) size analysis, (c) SEM image of smooth-surfaced, PMMA colloidal-NPs-based adhesives, (d) the number averaged DLS size analysis of SC particles, (e) frequency sweep rheology data, (f) schematic representation of HRCs and HSCs hydrogels formulation, (g)shear adhesion strength of three hydrogels [48]. Open Access CC BY-NC-ND 4.0.

3.3. Thermal Properties

The thermal state of the nanofluid adhesive can be measured by some typical techniques such as thermogravimetric analysis, differential scanning calorimetry, and thermo-mechanical analysis [39, 41, 46]. The temperature at which the curing of this system starts and the changes taking place during curing help to find the stability of the adhesive at higher temperatures. The presence of nanofiller in the adhesive could form clusters or agglomeration, causing a mesoscopic structure since the processing conditions of nanofluid adhesive may not be enough to disperse them at a molecular scale. The changes in the thermal behavior of the curing process are analyzed by differential scanning calorimetry. The thermal behavior of crosslinking reactions was evaluated by differential scanning calorimetry. Thermograms of neat epoxy resin and nanofluids with diverse ratios of carbon nanotube (CNT) and Al2O3 showed the exothermic peak temperatures of the neat epoxy resin show decreases, while the peak exothermic temperature with a dominant peak of the exothermic reaction also decreased from 83.84℃ to 83.02℃ [52-53]. The heats of crosslinking reactions of the prepared nanofluid thermosetting adhesives were also reduced with increasing CNT content in the nanofluids. Additionally, in the case of the nanofluid with 3 wt% CNT, only an endothermic-rich needle, an exothermic valley, and a broad peak at the curing temperature could be observed. Such behavior of a curing reaction is attributed to the spatial orientation of adjacent CNT. Moreover, the presence and high aspect ratio of adjacent CNT could improve the thermal properties of the hybrid dial in the final cured epoxy resin.

Curing conditions should be particularly controlled as they decisively determine mechanical and thermal properties. Curing may occur at dwelling temperature or through accelerating methods, such as infrared, microwave, induction, or ultraviolet mechanisms. Among these techniques, ultraviolet curing is recognized as an instantaneous process with efficient energy utilization. After complete curing, nanofilm surface roughness and the improvement of mechanical properties at the adherend/nanofluid adhesive interface led to optimized wettability and adhesion performance [54]. Applying adequate curing time and intensity results in obtaining cured nanofluid adhesive with mechanical, thermal, and adhesive properties. Uniformly distributing nanoparticles through the adhesive process is a key factor in obtaining the targeted thermosetting nanocomposite adhesive. However, significant challenges arise from the possibility of either nanoparticle agglomeration during adhesive mixing, poor stability of nanoparticles during the curing process, or the migration of nanoparticles during the curing phase, which may form various amounts of defects, such as crack initiation and propagation, and areas of weak points in the nanocomposite-assisted adhesive. Practically, these nanofluids are applied as adhesives on surfaces using different techniques to establish adhesive force.

4. Application of Nanofluids Thermosetting Adhesives

Utilization of nanofluids within thermosetting adhesives to manufacture these advanced composites, which are termed nanofluid thermosetting adhesives [9, 37]. Nanofluid thermosetting adhesives are desirable for various practical applications due to their environmental benefits, high adhesion strength, and multifunctional performance for bonding lignocellulosic materials. The utilization of nanofluid thermosetting adhesives for lignocellulosic adhesion applications is promising due to their rapid bond strength development, grafting from the adhesive-substrate, high adhesive joints, and multifunctional adhesive performance that can be tailored by controlling the nanofluid design. These multifunctional performances allow nanofluid thermosetting adhesives to be used for a wide range of lignocellulosic composite applications, including fiber composites, particleboard, laminated veneer lumber, adhesive joints, and plywood [9].

Consequently, nanofluid thermosetting adhesives for bonding lignocellulosic materials are also very interesting. When epoxy thermosetting adhesives are used for bonding wood substrates or other lignocellulosic-based materials, thermal curing processes are commonly required [37]. During the curing process, chemical reactions begin in epoxy adhesive systems to form a highly crosslinked network, which provides excellent mechanical strength and enhances the cured resin's thermal, chemical, and mechanical stability. Curing speed and cure state during the process are important parameters for the adhesive systems. However, an incomplete reaction will occur due to poor wettability of solid epoxy resins with substrates and the thickness of as-prepared adhesive films, affecting the adhesive properties of wood composites. In addition, direct blend preparations generally never show a promising improvement in adhesive performance in those systems and sometimes exhibit a reduction in performance during industrial emergence.

Silane coupling agents, epoxy dispersion, and nanoparticles can modify wood substrates, improve performance, and simulate wood adhesion with thermosetting epoxy adhesive resins [37]. Currently, nanoparticles are of great interest when used as modifiers in epoxy systems because they cannot only modify the mechanical performance of the thermosetting epoxy adhesive resins but can also change the surface state and wettability of substrates, bonding interfaces, and bulk epoxy resins. Lignocellulose surfaces present a rough or semifluid-like state, perhaps causing penetration or infiltration of nanoparticles into substrates. These nanoparticles are also dispersed into epoxy resins during the curing process. Consequently, wood-epoxy composites yield a nano-colloidal system. This overview will give an overview of various nanoparticles that have been reported to be used for industrial wood bonding using thermosetting epoxy adhesives and will also discuss the possible chemistry of these developed wood-epoxy nanofluid adhesive systems.

The paper and packaging industry consumes many thermosetting adhesives, particularly in the form of water dispersions or hot melts [37, 55]. In contrast to solvent-based counterparts, water-based resin technology is perceived as cleaner and safer. Water-based adhesives also allow our modern society to meet the demands of the environmental and regulatory communities with respect to volatile organic compound abatement and reduction. Exploring renewable resources for adhesive formulation also represents another recent development in adhesive technology. The thermosetting water-based resin must be compatible with a high alkalinity level because of the equilibrium moisture content and hydrophilic nature of paper and cellulose fibers. These resins form adhesive bonds with hydroxyl cells of fibers and crosslink with them.

5. Future Perspectives

Thermosetting adhesives show attractive bonding performance, as they may be obtained with very high mechanical strength, high thermal stability, and resistance to aging [56]. However, their final properties strongly depend on the chemical structure and the compatibility with the adherends. Furthermore, they come with severe health, safety, and environmental concerns as their chemical composition includes extremely reactive functional groups. Consequently, there has been a continuous search for new and useful substitutes to the traditionally used adhesives. Thermosetting adhesives with nanofillers demonstrate the most potential due to their unique physicochemical properties. Unfortunately, the research in this area is still very scarce. Nevertheless, nanofluids combined with green metrics will soon present an intriguing possibility for industrially important wood-bonding applications.

This review emphasized the main achievements in the formulation of nanofluid thermosetting adhesives. However, we believe introducing metallic or metal oxide nanoparticles that find diverse wood adhesion-promoting applications could bring additional beneficial properties to the product, thus supporting the overall performance [57-58]. Such improvement of nanofluids in bonding wood opens an intriguing possibility for the industrial application of a component for the adhesives for bonding wood harvested from fast-growing plantations. After all, the experimental bond strength data results have shown that wood bonded with resin shows the same mechanical strength as is observed from the resin without modification. Moreover, it has been concluded that a resin from fast-growing eucalypts as a component for the adhesive formulation has been less exothermic as compared to commercial UF, which is a good indication of lower adhesive reactivity, lesser cure stresses and less thermal degradation of wood elements in the increasing temperature range than UF with and without the additive [59-61]. So, combining the low price of eucalypts with the benefit of several of their nanometric additives or their effect in different types of thickening without compromising the product's performance will be an interesting challenge for future research.

The emerging trends in using nanofluid thermosetting adhesives for bonding lignocellulosic composites are compared with using pristine nanoparticles to develop green nanocomposites bonded with conventional thermosetting adhesives. The potential applications of the nano-adhesives in various advanced lignocellulosic materials developed for building and construction purposes are addressed. To conclude the mini-review section, the advantages, challenges, and potential research directions in developing nano-adhesives from research to commercial scale are discussed.

Modifying and reinforcing thermosetting adhesives with green nano-additives provide a promising, innovative, and cost-effective means for developing advanced materials, particularly bio-based construction materials. An attractive strategy for the development of innovative materials from the combination of bio-based accommodating nanoparticles and thermosetting resins can involve the encapsulation, infusion, immobilization, or hybridization of these within proper thermosetting adhesive polymers during the curing or solidification process. The designed materials feature important properties. From simple additives or reinforcement of thermosetting polymers, enhancing nanofluid thermosetting adhesives' physicochemical properties is the research topic's major focus.

The nano-adhesives used for bonding lignocellulosic materials with porous and cellular microstructures provide advanced features when applied in various construction materials, including lightweight, cored, and energy-efficient materials. Nanocomposites connected by thermosetting adhesives loaded with appropriate nanoparticles show various functionalities. Significant accomplishments include enhanced dynamic and static mechanical properties, heat stability, super-hydrophobicity, dynamic shape stability, and flame retardancy. Foamed materials cured from the nanofluid adhesives with low surface tension filler nanoparticles show a closed-cell structure, are lightweight, have water resistance, and have sound absorption performance. These lightweight, sound-absorbing, water-resistant materials with a strong structure are suitable for lightweight building and construction applications.

Based on nanofluid thermosetting adhesives' synthesis, characteristics, and application studies, the following potential research directions can be proposed. Firstly, the fundamental principles of characterization and performance measurement of thermosetting adhesives and adhesive joints raise the challenge of adhesive formulations and the bonding process. The correlation between adhesive properties and their performance for lignocellulosic materials remains to be studied further. However, this work focuses not only on nanofluid thermosetting adhesives for their workable improvements through the introduction of various functional nano additives but also on the performance of adhesive joints.

The compatibility among the lignocellulosic fiber, the thermosetting resin, and the nano additives in the adhesive bonding system should be considered. Using functional natural fibers as reinforcing agents or active fillers could also be beneficial. Therefore, developing environmentally friendly nanofluid thermosetting adhesives is comparatively more feasible and effective. Secondly, de-bonding treatment, such as low adhesive mass loading, sound bonding processes, suitable sizes and shapes of nano additives, and the development of advanced surface modification, are necessary to maintain the intrinsic properties and functionalization of nano additives effectively.

6. Conclusions

This review summarizes nanofluid thermosetting adhesives' recent progress and status for bonding woodworking materials. General fitness and function, the advantage of nanoparticles, important factors, and adhesive fabrication are first discussed to propose the impetus and function of nanoparticles that have spilt over to nontraditional wood bonding applications. Fundamental features, nanofluids formation, mechanisms for synthesizing nano-adhesives, characterization methods, and grafting methods are introduced to reveal the current conditions of these innovative adhesives. Three different wood bonding applications, including preparation of bamboo, interface protection of wood-based composites, and preparation of novel wood adhesives, are presented to elucidate what researchers have already achieved and to inspire them to potential applications of such advanced adhesives.

In recent years, researchers have paid great attention to nanofluid thermosetting adhesives for bonding lignocellulosic materials. Many excellent works have been published, leading to the launch of this exceptional and important field. We summarized those reports and presented this mini-review article to elucidate the importance of nanoparticle-based technology development in wood adhesive and to point out their great potential in future non-traditional applications. It would be expected to provide a thorough understanding of those studies and stimulate further investigation on this important and fascinating research area for a broad audience of researchers, including material scientists, material engineers, chemical engineers, mechanical engineers, and material experts active not only in various related research areas of wood bonding but also in many other areas related to thermosetting adhesives for both academic and industrial purposes.

As a concluding remark, using nanocarbons as nanofillers in thermosetting adhesives offers many possibilities regarding physico-mechanical properties, adhesive performance, and advantageous properties. This review highlights the potential of using nanocarbons as functional nanofillers in thermosetting adhesives, from synthesis and properties to application. The incorporation of nanocarbons may provide a balance between the high viscoelastic modulus and the improved stiffness in the dry state, as well as an extraordinary enhancement in the thermal, barrier, and mechanical strength of the adhesive, especially in the case of lignocellulosic materials. Since nanocarbon and thermosetting adhesives are feasible, low-cost materials, and easily scalable, they may fully meet the demand for technical and high-performance thermosetting adhesives in the future. Their application in a green and sustainable manner is the right way forward in this context. In the meantime, the adhesive properties in the wet state remain unanswered but may be relatively achievable owing to their inherent hydrophobic nature. Nevertheless, the interfacial reactivity with hydroxyl-rich surfaces is one of the most interesting topics yet to be explained. These issues are potentially challenging questions that need to be addressed and that we may tackle. In the future, thermosetting adhesives will have the opportunity to evolve into other multifunctional nanocomposites owing to the use of nanocarbons in the design of the adhesive.

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