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State of Research and Trends in the Development of Polyvinyl Acetate-Based Wood Adhesive

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Abstract

Synthetic wood adhesives, consisting of urea-formaldehyde resins (UF), phenol-formaldehyde resins (PF), melamine-formaldehyde resins (MF), and polyurethane resins, are widely used. For UF and MF, most investigations are concerned with reducing free formaldehyde content; for PF, most studies focused on finding new alternative chemicals to replace phenol. These adhesives come under the Carcinogenic, Mutagenic, and Reprotoxic chemicals (CMR) category. Due to global energy issues and dependency on petroleum sources, the focus has shifted to look for alternative and renewable raw material sources for wood adhesives. Conventionally available wood adhesives are polyvinyl alcohol (PVA) stabilized, with drawbacks like poor water resistance, poor heat resistance, low-temperature workability, and it's based on petroleum resources. Polyvinyl acetate (PVAc) is non-resistant to moisture polymer, and if such adhesive joints are exploited in a moist environment, its strength substantially decreases. Sufficiently moisture-resistant adhesive joints are obtained by modifying PVAc dispersion with special compounds like reactive comonomer, Silanes, and modified PVA. To improve the workability at low temperature, Vinyl acetate (VAc) is copolymerized with specific comonomers like butyl acetate without affecting the performance properties. Here, we aim to present an overview of the research trend of PVAc-based adhesives in the wood industry. The review summarizes the current state of research PVAc-based adhesives.

Keywords

Polyvinyl Acetate Emulsion, Polyvinyl Alcohol, Bio-Polymers, Wood, Water Resistance, Adhesives

1. Introduction

Wood adhesive

Wood is a porous material with many inherited anatomical characteristics. Major characteristics are longitudinal tracheids in softwood species and vessel elements and longitudinal fibers in hardwood species. The lumens of their cells are large enough to provide a promising pathway for the flow of liquid resin. Interconnecting pits are often adequate to permit resin flow. However, high-molecular-weight polymeric resins or occlusions in the pits or lumens may inhibit flow. This conglomeration of resin and wood substance is called the "interphase region." Two substrates, each with its interphase, and the interface between them comprise the "bond line." The geometry of the interphase region varies as a result of many factors, such as wood anatomy, permeability, porosity, resin viscosity, surface energy, consolidation pressure, and others [1]. Glue in all industrial sectors is a modern need; it is also essential in the furniture industry. Recently focus has shifted to green adhesives [2].

Wood adhesives account for a considerable part of manufacturing costs. To decrease the manufacturing costs, wood industries use lower-cost economical adhesives, sometimes compromising the quality of the products [3]. Many furniture was made using mechanical connectors, but humans were also looking for wood adhesives from plants and animals [4]-[19]. In the light of increasing public concern about human health and the environment, a decrease of formaldehyde and other carcinogenic, mutagenic, and reprotoxic chemicals (CMR) emissions arising from adhesives is highly desirable. To that end, developing environmentally benign materials that can replace CMR-based wood adhesives is a vital objective [20]. It needed a lot of research on environmental and human-friendly adhesives. Wood glue is a major area of importance for industrial and commercial activities [2].

History of wood adhesive

The first proof of a substance that was used as an glue dates back to 4000 B.C. Archaeologists have uncovered statues from Babylonian temples with ivory eye balls glued into eye sockets. This tar-like glue has been held for almost 6000 years. Between 1500 - 1000 B.C., the period gave further proof that glue had become a method of assembly. Paintings and murals showed details of wood gluing operations [21] [22]. The first commercial adhesive factory was started in Holland to manufacture animal glue from hides. About 1750, the first glue patent was issued in Britain for fish glue. Patents were then rapidly issued for adhesives using natural rubber, animal bones, fish, starch, and milk protein. By 1900, the United States had several factories producing glue from these bases. The industrial revolution caused an explosion in technical breakthroughs that resulted in new materials becoming available for formulating adhesives. The era of plastics began with the production of Bakelite phenolic, a thermoset plastic, in 1910. Within a year, adhesives using phenolic resin were put on the market. The 1920s, 30s, and 40s saw many new plastics and rubbers synthetically produced, many out of an urgent necessity developed during World War II [23]. Environmentally friendly adhesives Glue is the most critical raw material coming after wood in furniture industries. Especially after World War II, glue ameliorated its time and bonding techniques and developments occurring in plywood block board and chipboard production. In the past, plant and animal glues were used. Later they left the place for the synthetic resin. Animal glue has to fight against instability and resistance to hot water and microorganisms, and the lack of block board limits their usage, though the use and application of synthetic resin in plywood production eliminate these drawbacks [24]. From this art, animal and fish glues were refined, and other adhesives were developed, such as an adhesive from egg whites to bond golf leaf. In addition to egg whites, other natural ingredients were used to prepare the glue, such as blood, bones, hide, milk, cheese, vegetables, and grains [25] [26].

2. Classification of Adhesives Based on Chemistries

1) Animal glue

This glue is obtained from skin, bone, and fish residues. Blood is obtained from the raw with blood from slaughterhouses and casein derived from an animal milk protein [27]. They are obtained from waste and by-products of the animal industries. Raw materials of animal adhesives are hides, ligaments, and bones of cattle and other animals. The scraps of the leather industry are also utilized. Adhesives made from hides are of a higher grade than glue obtained from bones and tendons [28].

2) Plant botanical adhesives

Environmentally friendly adhesives obtained from botanical plants are mostly obtained by processing starchier plants. Plant-derived adhesives are divided into two groups as starch- and cellulose-derived. The first group is adhesives derived from starch extracted from plants, such as corn, rice, potatoes, and wheat, and is generally used in bookbinding, paper bags, and cardboard boxes. The second group of adhesives is made from cellulose, derived from trees, shrubs, or fruits such as bananas, which are used more in stickers affixed to glass.

Protein-based adhesives

Protein is the oldest kind of adhesive among different raw material sources and primarily includes animal and plant protein [29]. Soybean proteins are the easiest to obtain and account for most of their production of the other plant proteins. The performance of soybean proteins is closely related to the particle size of adhesives, the original condition of surfaces, viscosity and pressure temperature, pressure, and time during processing [30]. Hettiarachchy *et al.* [31] developed an alkali that changed the performance of soybean protein adhesives to bond lumber and compared it with natural protein adhesives. This change in performance of protein adhesives has the advantages of much better glue strength and water resistance.

Starch-based adhesives

As an environmentally friendly natural adhesive, Starch adhesives have become of growing interest to scientists. Since starch has outstanding features, such as naturally large molecules, active functional groups, meets environmental requirements, and is low priced, it usually is used as office adhesives. The use of starch as an adhesive in the wood industry is limited, *i.e.*, lousy water resistance, poor storage stability, inadequate liquidity, and molds easily. Therefore, modification to starch is necessary. To improve water resistance and bonding qualities of starch adhesives, the most effective way is to form compact structures of net cross-linking after adhesives have been molded to prevent bulking for the water molecules wedging and causing the destruction of hydrogen bonds. To improve starch adhesives' stability, we can add a stabilizing agent into the adhesives to extend their storage time [32].

Lignin based adhesives

Lignin is one of the essential natural polyphenols. It is made of phenylpropanoid monomers which become high molecular weight because of their linked C-C and ether bonds. The lignin structure is similar to the microscopic structure of phenol-formaldehyde resin. Hence, some references suggest using lignin to replace phenol to make adhesives. Lignin is a compound that has phenyl propane as its skeletal structure and is also an active polymeric compound. Condensation or a cross-linking reaction with urea-formaldehyde can produce lignin-urea formaldehyde adhesives.

Tannic based adhesives

Tannin is a natural phenolic compound with several active hydroxyl and carboxyl groups, replacing some phenols as raw material for industrial use. As a replacement for phenol or resorcinol, Tannins are produced as a wood adhesive with a neutral glue layer and, compared with UF, solidify rapidly. So far, tannin adhesives have been successfully applied in plywood, particle board, bamboo plywood, and other fields. Problems of tannin glues are primarily those of rapid reactions between tannins and formaldehyde, short adhesive activity, poor water resistance, high viscosity, high dosage, component variation, and easy chemical reactions [33] [34].

3) Synthetic adhesives

Synthetic adhesives have many advantages, such as extensive application, easy-to-use, high economic efficiency, and rapid development. All synthetic adhesives are not toxic in nature. Some of synthetic adhesives like UF and PF, they are formaldehyde realising adhesive. To reduce the toxicity of such adhesives, we can blend natural biopolymers like starch with them. In the wood industry, urea-formaldehyde resins (UF), phenol-formaldehyde resins (PF), polyvinyl acetate (PVAc) emulsion, and isocyanate adhesives have extensive ranges of application with promising market prospects. In the 1930s, synthetic resin adhesives were used in the woodworking industry. They have many advantages for use in the woodworking industry and some of disadvantages like based on petroleum sources, toxicity and costly. In outdoor furniture, synthetic resin adhesives can be used in joints that remain as strong as the wood even in unprotected exposure to the weather. Inorganic adhesives are based on typical compounds, such as sodium silicate, magnesium oxychloride, lead oxide, sulfur, and various metallic phosphates [35].

Polyvinyl acetate adhesives

Polyvinyl resin emulsions are also called white glues, are thermoplastics, softening when the temperature is increased to a particular level and hardening again when cooled. PVAc adhesives are copolymer-based. PVAc adhesive solidifies by evaporation or absorption of water by the gluing material [36]. PVAc is used for general assembly applications, film overlay and high-pressure lamination, edge gluing, wood veneer, and edge bonding as a furniture adhesive.

Hot-melt adhesives

To spread and for adhesion of substrates, adhesives should have the "soaking" feature. In most adhesives used in packaging, an easily evaporating agent such as water flow is used to dissolve the adhesive. It evaporates, leaving behind a sticky substance, and it easily glues. On the other hand, a solvent is used in Hot-melt before applying instead of dissolving it. The solidification of hot melt adhesives can cause the unifying feature. Heat dissipates more quickly in the case of a volatile liquid, even for a waterproof layer. Fast heat dissipation provides quick bond formation. Hot-melt adhesives are furnished in the solid form [37] [38] [39].

Contact adhesives

Contact adhesives are generally based on synthetic rubber, obtained by dissolving in suitable liquids. As a result of evaporation of the flux contained in the glue, the glue dries. Bonding of large surfaces with contact adhesive is difficult Contact adhesives are usually used to bond:

- Plastic laminates to plywood or particleboard for counter-tops,
- Restaurant and kitchen tables,
- Edge of particle boards and medium-density fiberboard (MDF),
- Upholstering of sofas, and
- Polyvinyl chloride (PVC) edge to panels [40].

Urea-formaldehyde resin adhesives

Urea-formaldehyde resins are widely used in chipboard or plywood production. UF resin is produced by heating suitable urea and formaldehyde at 115˚C for 5 hours. They are usually produced during the production of high-quality glue E3 formaldehyde emissions. UF resins came into the market in the 1930s. UF resin can be formulated for hot pressing or room temperature curing by different types and amounts of catalyst. They are also marketed as dry powders, with or without incorporating the catalyst [41].

Melamine resin adhesives

Melamine-formaldehyde resin (MF) is obtained from polycondensation of melamine and formaldehyde. In the reaction between formaldehyde and melamine, the melamine gives derivatives containing different numbers of methyl groups participating amine group. The number of methyl groups may be up to six. Applications and Properties MF resins are usually used in the impregnated decor paper, barrier lining the balance and preservation, post-forming craft, and overlays [42].

Phenol-formaldehyde resin

Phenol-formaldehyde resins (PF), the second-largest wood type of adhesives after UF, have excellent properties to resist weather, water, and temperatures, have high bond strength after their solidification process, and are commonly used in outdoor structures of wood-based panels.

Silicone adhesives

Silicone adhesives are known as polysiloxanes. In the chemical structure of silicones, silicon (Si) and oxygen (O) atoms are sequentially arranged instead of carbon (C) contained polymer is the common name. Silicone rubbers are also electrically insulating and chemically resistant and maintain flexibility in a wide temperature range. These are the crucial features. It is most commonly used in a protective sheath and insulating varnishes [36] [43].

3. Polyvinyl Acetate Emulsion

PVAc is most widely used as an emulsion of PVAc polymers in water. PVAc emulsions are prepared by free radical polymerizing vinyl acetate (VAc) monomers in the presence of polyvinyl alcohol as a protective colloid [44] [45]. Polyvinyl Acetate PVAc is commonly known as "white glue". Polyvinyl acetate (PVAc) emulsion is an odorless and non-flammable adhesive widely used in furniture and other wood product manufacture at room or low temperatures [46] [47]. Polyvinyl acetate (PVAc) adhesive emulsions are commonly used in bonding many porous materials at room temperatures, such as in wood processing, furniture packaging, building decoration, texture bonding, and print bonding [48] [49] [50].

Water-based PVAc dispersions are the most used among the thermoplastic polymers as the basis for glues to be used with wood and wood products [51]. Protective colloids like polyvinyl alcohol (PVA) play an important role in the emulsion polymerization of vinyl acetate (VAc) concerning the viscosity and stability of the emulsion and the mechanical properties of the bonds formed in glued wood joints [52] [53]. Emulsion polymerization of vinyl acetate to PVAc needs colloid for stability and enhancing the mechanical properties of the prepared adhesive as shown in **Figure 1**. DH, molecular weight, and molecular weight distribution of PVA are the main factors determining the colloidal stability.

Water solubility and flexibility increases when the low molecular weight grade of PVA is used as protective colloid. DH affects the water solubility of the colloid. Because of the crystallinity of fully hydrolyzed PVA, it needs to be heated to the boiling point of water for its complete dissolution. In partially hydrolyzed PVA, reduction in crystallinity due to the presence of residual acetate groups makes it soluble in normal water [54] [55]. Modifications are done in PVA with the help of fluorine substituted silanes and Glyoxal Bis (Sodium Hydrogen Sulfite) Adduct to improve the properties [56] [57] [58] [59] [60]. The curing

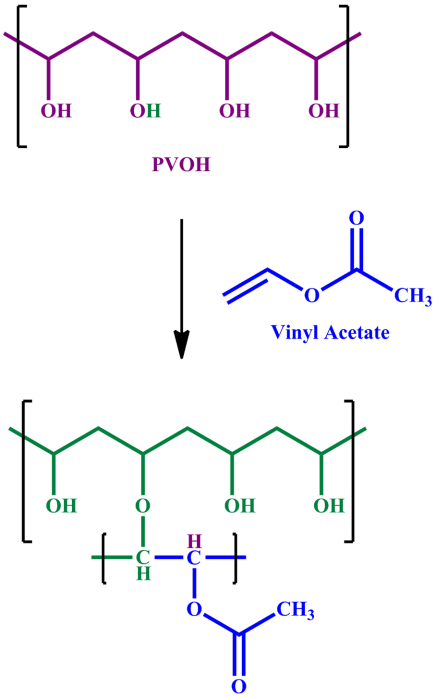

Figure 1. Polyvinyl alcohol stabilized polyvinyl acetate.

process of PVA only includes water evaporation and subsequent formation of hydrogen bondings, which are very much vulnerable to water and elevated temperatures. Of course, there are some cross-linked grades of PVA with improved performance at high temperatures and humid conditions. Research conducted on PVA has focused primarily on improving the water resistance of PVA by several crosslinking mechanisms [61] [62].

4. Current Issues Using Conventional Polyvinyl Acetate Emulsion Adhesive

The PVAc-based adhesive is one of the relatively economical adhesives that the wood industry has used for decades. Despite being a non-toxic impact on the environment, PVAc suffers the main drawback. From a physical and chemical standpoint, Wood adhesives are affected by temperature changes and moisture. As regards temperature, this dependence is a common characteristic of thermoplastic polymers. Instead, the water dependence in PVAc wood adhesives is related to these products being applied as water-based dispersions. Therefore surfactants, colloid protectors, and other hydrophilic compounds are present in formulations [63], thus increasing the water affinity of the dispersion compared to the original pure polymer [64] [65]. PVAc has inferior performance in fire and wet conditions. The mechanical performance of PVA adhesive deteriorates with increasing temperature, and it loses its bonding resistance capacity at over 70˚C [66] [67]. The poor performance of PVA at elevated temperatures stems from the fact that PVA is a thermoplastic polymer, which reaches Tg at relatively low temperatures. The curing process of PVA only includes water evaporation and subsequent formation of hydrogen bondings, which are very much vulnerable to water and elevated temperatures [68].

The wood adhesive should have excellent flexibility, toughness, and fatigue resistance. In addition, the adhesive should be applied in low-cost, high-speed processes and be able to survive storage conditions and repetitive stress [69]. Water-based polyvinyl acetate adhesive (PVAc) has many desirable features and advantages, with only a few limitations [70]-[76],

Advantages:

- Low cost and availability
- No toxicity problems
- No aging problems
- The dried film holds high joint flexibility
- It does not damage the equipment
- Provides invisible, colorless, and transparent glue lines
- Easy and wide for application

Limitations:

- Low resistance to weather and moisture
- Poor resistance to most solvents
- Slow setting speed
- Curing for 1 - 7 days is recommended before handling

Of course, there are some cross-linked grades of PVA with improved performance at elevated temperatures and humid conditions. Research conducted on PVA has focused primarily on improving the water-resistance of PVA by several approaches [77]-[85], and little attempt was made on the area of heat resistance.

5. Research Trend in the Development of Wood Adhesive Based on Modified Polyvinyl Acetate Emulsions

1) Filler encapsulated Polyvinyl acetate emulsion

Some of the study clays are encapsulated in PVAc emulsions. The study relates to the field of PVAc emulsion adhesives, particularly to a Nano clay or montmorillonite (MNT) contained toughened and modified polyvinyl acetate emulsion adhesive and a preparation method for the adhesive. To effectively improve the water-resistance of a polymerization product, through nano clay added in the reaction process, the mechanical property of the adhesive is effectively improved, the toughening and strengthening effect is realized, the polymer viscosity is improved, and the bonding strength is higher [86] [87] [88]. In [89] study investigated the shear strength of heat-treated solid wood of three species (beech, poplar, and fir) bonded with PVAc adhesive reinforced by nano wollastonite (NW). Heat treatment decreased the shear strength of the bonded specimens considerably. This was attributed to several factors, such as a reduction in polar groups in the cell wall, increased stiffness of the cell wall after heat treatment, and a decline in the wettability of treated wood. Nano-clay impacted the bond strength of PVAc with different magnitude depending on the type and loading of nano-clay. Shear strength of joints at dry state increased by the addition of nano-clay. The increase was more evident in the nano-clay compatibility with the matrix. Shear strength of joints in the wet state improved as nano-clay loading increased, showing the effectiveness of nano-clay on imparting water resistance in the glue line [90].

PVAc adhesive with fumed silica was prepared, and it has uniform viscosity and good binding strength, moisture resistance, cold resistance, and mechanical stability [91]. PVAc nanocomposites for wood adhesives containing different amounts of colloidal silica nanoparticles (CSNs) were synthesized via in situ one-step emulsion polymerization. The obtained results showed that PVAc nanocomposite's shear strength, including one weight % CSNs, has the highest shear and tensile strength, about 4.7 and 3.2 MPa [92]. The semi-continuous seeding emulsion polymerization prepared PVAc hybrid emulsions with nanoparticles SiO_2. Adhesion strengths of PVAc emulsions modified with nanoparticles SiO_2 were improved. Dynamic mechanical analysis (DMA) results indicated that the films of PVAc/SiO_2 hybrid emulsions had the higher storage modulus than the film of PVAc [93] [94].

The nano-titanium dioxide (TiO_2) was utilized to improve the bonding performance, structure stability, and film-forming properties of renewable starch-based wood adhesive. The results showed that 4% nano-TiO_2 resulted in 6.5 MPa of shear strength and 6437 Pa·s of viscosity. In conclusion, the 4% nano-TiO_2 can be employed to prepare starch-based wood adhesives with superior properties for wood application [95].

2) Vinyl acetate grafted on Biopolymer based emulsions

Grafting was an important technique for modifying polymers physical and chemical properties [96].

Starch-based PVAc emulsions

Graft polymerization of vinyl acetate monomer starch, as shown in **Figure 2**, and its usage in wood adhesives have gained researchers and industries' interest [97] [98] [99].

Improvements in thermal stability along with bonding strength and water resistance were shown by graft polymerization of vinyl acetate on corn starch [100]-[106].

Cellulose-based PVAc emulsions

Geng et al. conducted a study in which incorporation of cellulose nanocrystals (CNC) to the crosslinked PVAc matrix by sodium tetraborate (borax) and in-situ polymerization of vinyl acetate in the presence of CNCs [107]-[113]. Cellulose nanocrystals were successfully grafted by reversible addition-fragmentation chain transfer and macromolecular design via the interchange of xanthates polymerization (SI-RAFT/MADIX) of VAc in a controlled manner, as shown in **Figure 3**.

Chaabouni et al. investigated the effects of the addition of CNFs on the properties of waterborne polyvinyl acetate (PVA) adhesive [114]. A study investigated the effect of the addition of cellulose nanofibrils and nano clay on PVAc

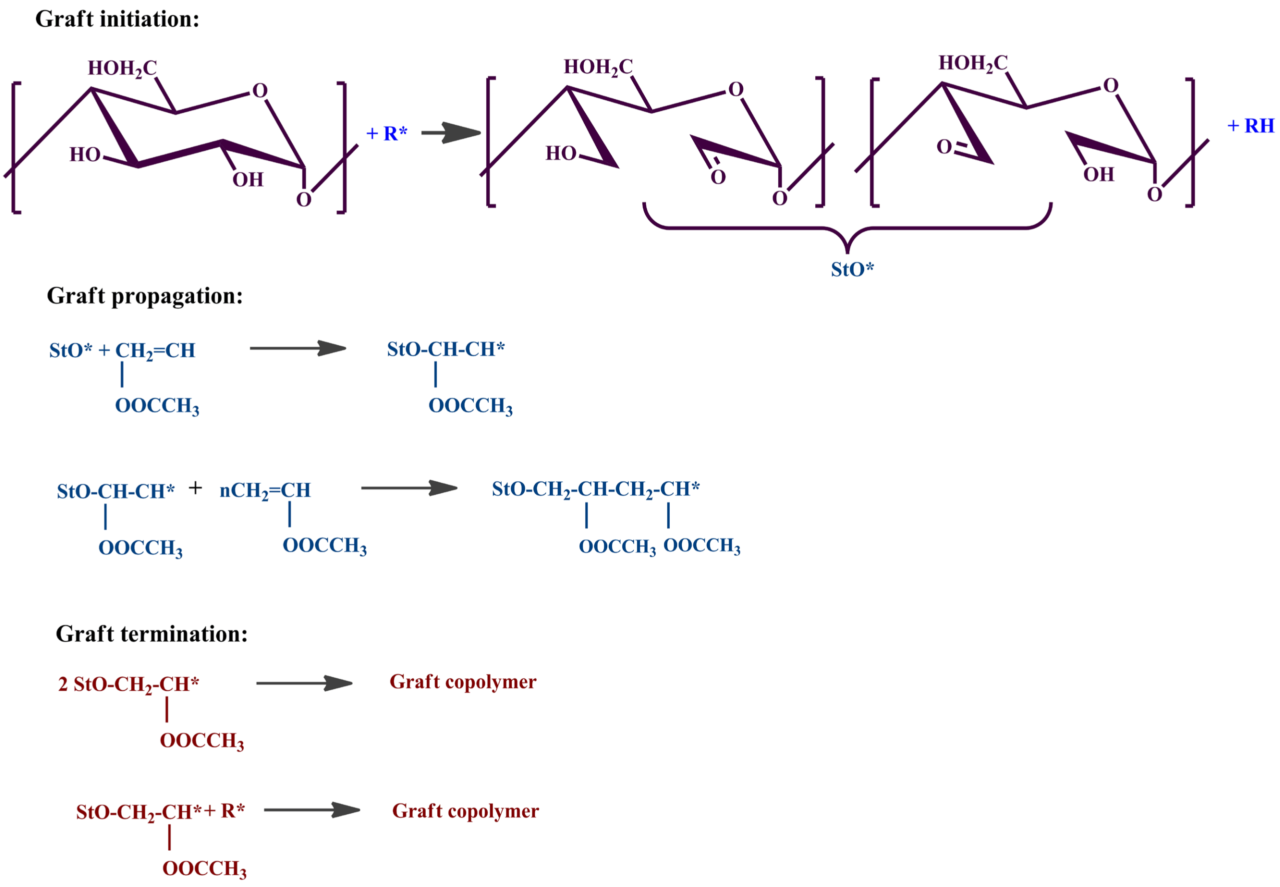

Figure 2. Vinyl acetate grafting on starch.

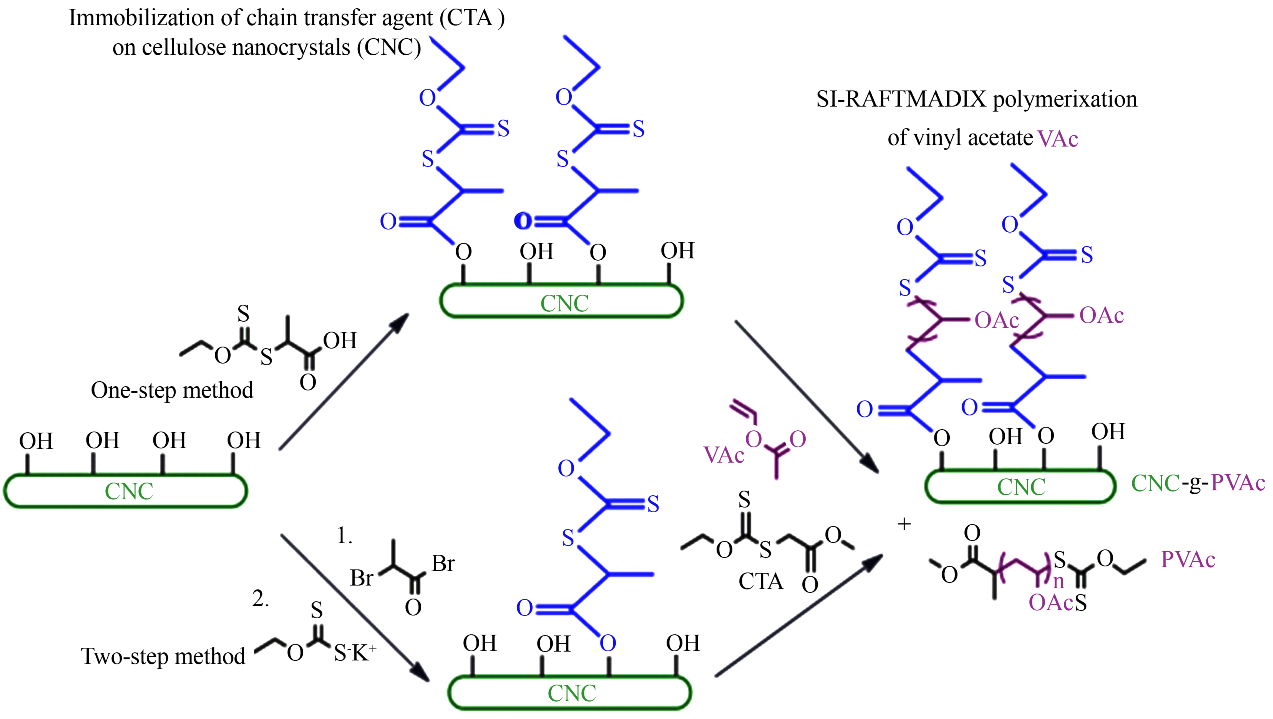

Figure 3. SI-RAFT/MADIX polymerization of vinyl acetate on cellulose nanocrystals.

adhesive [115]. In the presence of CNC, a persulfate/metabisulfite initiator was employed for in-situ emulsion polymerization of VAc without any surfactant [116]-[121].

Lignin based PVAc emulsions

Recently, lignin has been copolymerized with some vinyl monomers via the graft-onto method, graft from, and click chemistry techniques [122]-[129]. These studies showed significant enhancement in the physical and thermal properties of the copolymers [130] [131]. Therefore, VAc was grafted onto lignin to prepare lignin-VAc monomer (LVAc), and later it was copolymerized with VAc monomer through a free-radical copolymerization, as shown in **Figure 4**.

In some studies, vinyl acetate was grafted from chitosan by emulsion polymerization to combine the excellent bonding properties of chitosan with the applicability of PVAc. The bonding performance was investigated by bonding thin wood veneers and measuring the tensile shear strength after conditioning. The resulting bonding performance of the chitosan-graft-PVAc adhesive was outstanding, especially regarding the wet strength of the bond line, which is superior to that of the com. benchmark PVAc-based wood adhesive [132].

3) Water-resistant polyvinyl acetate emulsions

However, PVA stabilized PVAc emulsion-based adhesives also have some defects, its cold tolerance, mechanical stability, thermal stability, and water resistance are poor. Till now, many studies have been done on this topic, including the preparation methods, radiation preparation, co-polymerization, co-blending, and so on [133]. PVAc water-resistant glues used in the wood industry and belonging to the class of durability D3 as per EN 204 - 205 show high resistance to both water and heat compared to the usual PVAc-based thermoplastic products. Conventionally synthesized adhesives are attained by cross-linking the linear PVA chains and using Lewis acid, such as aluminum chloride [134]-[140].

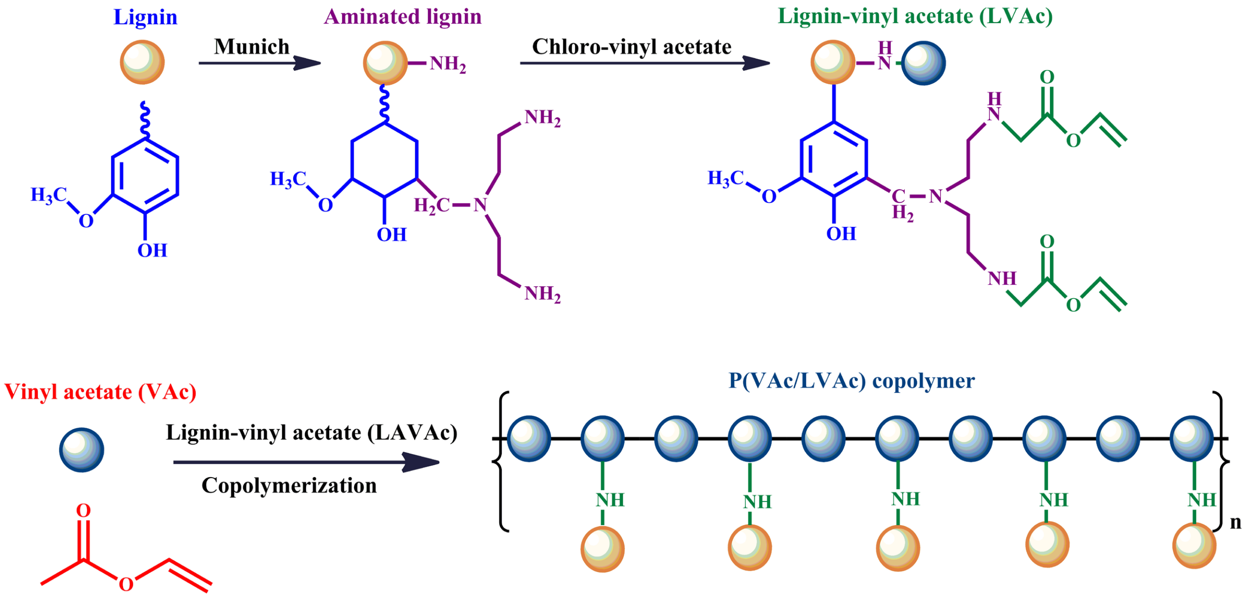

Figure 4. Schematic representation of the preparation of LVAc and its copolymer with VAc.

Vinyl acetate-N-hydroxymethyl acrylamide copolymer emulsions

In some of the studies, to improve PVAc's chemical, physical, mechanical, and thermal properties, and active monomer named N-hydroxymethyl acrylamide (NMA) was introduced to modify PVAc based emulsion adhesives. Here, NMA was an amide derivative from unsaturated carboxylic acid, it could polymerize with VAc, and the cross-linkable thermosetting copolymer of PVAc-NMA could be obtained. The molecules could further get cross-linked and cured under suitable acidic conditions [140].

Crosslinking reactions

Usually, NMA shows the reaction mechanism of that cross-linking agent: two molecules of NMA condense through the hydroxyl-methyl groups by leaving one molecule of water to form bis-(acrylamide-methyl) ether and, in a second step, by releasing one molecule of formaldehyde to form N, N–methylene-bis-acrylamide as shown in **Figure 5**. The reaction has been affected by acid catalysis or simply by heat [141]. As soon as the polymer dispersion is made, the product is modified by adding an external crosslinking agent able to act on the protective colloid (usually polyvinyl alcohol). The choice of this external agent is driven by the need to lower the pH of the system and, at the same time, block the hydrophilic action of the protective colloid, as shown in **Figure 6** [142].

A new biodegradable, renewable, and environmentally friendly starch-based adhesive for wood-based panels was synthesized. The synthesis was conducted by grafting polymerization of vinyl acetate (VAC) monomer onto corn starch and crosslinking polymerization with NMA. Compared with the traditional starch-based wood adhesive, the water-resistance of starch-based adhesive with NMA was greatly improved [74] [92] [143]-[155].

Acrylic comonomers based emulsions

A recently developed, successful approach to achieving controlled thermosetting of PVAc emulsions involved novel polymer latex particles bearing functional groups introduced via the reactive monomer acetoacetoxyethyl methacrylate

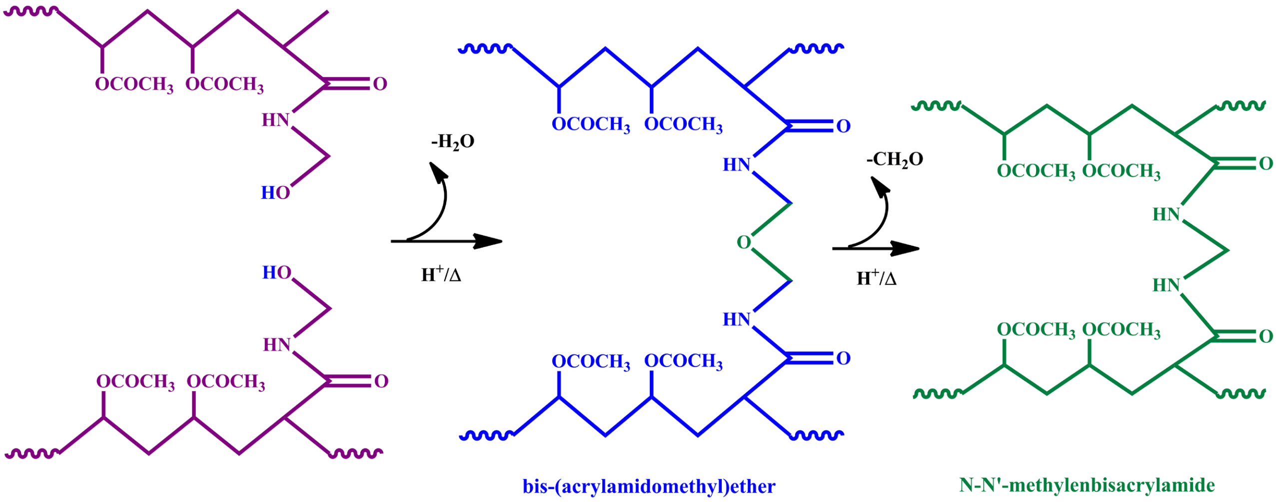

Figure 5. Cross-linking reaction of PVAc in the presence of N-methylolacrylamide (NMA mechanism).

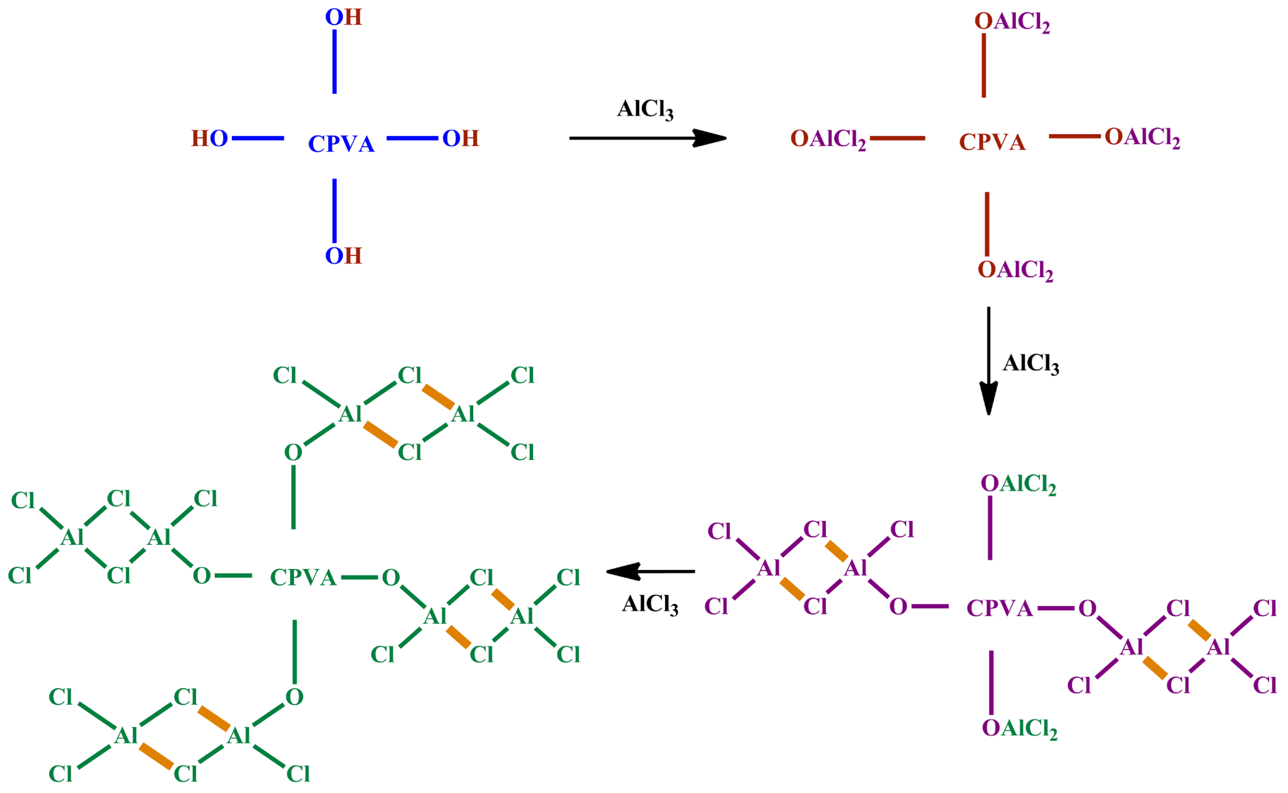

Figure 6. Reaction mechanism between the protective colloid and the external crosslinking agent.

(AAEM) which had been recognized for its ability to provide a versatile crosslinking site in thermoset adhesives [156]. To improve polyvinyl acetate emulsion adhesive's bonding strength and water resistance, a new kind of four component copolymer emulsion adhesive suited for plywood was prepared by semi-continuous emulsion polymerization with vinyl acetate, Bu acrylate, Me methacrylate, and acrylic acid as monomers [157] [158]. The invention further pertains to a dispersion incorporating said vinyl ester-based polymer latex composition, products comprising said dispersion, and various uses of the dispersion. A latex was prepared from acrylic acid, Bu acrylate, ethylene, N-methylol acrylamide, sodium vinyl sulfonate, Veova 10, and vinyl acetate [159] [160] [161]. Water-resistant copolymer latexes of vinyl acetate (VAc)/vinyl ester of versatic acid (Veova)/methacrylic acid (MAA) were prepared by the semi-continuous seeding emulsion polymerization. The water resistance of these latexes was greatly dependent on the M AA content, the introduction method of MAA, and the neutralization degree of MAA [156] [158] [160] [162]. This paper aims to enhance the water resistance and the heat resistance of poly (vinyl acetate) (PVAc) emulsion adhesive by providing the emulsion with controllable thermosetting capability. Emulsion polymerization was used to synthesize PV Ac/Veova 10 copolymers with varying proportions of acetoacetoxyethyl methacrylate (AAEM) incorporated in the copolymer chains [163] [164]. Water-resistant copolymer latexes of vinyl acetate (VAc)/vinyl ester of versatic acid (Veova)/methacrylic acid (MAA) were prepared by the semi-continuous seeding emulsion polymerization.

The water resistance of these latexes was greatly dependent on the MAA content, the introduction method of MAA, and the neutralization degree of MAA. The results showed that water-resistant VAc/Veova/MAA latex had 9.51 MPa of dry compression shear strength, 3.77 MPa of wet compression shear strength, and 47.0% water absorption [162] [165] [166] [167] [168]. The experimental method of copolymerization of acrylic acid with vinyl acetate was introduced, and optimum technical conditions were determined. The modification improved the adhesive's shear strength and water resistance [169] [170].

Vinyl formal comonomer based emulsion

In some study, to improve the performance of PVAc (polyvinyl acetate), vinyl acetate white emulsion was modified by copolymerization with polyvinyl formal [171].

Modified PVA stabilized emulsions

The methods of improving water-resistance of PVAc emulsion are reviewed, mainly including copolymerization, addition of compounding agent and modification of protective colloid [172]. A study was conducted to determine whether the water-resistance of PVAc emulsion can be improved by using PVA as a protective colloid, in which an acetoacetyl group is introduced into the protective colloid. Compared with PVAc with generic PVA, the PVAc using acetoacetylated PVA produces good numerical values in film properties and lumber bonding capacity, thus exhibiting improved water resistance [173] [174] [175].

Vinyl acetate was polymerized in the presence of acetoacetylated PVA (acetoacetyl content 5.5 mol%; average saponification degree 99 mol%) and subsequently mixed with propionic hydrazide to give an emulsion. Then, one woodblock was coated with the emulsion, laminated with the other block, and compressed to provide a test sample showing compression shear adhesive strength ≥ 30 kg/cm after boiling for 4 hr [176]. With acetoacetyl polyvinyl alcohol (AA-PVA) as protective colloid, Butyl acrylate (BA) and vinyl versatate (Veova10) as modified comonomers of polyvinyl acetate (PVAc) emulsion, a modified PVAc emulsion adhesive was prepared. The research results showed that the corresponding modified PVAc emulsion had good shear strength and good water resistance [177].

Silane modified PVAc emulsions

The aqueous emulsion comprises a vinyl acetate copolymer with mol. wt. 1000 - 800,000, such as vinyl acetate-vinyltrimethoxysilane copolymer. The polyvinyl acetate aqueous emulsion is free of formalin and is either used alone or combined with an additional crosslinking agent to improve the water resistance [178] [179] [180]. Polyvinyl acetate was emulsion-polymerized in the presence of Gohsefimer Z 210, and Exceval RS 2117 as a protective colloid using hydrogen peroxide and 1-part glycidyloxypropyltrimethoxysilane was added therein to give an aqueous adhesive, showing good storage stability and adhesion [181].

4) Blending with other crosslinkers

Various approaches were taken to improve the water resistance of PVAc emulsion adhesives. The polymer films' tensile storage modulus and glass transition temperature (Tg) were measured using dynamic mechanical analysis to quantify the influence. The polymer films' gel fraction and swelling ratio were measured to evaluate internal crosslink density. A blending of the PVAc emulsions with melamine/urea/formaldehyde resin modified the water resistance considerably. The film had a high tensile storage modulus because of the formation of an interpenetrating network-type structure [181]. Starch was oxidized and then condensed with urea; then, the modified oxidized starch was blended with polyvinyl acetate emulsion synthesized in the laboratory to prepare the main agent of aqueous polymer isocyanate (API) adhesive for plywood. The new main agent of API has excellent economic profit and no pollution [182]. The influence of glyoxal on the water resistance of pine-pine and beech-beech wood compounds formed by adhesives based on vinyl acetate dispersion is studied. A noticeable increase in water resistance is observed for pine-pine compounds if the adhesive composite contains not only glyoxal but also aluminum chloride and "glyoxal" additives [183].

5) Low temperature working polyvinyl acetate

Some problems about typical PVAc emulsion's stability, freezing resistance, and flowability at low temperature were successfully solved by adding Butyl acrylate (BA) [184], Methyl methacrylate (MMA) [185] [186], acrylic acid (AA) [187] [188], and 2-Ethyl Hexa-acrylate [189] co-monomer with means of emulsion copolymerization using PVA as stabilizing and emulsifying agent [190]. The properties of copolymer emulsion have no significant changes after five freeze-thaw cycles, frozen for six months, even frozen-thawed alternatively for six months out of the warehouse. The emulsion also exhibits good flowability at 0˚. It can be an excellent emulsion adhesive for porous materials [191] [192]. The adhesive does not generate low-temperature gel and has suitable construction properties and high low-temperature strength [193] [194].

6. Conclusion

Adhesive for wood bonding is not only key to the efficient utilization of wood; it has been a key factor in the development and growth of the forest products industry. Because of the importance of adhesives to the utilization of wood, it is expected that improvements in adhesive systems will continue to be made with considering health and safety aspects. Future areas for the advancement of Polyvinyl acetate adhesive systems will concentrate on increased water resistance, heat resistance, faster cure, applicability at low temperature, and based on sustainable raw material for the wood being bonded. For this review we used Scifinder as search engine to compile all the information on research trend in PVAc based wood adhesive. More researches should be carried out for adhesives along the following lines: 1) Studying the modification of polyvinyl acetate adhesives should be continued. Modified adhesives will have better properties and meet requirements under more harsh conditions like applicability at low temperatures. An important aspect will be to simplify the process of modification, reduce costs without affecting the performance properties with the help of new methods like core-shell polymerization and graft polymerization. 2) Developing natural polymer grafted adhesives. Developing environmentally friendly adhesives, low-cost, improved properties, and renewable raw materials have become increasingly essential.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Abbreviations

CMR: Carcinogenic, Mutagenic, and Reprotoxic chemicals
PVA: Polyvinyl alcohol
PVAc: Polyvinyl acetate
UF: Urea-formaldehyde resins
PF: Phenol-formaldehyde resins
MF: Melamine-formaldehyde resins
MDF: Medium-density fiberboard
PVC: Polyvinyl chloride
DH: Degree of hydrolysis
MNT: Montmorillonite
CSNs: Colloidal silica nanoparticles
DMA: Dynamic mechanical analysis
CNC: Cellulose nanocrystals
NMA: N-hydroxymethyl acrylamide
AAEM: Acetoacetoxyethyl methacrylate
Veova: Vinyl ester of versatic acid
MAA: Methacrylic acid
AA-PVA: Acetoacetyl polyvinyl alcohol
API: Aqueous polymer isocyanate
BA: Butyl acrylate