

Polyurethane Hybrid-Based Wood Adhesive: Review

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Abstract

Based on commercially available polyvinyl alcohol (PVA) stabilised polyvinyl acetate (PVAc), emulsion adhesives are neither heat nor moisture-resistant and show weak strength at high relative humidity and high temperatures. Pre- or post-crosslinking is another method used to manufacture a conventional vinyl-based homopolymers or copolymers system with improved water resistance. Vinyl neodecanoate (Veova), N-methylolacrylamide (NMA), Methacrylamide, methacrylic acid (MAA), and other self-crosslinking comonomers are typically inserted to produce highly water-resistant vinyl based homopolymers or copolymers. Additionally, organic crosslinkers like glyoxal, glutaraldehyde, citric acid, tartaric acid, and the like, as well as inorganic crosslinkers like acidic metal salts like aluminium chloride, aluminium nitrate, boric acid, and the like, can be used to prepare the highly water-resistant vinyl based homopolymers or copolymers. It is also possible to combine the self-crosslinking comonomers with the organic crosslinkers. Recently, a different hybrid chemistry has been developed that improves lap shear strength, has outstanding water resistance, good durability, and doesn't require any additional crosslinker agents. Two distinct polymers were combined to develop hybrid polymers. They usually involve mixing an organic polymer with a polymer. There are many capping agents that are used for polyurethanes to produce acrylics that are capped with polyurethane and used as an oligomer in PVAc wood glue. Here, in this paper, we reviewed the different hybrid chemistry based on polyurethane chemistry for wood bonding applications.

Keywords

Vinyl Acetate, Hybrid, Polyurethane, Wood, Adhesive

1. Introduction

Wood adhesive: Conventional system

A significant amount of production expenses are related to wood glue. The most popular types of wood adhesives are still polyurethane and polyvinyl acetate (PVAc), often known as epoxies and aliphatic resins [1]-[10]. The most popular thermoplastic polymer for use in adhesives with wood and wood-based products is water-based PVAc dispersions [11]. PVAc glue is frequently used in décor, paper goods, textiles, and carpentry [12] [13]. Dispersion stabilisers, including polyvinyl alcohol (PVA), are essential for the application, stability of the dispersion, and mechanical properties of the attached specimen in the emulsion polymerization of vinyl acetate (VAc) [14]. PVA colloid stabilised PVAc is a polymer that is made through the emulsion polymerization of VAc using free radicals [15] [16] [17]. The hydrolysis degree, polymer chain length, remarkable rheological characteristics with great wet tackiness, and porous surface compatibility of PVA can all be beneficial to wood bonding. Its many benefits as an adhesive include low cost, ease of use, practicality, and environmental friendliness. However, there are several intrinsic drawbacks to PVAc emulsions that restrict their application. PVAc homopolymer, lacking a protective colloid such as PVA, typically exhibits low stability, heat resistance, and water resistance. As a result, it is frequently altered through processes to enhance emulsion performance [18] [19] [20] [21]. As demonstrated in **Figure 1**, emulsion polymerization of VAc to PVAc requires colloid for stability and improving the mechanical characteristics of the produced adhesive [22] [23] [24] [25].

The utilisation of a low molecular weight grade of PVA as a protective colloid was found to enhance both water solubility and chain mobility. Hydrolysis degree has an impact on the colloid's water solubility. Fully hydrolyzed PVA is crystallinity, thus to dissolve it fully, and heat it to the water's boiling point. Partially hydrolyzed PVA loses crystallinity due to the presence of residual acetate groups, becoming soluble in regular water [24] [25] [26]. Research is being done on PVA modifications to improve its properties [27] [28] [29]. The main goal of PVA research has been to increase PVA's water resistance using different cross-linking techniques [30].

The disadvantages of PVA stabilised PVAc emulsion include low water resistance, mechanical resilience, heat resistance, and cold resistance. These defects directly affect its unsegregated processing and application value. To date, a great deal of research has been done on this topic, covering co-blending, co-polymerization, radiation preparation, preparation methods, and so forth [29] [31] [32] [33] [34] [35]. Unlike normal PVAc-based thermoplastic adhesives, PVAc-based moisture-tolerant adhesives are utilised in the wood and craft industries. They have a durability grade of D3 according to the EN 204-205 standard. Using Lewis acid, such as aluminium chloride, and cross-linking linear PVA chains are two popular methods used in the production of adhesives [36]. N-hydroxymethyl acrylamide (NMA), an active monomer, has been employed in several investigations to improve the chemical, mechanical, thermal, and physical properties of PVAc-based emulsion adhesives. PVAc-NMA is a cross-linkable

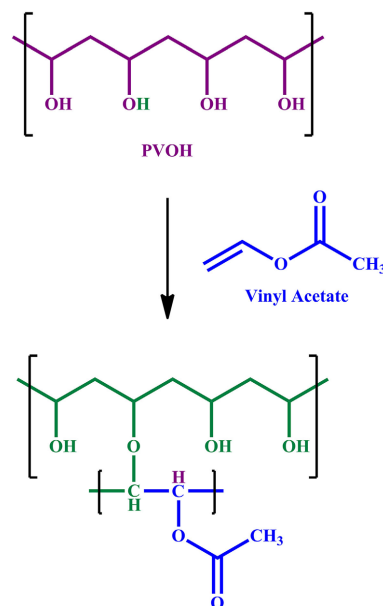


Figure 1. Polyvinyl alcohol stabilized polyvinyl acetate [23].

thermosetting co-polymer that can be formed when NMA, an amide analogue of unsaturated carboxylic acid, polymerizes with VAc. Lewis acid may cause the molecules to undergo more cross-linking and curing. According to a recent study, monitored thermosetting of PVAc emulsion was successfully achieved using an innovative polymer latex particle carrying functional groups presented via the reactive functional monomer, acetoacetoxyethyl methacrylate, which had previously been recognised for its potential to provide a cross-linking site in thermoset adhesives [29] [37]. Standard water-based D3 dispersions have an inherent cross-linking agent, unlike conventional PVAc wood glues. NMA frequently illustrates the reaction process of the cross-linking agent (as shown in **Figure 2**). Acid catalysis and heat and radiofrequency have all had an effect on the process [36]. As illustrated in **Figure 3**, the choice of this external cross-linking agent is motivated by the requirement to reduce the pH of the adhesive system while also blocking the hydrophilicity of the protective colloid [38].

2. Hybrid Adhesive

Combining two distinct polymers can result in the development of hybrid polymers. They usually involve mixing an organic or inorganic material with a polymer. For example, compounds based on epoxy resin are strong, cure quickly at ambient temperature, stick to most surfaces well, and exhibit good chemical resistance to a variety of diluted acids, alkalis, and solvents. These combinations incorporate certain properties of both components that were not achievable in a single polymer alone. By adding a polysulphide component, an epoxy resin's performance characteristics can be improved without affecting the system's current capabilities. Numerous polymers, including polyurethanes, alkyds, ACs,

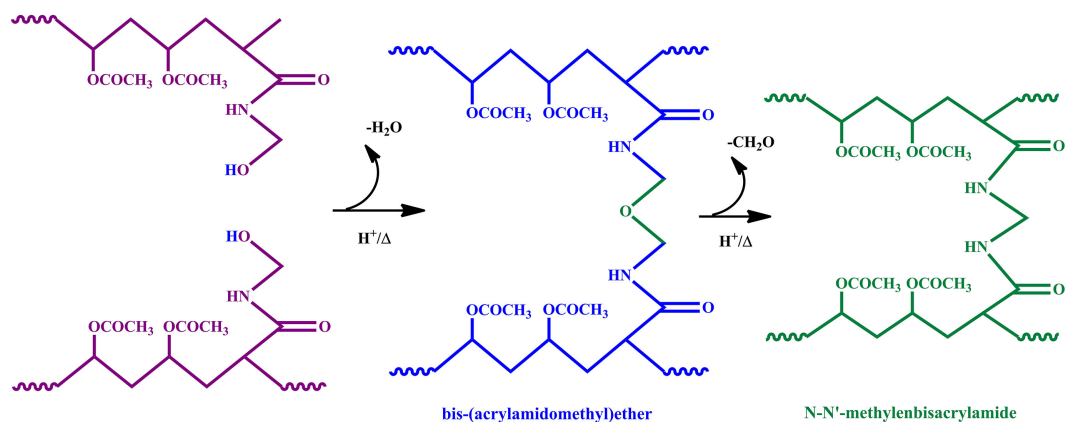


Figure 2. PVAc cross-linking in the presence of N-methylolacrylamide [36].

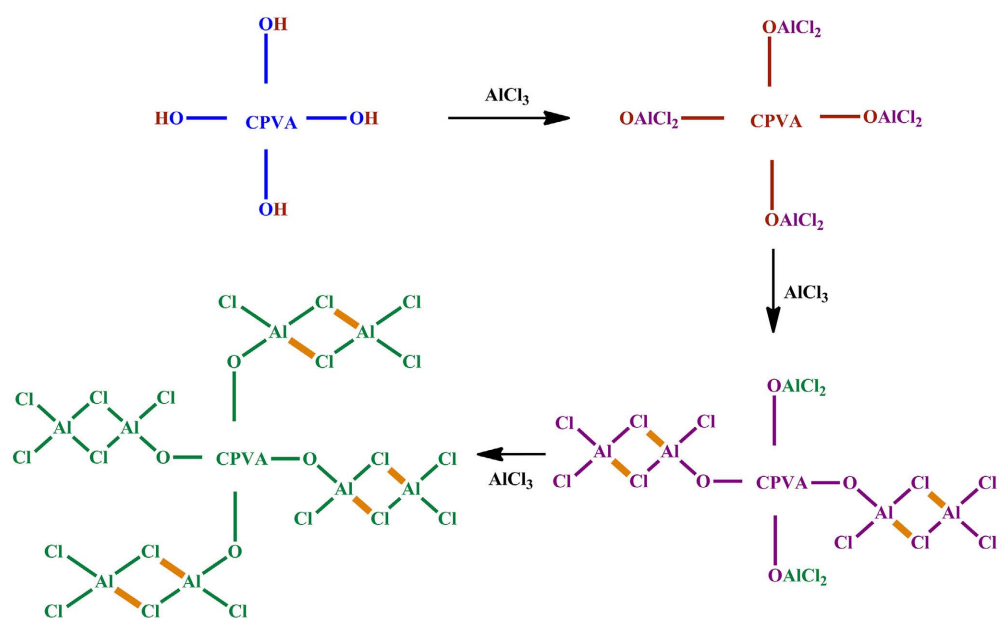


Figure 3. Mechanism of reaction of the protective colloid and the external cross-linking agent [38].

polyesters, silicones, etc., can perform better or provide desirable outcomes by hybridising these materials. Several hybrid systems have been introduced to the market as a result of the advancements in hybrid polymer technology. Aqueous polyurethane dispersions (PUD) are widely used in coatings and adhesives. Their films are very flexible, resistant to abrasion, and impact resistant at low temperatures. Although polyurethane (PU) coatings have been around for a while, new eco-friendly processes and products have been developed in response to the growing need for materials with low volatile organic content. The coatings industry uses water-borne PU synthesis quite frequently these days, even though the price of these products is typically higher than that of other goods. It is standard procedure to mix the low-cost AC component with the better chemical characteristics of PU resin in applications where funds are limited. Improving PU-AC adhesion to plastic surfaces, resilience to chemicals and solvents, abrasion resistance, and cost effectiveness are the main goals of recent advances in

this material [39]. PUD can be used to develop tinted topcoats and high gloss clear coatings. The films' remarkable mechanical properties and ideal hardness to flexibility ratio are retained at low temperatures. Polyurethane coatings also have a good scratch resistance. However, compared to pure PU-based paints, these hybrid-based paints offer a higher end gloss. After weathering, hybrid paints exhibit superior optical properties than pure AC-based paints [40]. Using a redox-initiated mini-emulsion polymerization technique, it was effective in developing nanosized PU/Polybutyl methacrylate hybrid latex particles (50 nm) with a range of compositions. Better mechanical and aesthetic qualities will be produced in films by using small-size latex particles. The PU prepolymer was treated with an intraparticle chain extension technique, which caused the PU chains to be stretched in order to raise the molecular weight of the PU and function as a "crosslinker-like" moiety by binding the pendant urethane chains together [41] [42]. Studies were done to find out how the latex characteristics were affected by various initiators, surfactants, PU-AC ratios, dimethylol propanoic acid, and other factors. Regardless of the kind of surfactant used—anionic, non-ionic, or anionic with a long chain of amphiphilic alkylphenyl polyethoxylate—particle size increased significantly in latexes prepared with 0.1% surfactant as compared to surfactant-free PU-AC latexes. Nevertheless, latexes with smaller particle sizes and a narrower particle size dispersion emerged when the amount of surfactant in the mixture increased [43]. The characteristics of PU-AC hybrid systems do not respond linearly with increasing AC content, as evidenced by the results of the synthesis of composite dispersions of water-based PU-AC physical blends. But the physical mixes' properties indicate a gradual shift from PU-AC [44]. When developing composite materials, inorganic fillers are frequently used to reinforce polymers. Recently, new opportunities for the synthesis of polymer-metal oxide hybrid materials have been made possible via sol-gel technology [45]. This article describes the production procedure for silica-polyimides hybrid materials. Tetramethoxysilane (TEOS) is hydrolyzed, polycondensed, and heated to 270°C in a polyamic acid solution. The concentration of silica in the hybrid films grew along with their density, decomposition temperature, and modulus; however, the tensile strength of the films decreased in that proportion [46]. The ethoxy-silyl group concentration of the matrix polyimide increased, causing the transparent-opaque shifting points to move to regions with higher silica levels [47] [48] [49]. The characteristics of the polyimide/silica (PI/SiO₂) hybrids and the size distribution of the silica (SiO₂) particles have been investigated in relation to the coupling agent. The compatibility between the two phases of PI/SiO₂ hybrids was greatly improved by the coupling agent γ -glycidyloxypropyltrimethoxysilane (GOTMS). The silica particle size in the PI/SiO₂ hybrids was considerably reduced using GOTMS. Consequently, the properties of the PI/SiO₂ hybrids were markedly improved [50] [51]. Less than 10% SiO₂ causes an improvement in the hybrid films' mechanical properties, which are ascribed to the development of interfacial contact and physical crosslinking. Dynamic mechanical analysis (DMA) studies revealed that the glass

transition temperature (T_g) of the hybrid materials increased by 15°C - 20°C with an increase in inorganic content [52]. For the purpose of developing epoxy-based organic/inorganic hybrid composites, silane alkoxide and bisphenol-A type epoxy resin were utilised as the organic and inorganic sources, respectively [53] [54] [55] [56]. Using hybrid systems is one way to potentially introduce the best qualities of vinyl-acrylics and alkyds into a water-based system with low volatile organic compound levels [57] [58]. An AC solution was combined with alkyd resin to develop an alkyd-AC hybrid, which finally had a 75% - 80% solids content [59] [60]. Simulating the large-strain deformation of alkyd-AC latex films using a combination of the Upper Convected Maxwell 25 model and the Gent model 26 allowed researchers to examine the evolution of the crosslinked network and its connection to the compatibilization of the alkyd and AC phases [61]. The synthesis of hybrid binders by free radical polymerization of AC monomers in the presence of an unsaturated alkyd resin was studied using an emulsion polymerization approach [62] [63]. By using a melt co-condensation reaction, an AC prepolymer with carboxylic groups and a long-oil alkyd resin were able to successfully synthesise hybrid aqueous alkyd-AC dispersions with 40% solid content without the need for an organic solvent or surfactant [64] [65].

Research on striking a balance between the advantages of PUD and AC latex's lower cost has persisted throughout the previous three decades. PUD-based coatings are widely recognised for their exceptional ability to balance water resistance, chemical resistance, hardness, flexibility, and film formation. However, as compared to coatings based on AC latex, PUD usually have greater prices and less exterior durability [66] [67] [68]. A lot of research has been done on PUD and AC latex hybrids, in which a PUD is present while the AC polymerizes [69] [70] [71]. Films of these materials are usually characterized by a PU continuous phase or interpenetrating network (IPN) of PU and AC domains [72] [73]. Particular emulsions known as waterborne polyurethanes (WPU) are utilised in a variety of industries, including membrane, artificial leather, packaging films, coatings, adhesives, and ink binders [74] [75] [76]. There is no toxicity, flammability, or environmental contamination associated with these biocompatible polymers. Moreover, these compounds' particular characteristics include excellent tensile properties, good chemical and abrasion resistance, correct rheological quality, great adherence to substrate, high flexibility, and good properties in cold temperatures [77] [78] [79]. Other polymers are added to WPU to improve performance. ACs are the most suitable option among them for this use [80]. ACs show low toughness, abrasion resistance, and adhesion, but they have strong water resistance and weather ability, hardness, low cost, chemical resistance, and gloss. As a result, the hybrid system possessed both attributes because to the PU and AC combination. Thus, the synergistic effect is possible [81]. Novel aqueous hybrid systems based on PU-AC have been synthesised in recent years. The waterborne PU-AC emulsion system can be synthesised either direct mixing or hybrid emulsion polymerization [82].

Athawale and colleagues developed physical blending and aqueous PU-AC hybrid emulsions at various weight ratios and studied their characteristics [83]. WPU are used as pressure-sensitive [84] and footwear adhesives [85]. This is due the PU backbone's addition of AC monomers increased the material's cohesive strength and shear holding duration. Lately, vegetable oils have been used for developing aqueous PU-AC hybrids [86].

3. Polyurethane Hybrid-Based Wood Adhesive

PUDs are a special kind of water-borne polymer colloids that have numerous benefits for the adhesives sector. All of these methods share the same steps for creating conventional PU, which are diols or polyols (soft segment) reacting with diisocyanates (hard segment) and then dispersed in water [87]. High molecular weight polyol components are the primary source of the soft segment, whereas isocyanates, low molecular weight diols, urethane, and urea bond sequences contribute to the hard section. PUDs have a distinct advantage over surface coatings in that they can produce a coherent film and regulate the microphase shape by varying the proportion of hard and soft segments in the polymer chain [88]. The two main techniques for combining the advantages of the two emulsions are emulsion polymerization and physical mixing [88].

The two components are incompatible, which restricts the progress of the blending system's performance even if physical blending is a workable way to create PU-AC hybrid emulsions. Emulsion polymerization, as opposed to manual blending, can be used to obtain the molecular compatibility of PU and AC. This maximises AC and PU's synergistic effects [89] [90] [91]. **Figures 4-6** illustrate the common di-isocyanate, polyol, and monomers that are used.

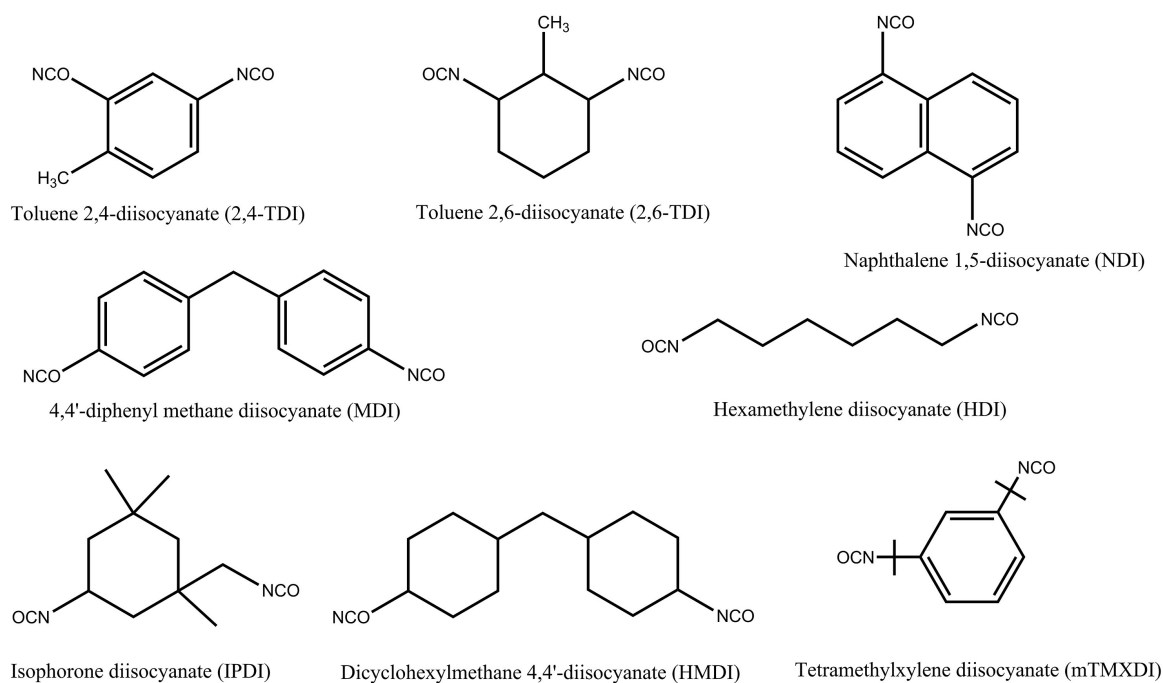
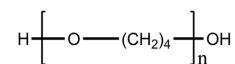


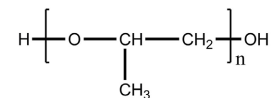
Figure 4. Di-isocyanate used in the synthesis of PU [90].

Polyether Macrodiols

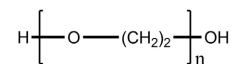
Poly(tetrahydrofurane) (PTHF) Or
Poly(tetramethylene ether) glycol (PTMEG)



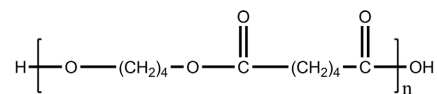
Poly(propylene) glycol (PPG) Or Poly(propylene) oxide (PPO)



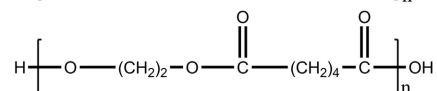
Poly(ethylene) glycol (PEG) Or Poly(ethylene) oxide (PEO)

**Polyester Macrodiols**

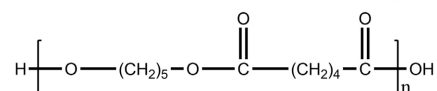
Poly(tetramethylene adiapate) (PTMA)



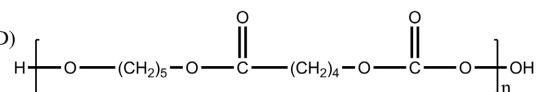
Poly(ethylene adiapate) (PEA)



Poly(caprolactone) glycol (PCL)

**Polycarbonate Macrodiol**

Poly(hexamethylene cartonate) glycol (PCD)

**Polydiene Macrodiol**

1,4- Polybutadiene diol

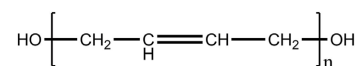


Figure 5. Polyol used in the synthesis of PU [90].

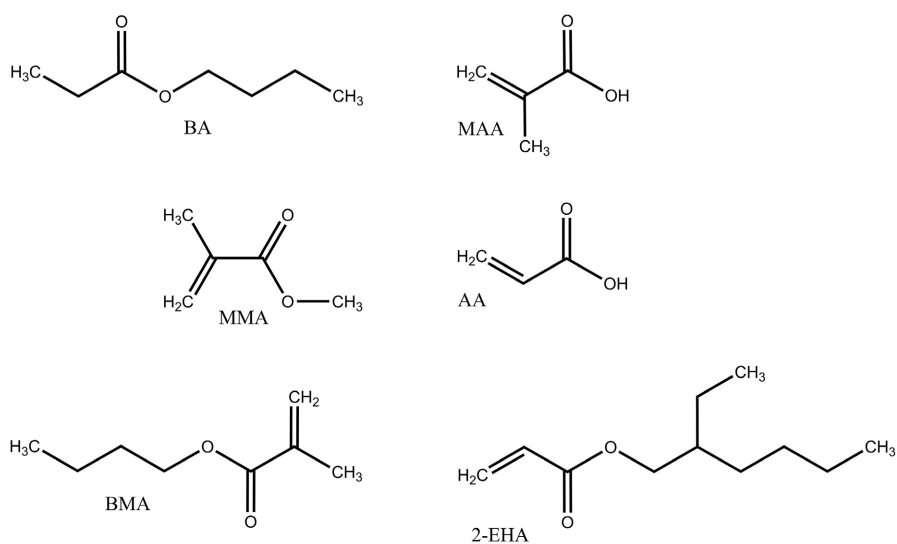


Figure 6. Monomer used to synthesis of acrylic based polyurethane dispersion.

However, their use in many industrial applications has been limited due to their relatively expensive raw material cost as compared to a standard AC emulsion. It is standard procedure to blend PUDs with other reasonably priced polymers in an effort to get around this and achieve a cost/performance balance [92]. Blending the two polymer systems physically is a common way to combine the advantageous properties of each polymer. However, because of the incompatibility of the two systems in which the various polymers are present as distinct particles, these blends frequently compromise the higher performance qualities. A more sophisticated method of achieving this equilibrium is by synthesising the PU-AC hybrid polymer [93]. AC latexes are the most significant binders in the same application because of their superior mechanical qualities, superior water resistance, and reduced cost [94]. Both anionic and non-ionic emulsifiers are usually required as critical components in their preparation, which has several detrimental consequences on their ultimate application, including emulsifier migration, changed polymer characteristics, and poor water resistance and adhesion [95]. PU-AC hybrid emulsions, which have gained a lot of interest recently, are always made by combining PU dispersions with AC latexes to provide cost/performance benefits [96] [97] [98] [99] [100]. The emulsion polymerization method that the researcher utilised to make the PUDs is described. First, the vinyl terminated PUDs were made in accordance with the previous report. Second, to make the WPU emulsion, vinyl-terminated WPU and methyl methacrylate (MMA) monomers polymerized [101]. To synthesise stable polyurethane-polystyrene (PU-PS) copolymer emulsions, azobis (isobutyronitrile), a radical initiator, and 4-((benzodithioyl)methyl) benzoic acid, a reversible addition-fragmentation chain transfer agent, were used to polymerize styrene and 2-hydroxyethyl acrylate (HEA)-capped polyurethane macromonomer [102] [103] [104] [105] [106]. According to the embodiment of the current disclosure, a preset quantity of a polyol and a predetermined quantity of a diisocyanate monomer are mixed and reacted to form capped polyurethane in a predetermined ratio. At a temperature between 90 and 100°C, this reaction occurs in the presence of a preset amount of a capping agent, a solvent that is compatible with hydroxyl termination, and optionally, a modifier and a catalyst. This adhesives has excellent mechanical, thermal properties without adding Lewis acids. In accordance with the existing disclosure, the capping agent is selected from the following: diisocyanate hydroxyethyl acrylate, hydroxyl propyl acrylate (HPA), hydroxyl butyl acrylate (BA), hydroxyl ethyl methacrylate (HEMA), hydroxyl propyl methacrylate (HPMA), and hydroxyl butyl methacrylate (HBMA) [107] [108].

One double bond and one hydroxyl group make up hydroxyalkyl ACs, which are frequently employed as coupling agents to create AC-PU terminated PU dispersion. This molecule serves as both an emulsifier and a macromonomer in the emulsion polymerization process that follows. Triethylamine is used to neutralise the carboxyl group when hydroxyalkyl ACs react with the isocyanic

(-NCO) groups of the PU prepolymer to create AC terminated PU. The PU double bond stays active after being dispersed with water, helping to copolymerize with later added AC monomers to create PU-AC hybrid emulsions by batch, semi-batch, or continuous emulsion polymerization processes [109] [110]. In the previous literature, different process parameters, such as PU and AC content, [111] the chain extender [112], polyol [113] and dimethylol propanoic acid of PU, initiator, have greatly influenced on the mechanical properties of their hybrid emulsions and resultant films [114]. Adhesives are essential items with a wide range of applications. PU-AC hybrids stand out from other polymeric adhesive types due to their exceptional adhesion, isolation, flexibility, colour stability, and resistance to ultraviolet degradation. As a result, these hybrids are used as interlayer adhesives in lamination, woodworking, construction, and shoe manufacturing. Solvent-free and emulsifier-free waterborne PU-AC hybrids were recently synthesised by Che *et al.* [115] and used for developing adhesive formulations for footwear applications [115]. Tsavalas *et al.* [116] [117] carried out mini-emulsion polymerization with a three-component AC system of MMA, BA, and acrylic acid (AA) in the presence of a Bayer Roskydal TPLS2190 unsaturated polyester resin. Synthesis and characterization of PU-AC hybrid latexes has been discussed in many technical papers [116] [117] [118] [119]. By grafting bisphenol-A-glycidyl dimethacrylate as an anchoring molecule into the PU macro-structure, an alternate way to the auto-emulsifying method is presented in this study for developing aqueous PU-AC hybrid dispersions. The PU and AC chains are encouraged to hybridise by means of a redox initiating system including hydrogen peroxide and ascorbic acid [120].

The polymerization techniques include seeded emulsion polymerization [121] or interpenetrating network (IPN) formation [122]. Hybrid emulsions based on PU and AC polymers are currently being studied. It is anticipated that these hybrid emulsions will offer the benefits of PUs, such as superior adhesion and toughness, together with the benefits of AC polymers, such as hardness, gloss, weatherability, and chemical resistance. A few research have shown that the hybridization of these two materials has advantages. There are several methods for making waterborne PU-AC hybrid emulsions [123]-[128]. To make hybrid emulsions, the most representative method is to polymerize AC monomers in the presence of a PUD. An alternative technique is the in-situ process, in which AC and PU polymerization happen simultaneously. The components that resemble IPN are transformed into PU-AC hybrid emulsions [124] [129] [130] [131] [132].

The carbon-carbon linkages in the primary polymer chain of AC polymers provide them good resistance to water, alkali, and weathering; nevertheless, they are not very elastic or abrasion resistant. Consequently, adhesive formulators have looked for ways to combine AC polymer and Waterborne polyurethanes (WPU's) benefits [133] [134] [135]. In applications where funds are few, it is customary to mix the affordable AC component with the outstanding chemical

capabilities of PU resin. The hybrids use a variety of methods, including seeded polymerization, core-shell type polymerization, and IPN formation, to combine both PU and AC polymers into a single emulsion particle with a multiphase structure [136].

4. Conclusion

Emulsion adhesives, which are based on widely available polyvinyl alcohol (PVA) stabilised polyvinyl acetate (PVAc), have weak strength at high relative humidity and high temperatures and are neither heat-nor moisture-resistant. An additional technique for producing a conventional vinyl-based homopolymer or copolymer system with enhanced water resistance is pre- or post-crosslinking. To synthesize extremely water-resistant vinyl-based homopolymers or copolymers, self-crosslinking comonomers such as vinyl neodecanoate, N-methylolacrylamide, Methacrylamide, and methacrylic acid are usually added. A new hybrid chemistry was recently developed that has excellent water resistance, good durability, enhances lap shear strength, and doesn't require extra crosslinkers. Hybrid polymers were developed by combining two different types of polymers. Typically, they involve combining a polymer with an organic polymer. For the manufacture of acrylics that are capped with polyurethane and utilized as an oligomer in PVAc glue, a variety of capping agents are utilized with PU. Interpenetrating networks (IPNs) of PU and acrylic domains were produced by hybridising PUDs and hydroxyl terminated acrylates, wherein the acrylic was polymerized in the presence of a PUD. In conclusion, an alternative hybrid chemistry has been developed that has excellent water resistance, good durability, enhanced lap shear strength, and no need for extra crosslinkers.

Conflicts of Interest

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

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Abbreviations

PVA: Polyvinyl alcohol
PVAc: Polyvinyl acetate
NMA: N-methylolacrylamide
VAc: Vinyl acetate
PUD: Polyurethane dispersions
PU: Polyurethane
PU-AC: urethane/acrylic dispersion
GOTMS: Glycidylxypropyltrimethoxysilane
T_g: Glass transition temperature
DMA: Dynamic mechanical analysis
WPU: Waterborne polyurethanes
HEA: 2-hydroxyethyl acrylate
PU-PS: Polyurethane-polystyrene
AA: Acrylic acid
IPN: Interpenetrating networks