

Starch Grafted Water Resistant Polyvinyl Acetate-Based Wood Adhesive: A Review

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Abstract

Global energy issues and the reliance on hydrocarbon resources have resulted in the reduction of petroleum sources, and the focus of the chemical industries has shifted to substitute raw material sources. The major raw materials used in wood adhesives, such as hydrocarbons like polyvinyl acetate, would be gradually replaced by renewable natural polymers. Currently, polyvinyl alcohol has the limitation of petroleum origin, which is non-economical and it will be replaced by biopolymers. Conventionally available wood adhesive emulsions are colloid-like polyvinyl alcohol stabilized. Starch, being a naturally available polymer, has gained interest from researchers for replacing polyvinyl alcohol as a stabilizer. New research on sustainable, economical, biodegradable, renewable, and environmentally friendly starch grafted polyvinyl acetate emulsion that was synthesized by the graft polymerization of vinyl acetate monomer onto starch. However, starch grafted polyvinyl acetate emulsion-based adhesive's properties, such as poor water resistance, weak adhesion, delayed drying rate and delayed setting speed, have resulted in limitations in its application as a wood adhesive. A detailed review of starch grafting on vinyl acetate and comonomers like acrylamides, and acrylic acid, and the addition of nano-fillers to enhance the water resistance and performance properties of sustainable adhesives has been explained.

Keywords

Starch, Water Resistance, Grafting, Polyvinyl Acetate, N-Methylol Acrylamide

1. Introduction

Recently, the emulsion polymerization technique has attracted adhesive industries and the adhesive market as the demand for eco-friendly and solvent-less

adhesives increased, which has the advantage of the absence of volatile organic compounds (VOC). In the carpentry and furniture segment, Polyvinyl acetate (PVAc) emulsion adhesives, which are also called white adhesives, are thermoplastics softening when the temperature is increased to a glass transition temperature and hardening again when cooled. PVAc adhesive solidifies by evaporation, absorption or penetration of water by the gluing material [1] [2]. Polyvinyl alcohol (PVA) which acts as a protective colloid for PVAc has a different degree of hydrolysis (DH) and polymer chain length, good rheological properties with high wet tack, and due to hydroxyl group, its affinity to porous substrates made them applicable in carpentry applications. Emulsion polymerization of Vinyl acetate (VAc) to PVAc needs PVA for stability and to enhance the thermomechanical properties of the prepared adhesive as shown in **Figure 1**.

In partially hydrolyzed PVA (DH = 88% - 90%), reduction in crystallinity due to the presence of acetate side groups makes it soluble in cold water [4] [5]. Modifications in PVA are done to further improve the properties of PVAc emulsion-based adhesives [6]. The white adhesive is used for assembly applications in carpentry, high-pressure lamination, wood veneer, and edge bonding as a furniture adhesive [7].

2. Need of Starch in PVAc Emulsion-Based Adhesives

Due to the increasing global energy crisis and shortage of petroleum sources, chemical industry' focus has moved their approach to new raw material resources. The main focus of raw materials in wood adhesives, such as hydrocarbon and natural gas [8] [9], would be gradually substituted by sustainable natural polymers [10] that are inexpensive [11] [12] [13]. The key raw materials of PVAc adhesive depended on non-renewable resources such as hydrocarbon and

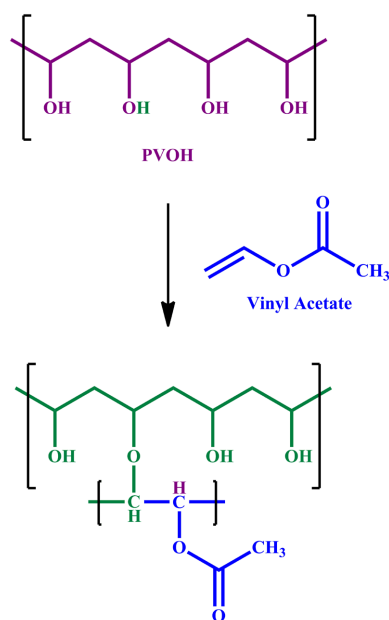


Figure 1. Vinyl acetate grafting on polyvinyl alcohol [3].

natural gas. With the aggravated global energy crisis, the key raw material used in wood adhesives is being replaced by sustainable biopolymers, such as cellulose, protein, tannin and starch [14]-[22].

Starch is a relatively inexpensive, sustainable, and renewable material from abundant plants. It is easy to be processed and has been used as adhesives, binders and pastes in various applications, but its bonding capacity is not strong enough to bond the woods [23] [24] [25]. Starch is a polysaccharide, basically polymers of the six-carbon D-glucose. Starch consists of D-glucose units, which are referred to as homoglycan or glucopyranose, and two major bio-macromolecules, amylose (strength chain) and amylopectin (branched chain) [26]-[48]. Extensive research has been carried out on improving the performance properties, especially water resistance of starch-based adhesives. In starch-based wood adhesive, many new research approaches have come forward for effective use of starch in wood adhesive and giving a comparable performance to synthetic adhesives [49]. Starch is one of the important materials in wood adhesive formulation influencing the polymerization mechanism with VAc and the performance of the end product [50]. This review paper aims to showcase the application of starch as stabilizing media for PVAc wood adhesive with improved water resistance. The starch-based adhesives are made with the focus on starch grafting on various comonomers for improving water resistance and performance properties.

3. Starch Grafted Polyvinyl Acetate Emulsions

Adhesives made of conventional materials when compared with natural polymer-based wood adhesives are usually too weak for practical use [51], so the structural strength and other performance properties of starch-based adhesive should be strengthened to achieve high-performance wood adhesive. Grafting was an important technique for modifying the physical, chemical and mechanical properties of polymers. The graft polymerization of synthetic polymers onto a natural polymer like starch backbone was one of the best ways of improving the mechanical properties of starch. There were many reports on the synthesis, characterization, and performance properties of starch graft copolymers [52]-[57]. Graft polymerization of VAc on starch was done to prepare wood adhesive which can be used and give excellent bonding performance [58] [59]. The improved properties were attributed to the modified structure of the graft-copolymerized starch-based adhesive [60] [61]. Renewable starch-based wood adhesive that could be used for wood bonding was prepared by the grafting VAc onto starch using ammonium persulfate as the initiator [62] [63]. Graft polymerization of VAc monomer on starch as shown in **Figure 2** and its usage in wood adhesives have gained interest among scientists and industries [64] [65].

Urea was often used in the starch system to bring about considerable rheology changes [67] [68] [69] [70]. Addition of urea changed the gelatinization and retrogradation characteristics of starch [71]. In aqueous suspensions, urea helps starch gelatinization and solubilization [72] [73] [74] [75]. Furthermore, urea

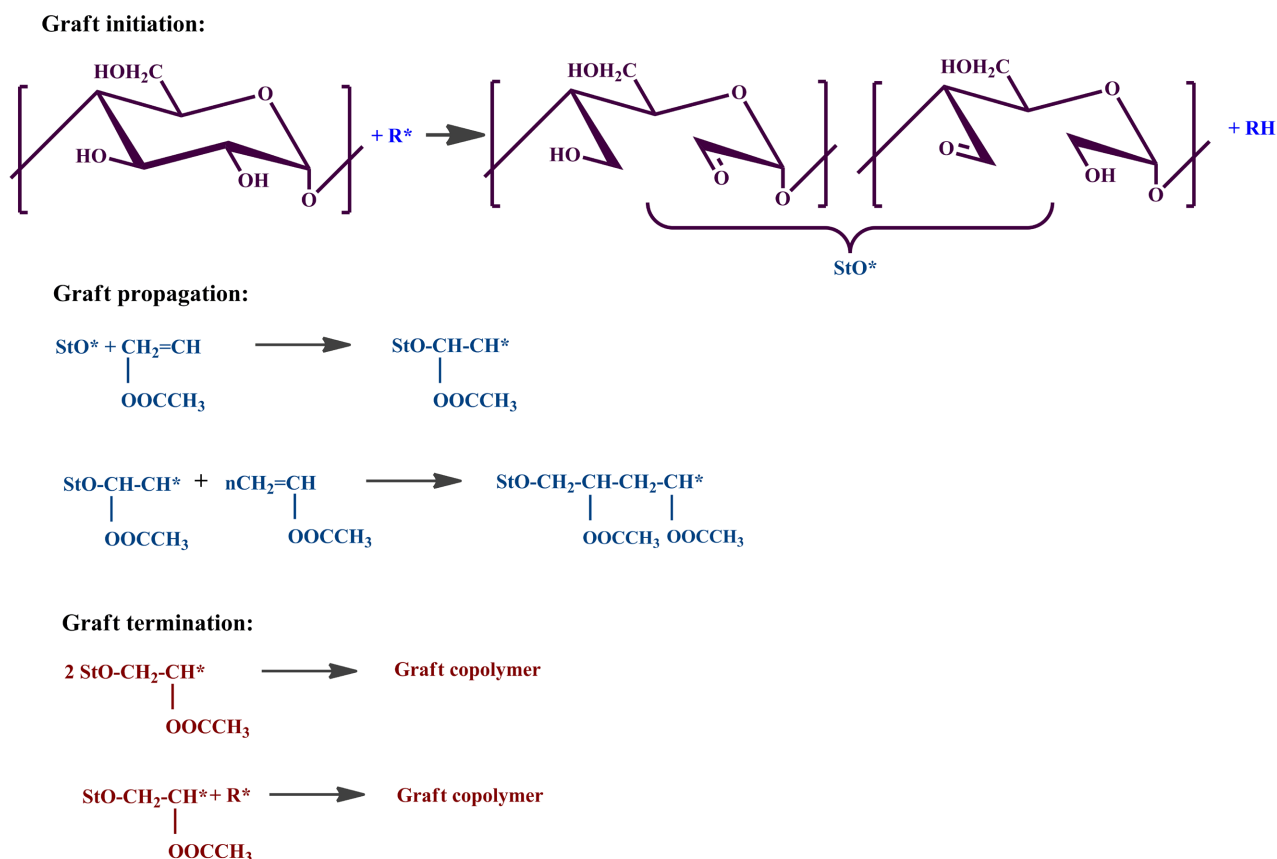


Figure 2. Vinyl acetate monomer grafting on starch [66].

could also effectively reduce the retrogradation process of starch [76] [77] [78]. Therefore, urea could likely be used to improve the freeze-thaw stability of starch grafted emulsion [79]. In some studies, before graft polymerization of VAc onto starch, sodium dodecyl sulfate (SDS) was added to improve the performance of the starch-stabilized wood adhesive. Compared with the starch-stabilized wood adhesive without SDS, both the mobility and storage stability of the adhesives were significantly enhanced by the presence of SDS [80] [81] [82]. The graft copolymerization of mixed grafting monomers VAc and butyl acrylate (BA) onto grafting skeleton of corn starch had been studied using ammonium persulfate as an initiator. Starch-stabilized adhesive prepared in emulsion synthesis have green material, superior property, and low cost [83]. According to some studies, designed and demonstrated the use of two co-monomers VAc and BA for promoting the graft copolymerization while improving the bonding performance of wood adhesive. The results showed that the properties of wood adhesive could improve dramatically by using two co-monomers [84]. For improving the performance of a cornstarch-based biobased adhesive, corn starch graft glycidyl methacrylate adhesive was prepared [85]. Graft copolymerization, which has improved the structural, physical, chemical and mechanical properties of adhesive, is considered to be one of the most effective methods employed to modify many different properties of starch-based polymers. Improvements in thermal

properties along with bonding strength were shown by graft polymerization of VAc on starch [86].

4. Water Resistance Starch-Based Emulsion

Currently, starch has been gaining increasing attention in chemical industry, due to its being abundant, inexpensive, renewable, sustainable and fully biodegradable. Consequently, it is a trend to produce a wood adhesive using starch grafted emulsion as base materials. However, starch grafted adhesive properties, such as lacking water resistance, weak bonding and delayed drying rate, are resulted in restrictions in its various application [87]. To improve the water resistance and performance of adhesive, some agents were used to enhance the adhesive strength. Addition of nanoparticles in the wood adhesive is one of the most effective ways to enhance the performance of starch-stabilized wood adhesive. Inorganic nanoparticles have unique characteristics to improve the performance of adhesive, such as small size, high surface energy and unsaturated chemical bonds on the surface. In the past year, nano-silica (SiO_2) and montmorillonite (MMT) were used to enhance the properties of adhesives [88] [89].

The wood adhesive showed significant improvement in the water resistant and bonding performance to some degree. In previous research, it is reported that the polymers with low content of nano-titanium dioxide (TiO_2) can obtain barrier, thermal and mechanical properties, showing the promising application of nano- TiO_2 in nano-composite adhesives [90]. As a kind of inorganic material, nano- TiO_2 can be dispersed into the starch grafted emulsions at a nanometric level to improve the physical and mechanical properties of wood adhesives [91] [92].

A series of starch graft polymers were prepared from commercial starch and vinyl monomers and were evaluated as adhesives. Adhesive strength of starch graft polyacrylamide copolymers containing little amount of polyacrylamide was considerably superior water resistance to the commercial starches as paper coating adhesives [93]. N-methylol acrylamide (NMA) is a water-soluble functional monomer with a condensed hydroxymethyl group. A number of studies on the emulsion polymerization of NMA with vinyl acetate or acrylate monomers have been reported [94] [95] [96]. There are also reports of NMA being used to make hydrogels. The synthesis was conducted by grafting copolymerization of VAc monomer onto corn starch and crosslinking polymerization with NMA. Compared with the traditional starch-stabilized wood adhesive, the water resistance of starch-stabilized adhesive with NMA was greatly improved [97] [98] [99]. The preparation method for water resistant adhesive comprises oxidation of corn starch by the use of sodium hypochlorite followed by co-polymerizing the oxidized corn starch with N-hydroxymethyl acrylamide and acrylic acid (AA). According to the preparation method, the NMA was adopted to replace the conventional acrylamide to copolymerize with the starch; the AA was added to provide protons for being beneficial for the starch to form the copolymer; the reac-

tion was stable; the starch grafting effect was efficient; the adhesive prepared by the preparation method was free from formaldehyde, was safer, and was good in bonding performance, and the problems such as poor water resistance of common starch adhesive were solved [100]. In one embodiment of the invention, the cross-linking monomer used NMA, N-methoxyl group Methacrylamide, N-isopropoxymethyl acrylamide, N-butoxymethyl acrylamide, N-hydroxyethyl acrylamide etc., which had copolymerized and condensed at acidic pH [101]. Synthesizing of described starch-VAc cross connect graft copolymer with starch was sustainable raw material, with N,N'-methylene-bisacrylamide was a comonomer, carried out polymerization reaction and synthetic starch-VAc cross-connect graft copolymer obtained [101] [102] [103] [104].

5. Conclusions

Conventionally, PVA's were used as a colloidal stabilizer for PVAc dispersion, but starch, which is a relatively cheaper and sustainable product obtained from large quantities of plants, is of easy processibility and can be used as a colloidal stabilizing media for PVAc emulsion. But starch adhesive exhibited poor bonding strength and water resistance preventing its use in practical applications. Urea and SDS were added to the starch so that starch could easily be grafted on VAc and other monomers to produce a graft-copolymerized emulsion. Also, nanoparticles like MMT, SiO₂ and TiO₂ were used to improve the mechanical and barrier properties of starch-stabilized wood adhesives. The properties of wood adhesive could be improved dramatically by using two co-monomers VAc and BA during the graft copolymerization reaction.

Therefore, in order to improve the water resistance and performance properties of starch-stabilized PVAc adhesive, starch grafts on vinyl acetate and comonomers like acrylamide derivatives; AA and the addition of nano-fillers improve the water resistance of sustainable adhesives. Taken together, the graft modification of starch with acrylamide derivatives, and AA and acrylic monomers can be an encouraging way to produce starch-stabilized wood adhesive with improving water resistance and good performance for wood adhesive.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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Abbreviations

VOC—Volatile Organic Compounds

PVAc—Polyvinyl Acetate

PVA—Polyvinyl Alcohol

DH—Degree of Hydrolysis

VAc—Vinyl Acetate

SDS—Sodium Dodecyl Sulfate

BA—Butyl Acrylate

MMT—Montmorillonite

NMA—N-Methylol Acrylamide

AA—Acrylic Acid