

Cellulose Stabilized Polyvinyl Acetate Emulsion: Review

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Abstract

The global energy crisis and overconsumption of non-renewable resources have depleted natural resources, climatic changes with global warming, and rise in sea level. The research on alternate sources and chemicals has resulted in the usage of green materials. These biomaterials are sustainable sources, biodegradable, and are abundant in nature. The replacement of petrochemicals with biopolymers has gained much importance in this aspect. Conventionally, polyvinyl alcohol is employed as a protective colloid in polyvinyl acetate adhesive. Polyvinyl alcohol has the limitation of petroleum origin, is replaced by biopolymers. Starch being a biopolymer, has gained interest in replacing polyvinyl alcohol as a stabilizer. Cellulose has a low cost, and the most abundant biomaterial finds application as a reinforcing agent in conventional adhesives. Exploring cellulose as a stabilizer for polyvinyl acetate emulsion polymerization with reinforcement has created potential applicability of cellulose in adhesives. Surface hydroxyl groups in cellulose act as sites for functionalization, making it material for the adhesive sector. This review paper aims to showcase biomaterials, namely starch, and cellulose, in the adhesive field. A detailed review of cellulose as functional filler for polyvinyl acetate emulsion adhesives has been explained.

Keywords

Cellulose, Nanocellulose, Polyvinyl Acetate, Wood, Adhesive, Renewable Material

1. Introduction

The adhesives industry is one of the most important applications for poly (vinyl acetate) (PVAc) emulsions, especially for wood product manufacture. It has many advantages as an adhesive, e.g., low cost, ease of use, and simplicity of ap-

plication. However, there are some inherent disadvantages of PVAc emulsions, which limit their wider usage.

Usually, the carcinogenicity of formaldehyde by its emission from conventional thermosetting resins for wood adhesives [1] [2] such as phenol-formaldehyde (PF), urea-formaldehyde (UF), and melamine-formaldehyde (MF), and considering the overexploitation of petroleum sources have accelerated scientists' in developing bio-based adhesives which are sustainable, low cost and renewable in nature [3]. Release of unreacted formaldehyde in bonded wood occurs under hot and humid conditions [4] [5]. Various biomasses have been exploited as green adhesives including cellulose [6]-[12], starch [13] [14] [15], lignin [16] [17] [18], tannin [19] [20] [21], natural rubber latex [22] [23], soy protein [24] [25] [26] and vegetable oils [27]. Researchers' acceptance of these biomaterials is due to the added advantages of renewability, eco friendliness, and very low emission of volatile organic solvents in adhesives [28] [29]. This acceptance made adhesive manufacturing industries promote green adhesives, where the low cost, easily available greener materials have been exploited even though these are in an introductory stage. Research on the partial or complete replacement of petrochemical-based raw materials in adhesives, without compensating on performance properties, provides a huge scope for commercializing bio-based adhesives [30] [31]. The importance of cellulose as a potential material to replace petrochemical-based polymer is mainly attributed to its free hydroxyls present in the cellulose structure. Moreover, being the most abundant biopolymer with biodegradability, film-forming properties, good chemical-mechanical and thermal properties, and importantly its adhesive properties can contribute to developing a better performance adhesive. Free hydroxyl groups provide the site for chemical modification which can be used for tailor-made applications [32].

1) Polyvinyl alcohol stabilized polyvinyl acetate emulsion

Water-soluble polymers have attracted coating industries and adhesive market as the demand for solvent-free adhesives increased, which have the advantage of the absence of volatile organic compounds (VOC). In this view polyvinyl alcohol (PVA) is highly important in developing organic solvent free adhesives. PVA has a controllable degree of hydrolysis (DH) and chain length, good rheological properties with high tackiness, and affinity to porous materials made them applicable in wood consolidation purposes. Moreover, the use of PVA as a protective colloid for polyvinyl acetate (PVAc) adhesives has further created a demand for its use [33]. Emulsion polymerization of vinyl acetate to PVAc needs colloid for stability and enhances the prepared adhesive's mechanical properties, as shown in **Figure 1**. The degree of hydrolysis (DH), molecular weight, and molecular weight distribution of PVA are the main factors determining the colloidal stability. The general schematic representation of the aim of this review paper is shown in **Figure 2**. Cellulose isolated from a natural source and further modifying it by various techniques and finally incorporating with PVAc can be a technique thereby the usage of conventional PVA as a stabilizing agent for PVAc can be replaced.

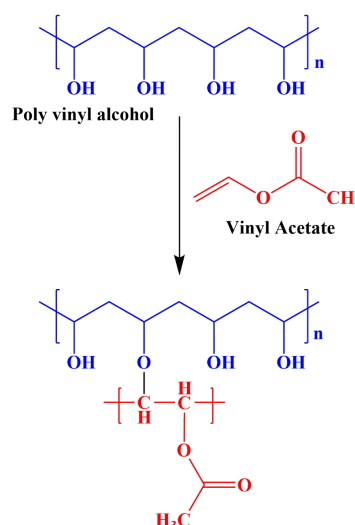


Figure 1. Stabilizing polyvinyl acetate (PVAc) with polyvinyl alcohol (PVA).

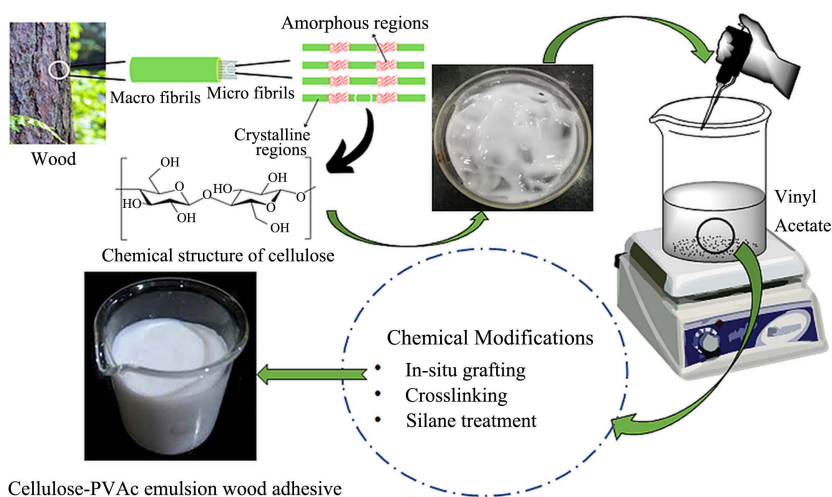


Figure 2. Schematic representation of preparing modified cellulose incorporated polyvinyl acetate (PVAc) emulsion.

Water solubility and flexibility increase when low molecular weight grade of PVA is used as protective colloid. DH affects the water solubility of the colloid because the crystallinity of fully hydrolyzed PVA needs to be heated to the boiling point of water to its complete dissolution. Whereas in partially hydrolyzed PVA, the reduction in crystallinity which is due to the presence of residual acetate groups makes it soluble in normal water [34] [35]. Modifications are done in PVA to further improving the properties [36]. Hence by tailor-making the properties, PVA act as an ideal protective colloid for PVAc emulsion-based adhesives.

However, despite all the mentioned benefits, Adding PVOH decreases adhesive water-resistance as the hydrophilic hydroxy groups are introduced into the system. Poly (vinyl acetate) is often partly hydrolyzed to form hydrophilic hydroxy groups and carboxy groups attached to the polymer backbone, usually on

the polymer branches during emulsion polymerization. This worsens the resistance to water. The third major explanation for the weak resistance to water is that several microscopic pores and water soluble surfactant molecules in the film enable water and steam to penetrate the adhesive film quickly.

2) Starch stabilized polyvinyl acetate emulsion

The scarcity and non-renewable nature of petrochemical sources with increasing concerns on global energy crisis and investigation on alternate sources have concluded by using biomaterials in the adhesive sector. Starch, the second most abundant biomaterial obtained from nature, is inexpensive and soluble in water and has many advantages. The binding property of starch can be advantageous in adhesives [37] [38] [39], paper coating applications [40], textile applications [41], etc. Starch consists of two polysaccharide parts of glucose with different shapes and structures, amylose and amylopectin. The amount of amylose and amylopectin, shape and its size depend on the origin from where the starch is obtained. Starch has both amorphous regions and crystalline regions. The hydrogen bonding between the molecules forms a crystalline region. Lowering of reactivity in starch is resulted from the inhibition of the crystalline regions. Hence, to improve the reactivity by lowering the crystalline regions, modifications are done. Heating in water results in the disruption of crystalline regions by gelatinization, starch helices connected by the hydrogen bonds gets broken, and water penetrates to this, forming a paste [37]. Chemical modification in starch [42] includes esterification, etherification, oxidation, and crosslinking [43]. The modification can also be made by physical treatments, including ultrasonic degradation, microwave treatment, heat-moisture treatment, etc. The blending of starch with PVAc opened a new dimension of possibly or completely replacing petrochemical-based polymer, including PVA [44]. Graft polymerization of vinyl acetate monomer starch as shown in **Figure 3**, and its usage in wood adhesives have gained interest among researchers and industries [41] [44] [45] [46]. Improvements in thermal stability with bonding strength and water resistance are shown by graft polymerization of vinyl acetate on corn starch [47].

2. Cellulose-Based Wood Adhesive

Cellulose is the most abundant biopolymer, and its ability to adhere makes it an ideal biomaterial for developing green adhesives and coatings [48] [49]. It is a polysaccharide with a linear chain of glucose molecules and the repeat unit consisting of two anhydroglucose rings connected by a β 1 - 4 glucosidic bond. Sources of cellulose are mainly softwood and hardwood, agricultural sources such as corn, jute, and sugarcane bagasse [50] [51] [52] [53]. From these sources, cellulose is extracted, isolated, and are then modified for a specific application. Based on extraction, treatments, it can be in micro size (micro fibrillated cellulose (MFC), microcrystalline cellulose (MCC)) [54], and nano size [55] [56] [57]. Nanocellulose, classified as nanofibers (CNF), nanowhiskers, and cellulose nanocrystals (CNC), is one among the cellulosic material with one dimension in the nano range [55]. Cellulose is widely used as a reinforcing agent in various

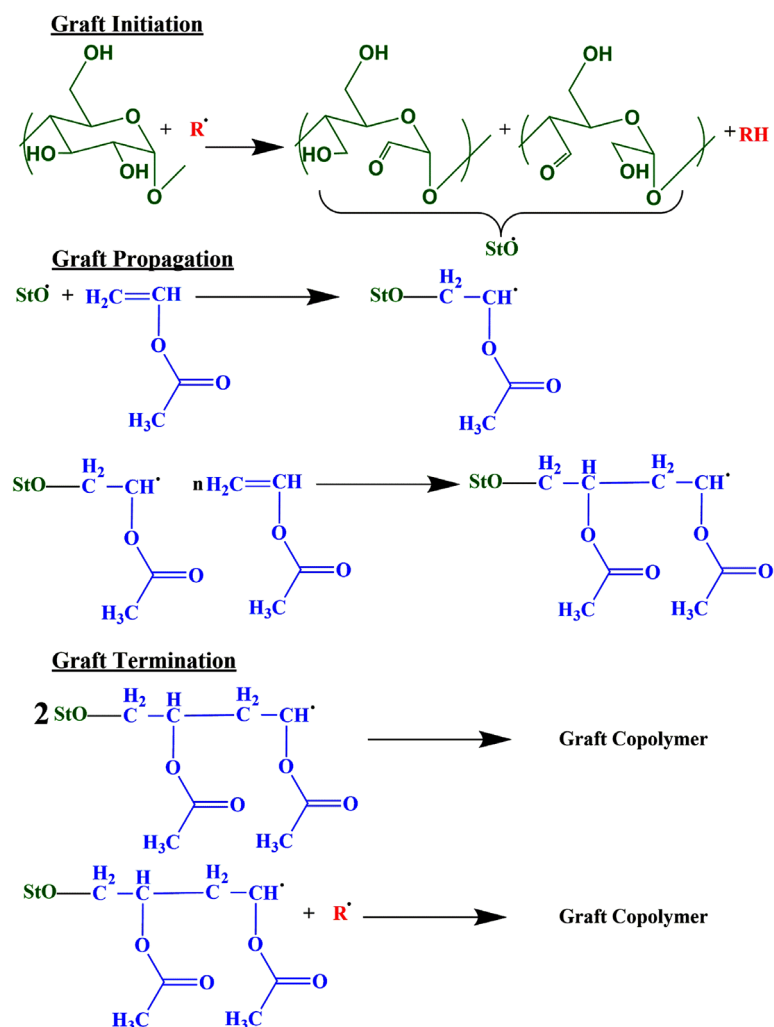


Figure 3. Mechanism of stabilized polyvinyl acetate (PVAc) using starch.

adhesive systems [58] [59] [60] [61]; **Table 1** shows works regarding the base binder with the type of cellulose used and the field of application. The hydroxyl groups of cellulose make the possibility for functionalization, and hence the binding property of nanocellulose has been enhanced [3] [48] [62]. This is because nanocellulose-monomer interactions are less repulsive since monomers are smaller than polymer chains. The initial dispersion of the final composite in this sense, is improved with less agglomeration. This is especially encouraged if the polymerization process is carried out in an aqueous medium with an aqueous distribution of nanocellulose. This is perfect since the polymerization process happens in the same medium as the nanocellulose previously spread. The nanocellulose in this process is left in the water and interacts during synthesis with the exterior surface of the polymer particle [63] [64].

The added advantage of using nanocellulose in adhesives for the consolidation of wood panels include the possibility of altering the properties of adhesives, gains in physical, mechanical, and thermal properties of panels, and reduction in formaldehyde emissions by using synthetic adhesives.

Table 1. Application of various types of cellulose used in wood joining application as adhesive.

Sr no	Base material	Type of cellulose used	Application	Reference
1	Poly(Vinyl Acetate) and Starch Adhesive	Cellulose Nanofibrils	Wood Joining	[65]
2	Urea-Formaldehyde-Adhesive	Cellulose Nanofibrils	Wood Adhesive	[59]
3	Urea-Formaldehyde and Melamine-Urea-Formaldehyde	Cellulose Nanofibers	Particle Boards and Oriented Strand Boards	[7]
4	Poly(Vinyl Acetate)	Cellulose Nanofibrils	Adhesives for Wood Bonding	[66]
5	Poly(Vinyl Acetate)	Nano Crystalline Cellulose	Wood Adhesive	[67]
6	Tannin Adhesives	Cellulose Nanofibers	Wood Adhesives	[68]
7	Urea-Formaldehyde Resin Adhesive	Modified Nanocrystalline Cellulose	Wood Adhesive	[69]
8	Polyethylene Glycol	Cellulose Nano-Whiskers	Plywood Bonding	[70]
9	Wood Flour	Cellulose Nanofiber	Binder in Wood Flour Board	[71]
10	Wood Flour	Ligno-Cellulose Nanofibers	Wood Flour Board	[72]
11	Urea-Formaldehyde	Micro fibrillated Cellulose	Laminated Veneer Lumbers	[73]
12	Sweetgum (Liquidambar Styraciflua) & Southern Pine (Pinus Spp.)	Micro Crystalline Cellulose	Particle Board	[74]
13	Wood Particles (80:20 Softwood: Hardwood)	Cellulose Nanofibrils	Particleboard	[75]
14	Adhesive-Free Fiber-Board	Ligno Cellulose Nanofibrils	Adhesive for Medium Density Fiberboard	[76]
15	Southern Pine Wood Particles	Cellulose Nanofibrils	Binder for Particleboard	[77]
16	Cottonseed Protein	Cellulose Nanofibers and Cellulose Nanocrystals	Wood Adhesive	[78]
17	Urea-Formaldehyde	Micro Fibrillated Cellulose	Particle Board	[10]
18	Zein and Gluten Adhesive	Cellulose Nanofibers	Plywood Bonding	[79]
19	Dialdehyde Cellulose	Dialdehyde Cellulose	Wood Adhesive	[80]
20	Urea-Formaldehyde	Micro Fibrillated Cellulose	Wood Adhesive	[81]
21	Polymeric Diphenylmethane Diisocyanate (pMDI)	Ligno-Ellulose Nanofibrils	Wood Adhesive	[82]
22	Poly Vinyl Alcohol	Micro Crystalline Cellulose	Wood Adhesive	[83]

3. Cellulose Stabilized Polyvinyl Acetate Emulsion

Polyvinyl acetate (PVAc) based adhesives are mainly used in wood bonding applications due to the binding property with room temperature curing, low toxicity, chemical resistance, and biodegradability. Because of poor performance towards elevated temperatures and humid conditions limits the usage where there is a need for high performance at these conditions. Researchers have put forward two approaches to improve the performance of PVAc: 1) vinyl acetate copolymerized with monomers that are hydrophobic [84], and 2) PVAc blended with hardeners, additives, or adhesives [85] [86] [87] [88]. PVAc has the advantage of organic solvent-free adhesive with ease of processing. At the same time, the ad-

dition of nano cellulose improves shear strength with the reduction in the size of the acrylic microsphere for pressure-sensitive adhesives [89]. Increasing content of CNF in PVAc matrix showed reinforcing effect [66] [90]. *Geng et al.* conducted a study in which incorporation of CNC to the crosslinked PVAc matrix by sodium tetraborate (borax) and in-situ polymerization of vinyl acetate in the presence of CNCs. Observation relating the crosslinking reaction observed to be tuned by pH rather than borax amount. Covalent grafting of polymers via controlled polymerizations represents another alternative route for surface modification of cellulose. Cellulose nanocrystals were successfully grafted by reversible addition-fragmentation chain transfer and macromolecular design via the interchange of xanthates polymerization (SI-RAFT/MADIX) of vinyl acetate (VAc) in a controlled manner [91]. The schematic representation of xanthates polymerization (SI-RAFT/MADIX) of vinyl acetate (VAc) is represented in **Figure 4**.

The in-situ nanocomposite with 10 wt% of CNC showed higher strength and storage modulus from thermo-mechanical analysis, and work opened the possibilities for using this material and method for green packaging and coating material applications. *Kaboarani et al.* observed enhancement of performance property when nanocrystalline cellulose was added to PVAc as wood adhesive [92]. With proper dispersion of nanocrystalline cellulose in the PVAc matrix, shear strength, hardness, modulus of elasticity, thermal stability and creep properties were significantly improved. The improvement of bonding strength evidenced enhancement in performance property at dry and wet conditions and the elevated temperature (100°C). *Chaabouni et al.* investigated the effects of the addition of CNFs on the properties of waterborne PVAc adhesive [93]. An increase

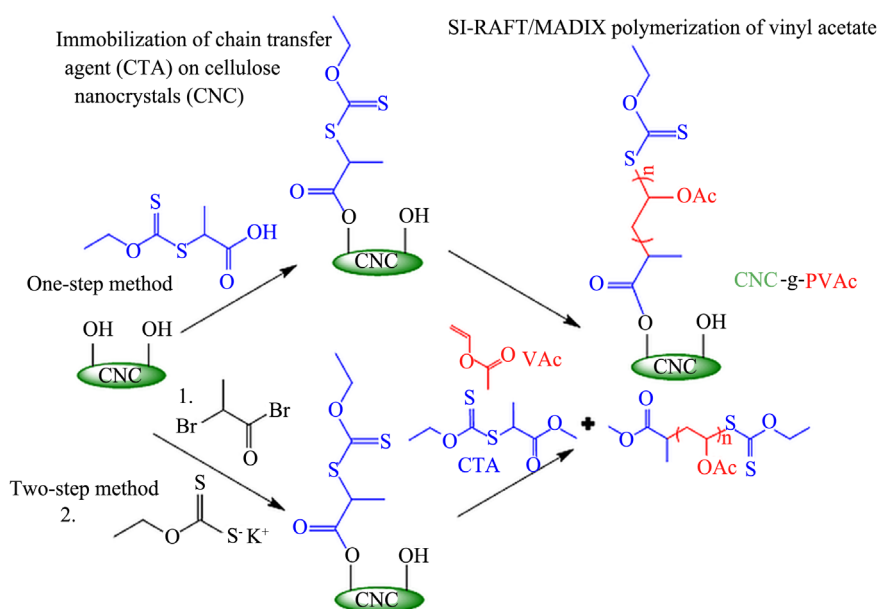


Figure 4. Schematic representation of xanthates polymerization (SI-RAFT/MADIX) of vinyl acetate (VAc) on cellulose nanocrystals (CNC).

in viscosity was observed as the concentration of CNF increased from 0 to 10 wt% while the solid content remains almost constant. Dynamic mechanical analysis (DMA) showed the reinforcing effect by CNF with the enhancement of shear strength and better cohesion of the adhesive. Improvement was shown in tensile strength, and tensile modulus of CNF filled PVAc films. A decrease in water absorption at high temperature (70°C) by increasing concentration of CNF confirmed the efficiency of bonding between the filler and matrix showed good interfacial adhesion due to hydrogen bonding. A study investigated the effect of the addition of cellulose nanofibrils and nano clay on PVAc adhesive [94]. Thermal characteristics were studied, showing enhancements on incorporating fillers. Lap joint shear strength of the adhesive increased as on addition of both the filler. Morphological studies were done with scanning electron microscopy (SEM) and observed clumps for 1 wt%, 2 wt%, and 4 wt%. Loadings for CNFs and nano clay fillers.

In the presence of CNC, a persulfate/metabisulfite initiator was employed for in-situ emulsion polymerization of vinyl acetate without any surfactant [95]. Polyethylene glycol methacrylate (MPEG) was employed as a co-monomer and helped in the stabilization by attachment of CNC into the polymer. In the presence of MPEG, a higher reinforcing effect of CNC was observed, and films showed better transparency when the dispersion produced is in-situ, which showed potential applicability in coating and adhesives. The presence of CNC improved the shear strength of the wood joint bond, and better values were shown in the dispersion when 5% MPEG was present.

4. Conclusions

Biomaterials are among the most studied materials by the scientific world due to their renewability, non-toxicity and biodegradability. Functionalization and its ability to alter the properties have made them compete against conventional petrochemicals and hence expanded the research targeted for specific applications. PVA was initially used to stabilize PVAc emulsions. Starch provides an option to replace PVA for stabilizing PVAc. Like the structure of starch, cellulose is a member of the polysaccharide family; it is also expected to function in the same manner. Cellulose has inherent binding properties but is too weak to bond the substrates. One way to improve is by incorporation in commercial adhesives, which the researchers establish. By this method, reinforcing effects are observed and lowers the VOC emission by replacing the usage of petrochemical additives. Hence cellulose is a potential material in adhesive industry with the added advantage of renewability and biodegradability.

On the other hand, PVAc adhesives have good bonding strength, high tack, and have the advantage of formaldehyde-free and water solubility. Reinforcement of cellulose in PVAc adhesives with improvements in bonding strength and thermo-mechanical properties, and decreased water absorption have been established in the literature. Various researchers have reported the advantage of

incorporating cellulose stabilizing the emulsion polymerization and in-situ emulsion polymerization of PVAc adhesives. Even though research and developments on cellulose-based adhesive are in their infancy, the works reported till now show the biomaterial cellulose has its applicability both as a reinforcing agent and a functional additive. Crosslinking is one such approach that can modify the cellulose as functional filler, enhancing the colloidal stability of PVAc emulsions and reduce the phase separation with filler and matrix. Hence by modifications, cellulose can be a material for stabilizing polyvinyl acetate emulsion.

5. Futuristic Development

The literature review established that cellulose's addition to adhesive matrix has a reinforcing effect, enhanced binding, and performance properties. The presence of hydroxyl groups provides an ideal site for functionalization, which can be an area of further research. The similarity in structure of starch and cellulose, both being polysaccharides, enables to study of the modifications in a similar way. Similar to the development of starch stabilization in PVAc, cellulose can also be employed in which research has been at the infant stage. Crosslinking can be one such way to enhance the colloidal stability of PVAc emulsions. Hence, to enhance the degree of grafting and reduce water susceptibility, cellulose will be modified, and further research will be carried.

Conflicts of Interest

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

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