

Silane Modification of Starch-Based Wood Adhesive: Review

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Abstract

Currently there has been a growing interest in substituting traditional synthetic polymers with biobased renewable polymers for adhesive applications. However, biobased renewable polymers such as starch suffer from few draw-backs like poor water resistance and mechanical strength. To become important potential alternatives of synthetic polymers, starch must have comparable physical, chemical, thermal and mechanical properties to that of synthetic polymers. To achieve this, starch has been modified by a series of crosslinkers like boric acid, citric acid, glyoxal, glutaraldehyde, etc. and silane modification. Silane modification by chloropropyl trimethoxysilane, γ -Methacryloxypropyl trimethoxy silane and vinyl trimethoxy silane is a suitable method to improve the performance in terms of mechanical and thermally. Silane forms covalent bonds with starch during starch modification resulted in enhanced shear strength and storage stability. A new research on biodegradable, renewable, environmentally friendly silane modification of starch-based wood adhesive that was prepared by reacting with various silanes. This paper, we reviewed silane as a modifying agent for starch-based wood adhesive.

Keywords

Starch, Silane, Wood, Adhesive, Coupling Agents

1. Introduction

Polyvinyl acetate (PVAc) emulsions are commonly used in bonding porous materials at room temperature. PVAc emulsions are prepared by free radical polymerizing vinyl acetate (VAc) monomers in the presence of polyvinyl alcohol as a protective colloid. PVAc adhesive manufacturing is depended on vinyl acetate

monomer which will get from petroleum resources. The effective use of renewable cellulosic polymers as wood adhesive, which has been shown to have some, promising properties comparable to traditionally used synthetic polymers can successfully reduce the use of petroleum resources [1]-[8]. With the development of wood-based composites, wood adhesives play a significant role in furniture, construction and building industries [9]. However, most of the wood adhesives are produced from petroleum resources such as urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde that cannot be sustained in the long run. Moreover, In the process of the production and application, a large amount of formaldehyde will be released leading to environmental pollution and harm to public health [10]-[15]. Therefore, it is very important to develop non-toxic and environmentally friendly wood adhesives based on renewable resources in future research [16]. At present, several renewable biopolymers, such as soybean protein, natural tannin and starch [17] [18] [19] [20], had been used to prepare environment-friendly wood adhesives.

Starch has many diverse applications in food production and other industries [21]. Chemically modified starches extend the range of physical properties available for various uses, because they exhibit excellent physicochemical properties that are markedly altered from those of their parent starches [22] [23]. Starches have been widely used in the adhesives industry, but their bonding capacity is insufficient for gluing wood. Never the less, these starch-based wood adhesives still lack the high bonding strength and water resistance. The molecular structure of starch adhesives must be strengthened to develop high-performance wood adhesive [24].

Starch oxidation, an alternative method for improving starch properties, is widely used in the industry. Oxidation is a chemical modification in which carboxyl and carbonyl functional groups can be introduced into the starch chains. At a suitable temperature and pH, starch can react with several oxidizing reagents [25] [26] [27] to form oxidized starch. Oxidized starch prepared from hydrogen peroxide has been of particular research interest [28] [29]. Hydroxyl groups, primarily at the C-2, C-3, and C-6 positions, are transformed into carbonyl or carboxyl groups via oxidation [30] [31]. However, the carbonyl and carboxyl groups exhibit high-activity, easily participating in various reactions, such as cross-linking [33]. Hydrogen peroxide decomposes into hydrogen ions and water, making it an environmentally friendly oxidizing reagent. The oxidized starch adhesive exhibited low bonding strength and water resistance preventing its use in practical applications. Therefore, in order to improve the performance of starch adhesives, sodium dodecyl sulfate [32], urea [33], however, during the last few decades, environmental friendly natural polymers have attracted greater attention all over the world due to the increasing environmental awareness as well as the depletion of petroleum-based resources [34] [35] [36]. Due to their inherent properties such as renewable nature, biodegradability, economic, easy availability, natural polymers are emerging as viable alternatives

to traditional petroleum-based materials [37] [38] [39].

The bonding strength and thermal properties of the starch-based adhesive have improved significantly, confirming the positive effect of adding the silane coupling agent and olefin monomer to the adhesive system. Silane coupling agent is commonly used to strengthen the interfacial interaction between starch hydroxyl groups. For the adhesive, organo-silanes can combine with starch to form a very thin coat, and the C-Si-O connects with the hydrogen bonding on the surface of the wood. In this paper, we reviewed modification of starch by silane to improve performance properties of starch-based adhesive.

2. Silane Modification of Starch-Based Adhesive

Silane coupling agent was added to the starch to produce a silane modified wood adhesive [40] [41] [42] as shown in **Figure 1**. The bonding strength and water resistance of the adhesive had improved significantly, confirming the positive effect of adding the silane coupling agent to the adhesive system [43] [44].

Cellulose fibers exhibit the potential to replace traditional synthetic fibers as reinforcement in the production of cellulose-fiber-reinforced green composites [45]-[51]. However, the hydrophilic nature of these cellulosic fibers limits their applications as it results in poor chemical as well as moisture absorption resistance. In the case of poly lactic acid (PLA) and silane treated starch blends, they were widely reported but mainly focused on the changes in mechanical and thermal properties [52] [53]. In the first step, a systematic study of coupling reaction between organo functional silane coupling agents and starch to clarify the optimal type of silane was carried out. In the second step, the use of the obtained starch coupling with silane for the reactive blend with PLA was shown as in **Figure 2**.

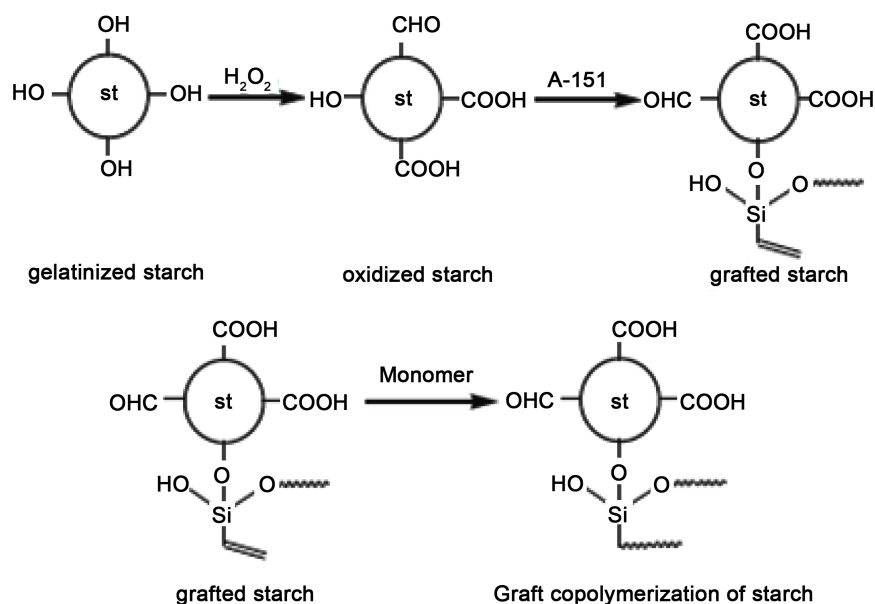


Figure 1. Silane modification of monomer grafted starch [2].

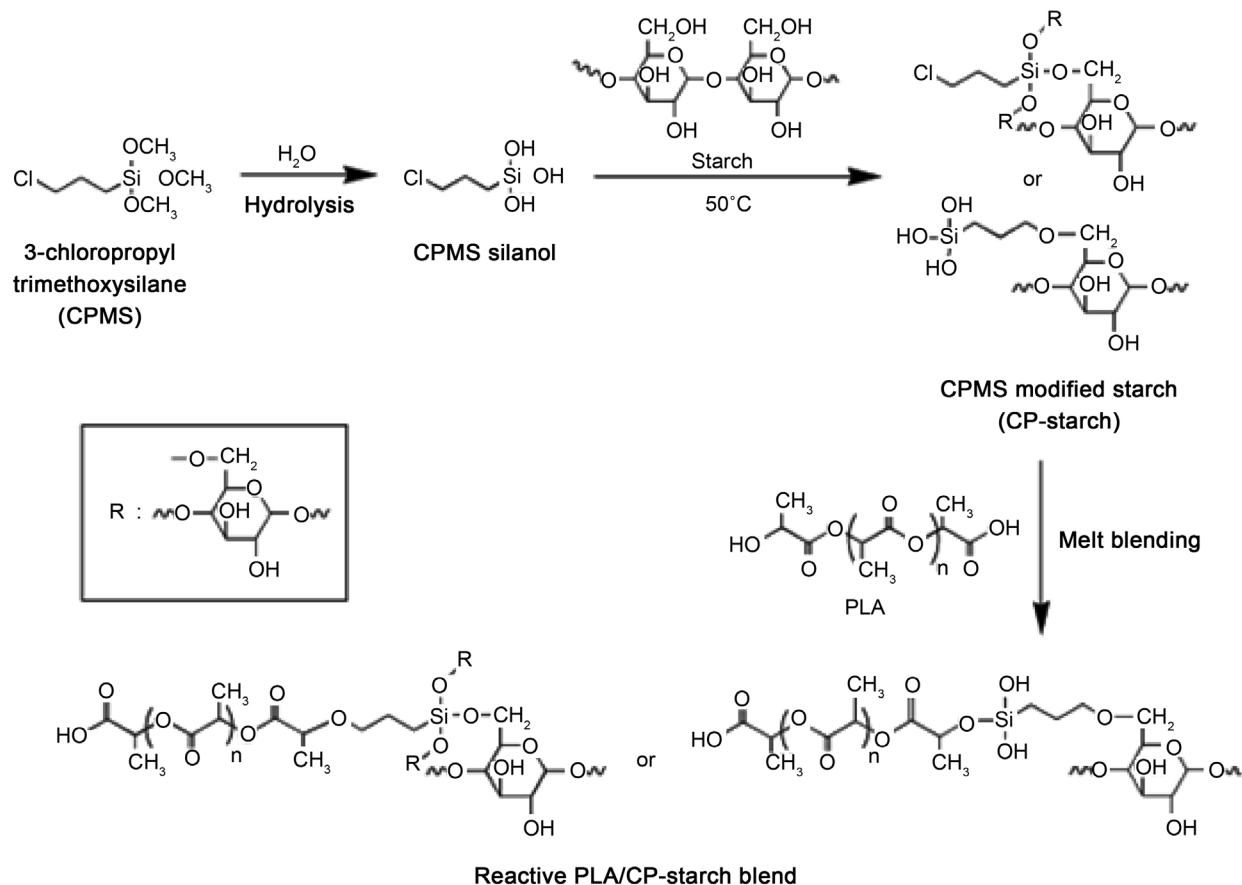


Figure 2. Starch coupling reaction with silane [54].

Starch-based wood adhesive prepared by grafting vinyl acetate onto the starch backbone shows better properties [55]. In addition, silane coupling agent was also used to produce the oxidized starch graft copolymerized wood adhesive with high bonding strength and water resistance [43] [56] and reinforced soy protein adhesive [57]. For the adhesive, organo-silanes can combine with starch or VAc to form a very thin coat, and the C-Si-O-connects with the hydrogen bonding in the surface of wood [58]. Silane coupling agents from the initial research are generally addition for the thermosetting resins, fillers and substrates to improve the dispersion forces and flow behavior [59]. However, KH570 is one of the most commonly used coupling agent with a better reactivity for vinyl acetate, and the acyloxy groups in KH570 as a coupling agent to prepare starch-based wood adhesives and investigated the improvements such as bonding strength, stability, structures and morphologies using different analytical techniques.

The alkoxy silanes have been demonstrated to be able to directly react with -Si-OH groups of silica thereby forming -Si-O-Si- bonds without any requirement of pre-hydrolysis. However, silanes do not undergo the same reaction with the hydroxyl groups of starch/PVA even at high temperature. This has been attributed to lower acidity of starch/PVA hydroxyl groups compared with silanol.

In addition, starch/PVA is generally un-reactive to many chemicals and the OH groups have very low accessibility [19]. Based on the fact, an optional strategy is to activate the alkoxy silane by hydrolyzing the alkoxy groups off thereby forming the more reactive silanol groups. As a result, the silanol may react with the hydroxyl groups of fibers or condense themselves on the surfaces of fibers and/or in the cell walls forming macromolecular network **Figure 3**.

3. Conclusion

High water resistance and bonding strength of starch-based wood adhesive can

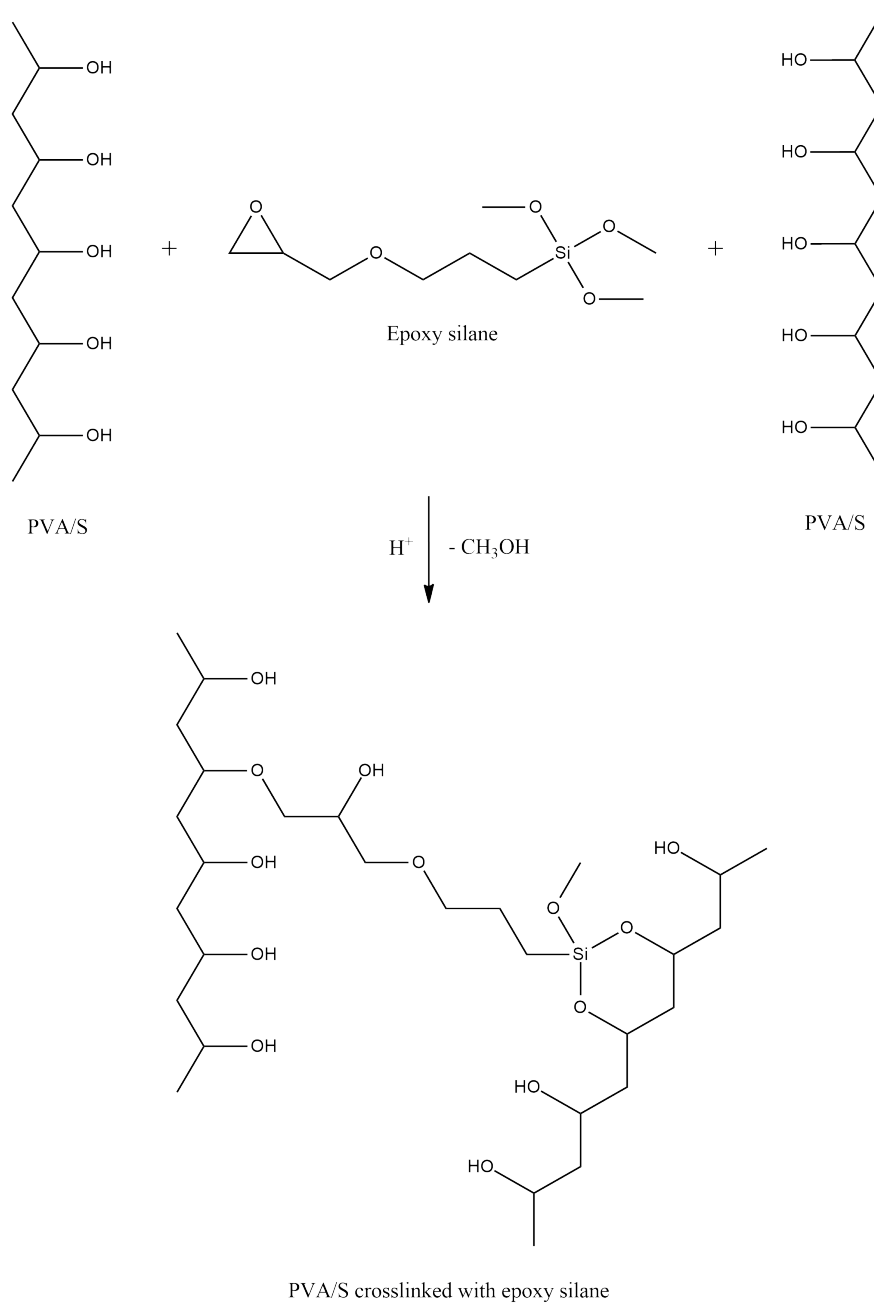


Figure 3. PVA/S crosslinked with epoxy silane [60].

be synthesized via the copolymerization of starch with a coupling agent and monomer. The improvement in the properties of the starch-based wood adhesive with the addition of the coupling agent was supported by its better compatibility and more covalent bonds formation that resulted in enhanced thermal stability and increased bonding strength. The cross-linking reaction had resulted in the formation of covalent bonds between the silanol bonds and hydroxy groups. The organic end of coupling agent reacted with starch, and another end was used for grafting and forming chemical bonds across the wood interface to enhance the bonding strength.

Conflicts of Interest

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

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