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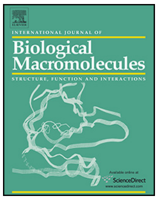

Effects of different durations of acid hydrolysis on the properties of starch-based wood adhesive

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ABSTRACT

In this study, the effect of different durations of acid hydrolysis on the improvement of the properties of starch-based wood adhesive was investigated through a variety of determination methods The improved properties were analyzed using the pasting properties, viscosity, shear performance in dry and wet states, fourier infrared spectrometer, dynamic time sweep, and low filed nuclear magnetic resonance spectroscopy. Starch hydrolysis improved the viscosity stability, bonding performance, and water resistance of the starch-based wood adhesive.

1. Introduction

Starch is the product of green plant photosynthesis and the main form of carbohydrate storage. Compared with petroleum chemical raw materials, starch is a low-cost renewable and biodegradable material that does not contribute to pollution. As a biodegradable polymer, starch has potential as a renewable resource for various material applications [1]. The natural state of starch provides its good film-forming and adhesive properties. Some studies showed different ways to synthesize starch-based adhesives using starch as the main raw material. Tannic acid and hexamine were added to corn starch to produce the starch adhesive [2]. However, this process did not change the structure of the corn starch, and thus, the adhesive has poor storage stability. The retrogradation limits the use of starch for the production of wood adhesives [3]. Modifying the hydroxyl groups on the starch is necessary to improve the stability of the adhesive [4].

Most domestic and foreign studies focused on the moderate degeneration of starch molecules. Sandip extracted amylase from potato starch [5]; Schwenke oxidized the starch [6]; Lanthong denatured the starch through acid hydrolysis, oxidation, crosslinking, and graft copolymerization [7]. Acid hydrolysis is one of the common modification methods. Hydrolysis of starch is involved in many biological and industrial processes [8]. Studies on acid hydrolysis are conducted to modify native starches and create products for their application in food, paper, textile, and other industries [9]. Omojola found that hydrolysis reaction presented important changes in the pasting, thermal transition and morphology of the native starch which is consistent with other modified starches that have found useful applications in pharmaceutical, food and confectionary industries [10]. The acid treatment was efficient in producing a potential fat substitute from pinhão starch variety [11]. Acid hydrolysis would also affects the amylose content of the starch, and the amylose content has significant effects on the structural and functional properties of starch [12]. Furthermore, acid-hydrolysis destroyed hydrogen bond between starch molecules and changed the crystalline of starch [13]. This would provide more chances for starch molecules to react with grafting monomers. However, excess acid hydrolysis damages granular structure [14], which is unfavorable to the adhesive system. In our study, we also found acid hydrolysis had an impact on properties of the adhesive. To sum up, acid hydrolysis may be an important step to obtain starch-based wood adhesive with good quality. However, few studies focused on the effects of acid hydrolysis on starch-based adhesives.

In the current study, different durations of acid hydrolysis were used to investigate the effects of acid hydrolysis on starch adhesives. Apparent viscosity, bonding strength, water resistance, and pasting properties were tested to confirm the positive effects of acid

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hydrolysis on the starch-based wood adhesive. Structural properties such as FTIR and LF-NMR were analyzed to show the interaction of the hydrolyzed starch and grafting monomers. In addition, rheological properties were examined to support the improvement effect of acid hydrolysis. Finally, we selected the suitable acid hydrolysis time for synthesizing stable starch-based wood adhesives.

2. Materials and methods

2.1. Materials

Ordinary corn starch, vinyl acetate (VAc), ammonium persulfate (APS), sodium bicarbonate ($NaHCO_3$), sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH), acetone, and hydrochloric acid (HCl) were provided by Wuhan Jinruicheng Co. (China). The chemical agents were of analytical grade and used without further purification.

2.2. Synthesis of the acid-hydrolyzed starch

The acid-hydrolyzed starch was prepared as follows. Approximately 50 g ordinary corn starch and 120 mL of HCl (0.5 M) were dissolved in a four-necked round-bottom flask and stirred at 60 °C for different durations (0, 0.5, 1, 1.5, 2, 2.5, and 3 h). The pH of the mixture was adjusted to 6.0–7.0 with NaOH, and the mixture was placed into 4 centrifugal tubes for centrifuging. The solid starch samples were mixed with 300 mL of deionized water for centrifuging. The acid-hydrolyzed starch was washed, centrifuged, and suction-filtrated until the supernatant does not produce precipitation with $AgNO_3$. Finally, these samples were freeze-dried.

2.3. Synthesis of the starch-based wood adhesive

The starch-based wood adhesive was prepared as follows. About 50 g ordinary corn starch and 120 mL of HCl (0.5 M) were dissolved in a four-necked round-bottom flask and stirred at 60 °C for different durations (0, 0.5, 1, 1.5, 2, 2.5, and 3 h). The pH of the mixture was adjusted to 4.0 with NaOH. Briefly, 2 g SDS and 60 mL of PVA were added into the mixture. After 20 min of stirring, 0.3 g APS was drop-wise added into the flask over a period of 10 min; the temperature was increased to 70 °C. Briefly, 50 mL of VAc was drop-wise added into the mixture at a speed of 3–3.5 s per drop. This step was conducted for about 2.5 h. After polymerization, the temperature was maintained at 70 °C for 30 min, then increased to 85 °C for 30 min, and finally cooled down to 50 °C. Afterward, 10 g urea was added into the flask. $NaHCO_3$ was added to adjust the pH to 6.0.

2.4. Synthesis of copolymer

The grafted samples (prepared following the above process) were precipitated with ethanol and washed with distilled water. These samples were then freeze-dried after centrifuging to obtain solid grafted starch samples. These solids were extracted with acetone in the Soxhlet extraction device at 70 °C for 48 h to remove the homopolymers of VAc. Finally, the products were freeze-dried until a constant weight was achieved.

2.5. Determination of pasting properties using the RVA

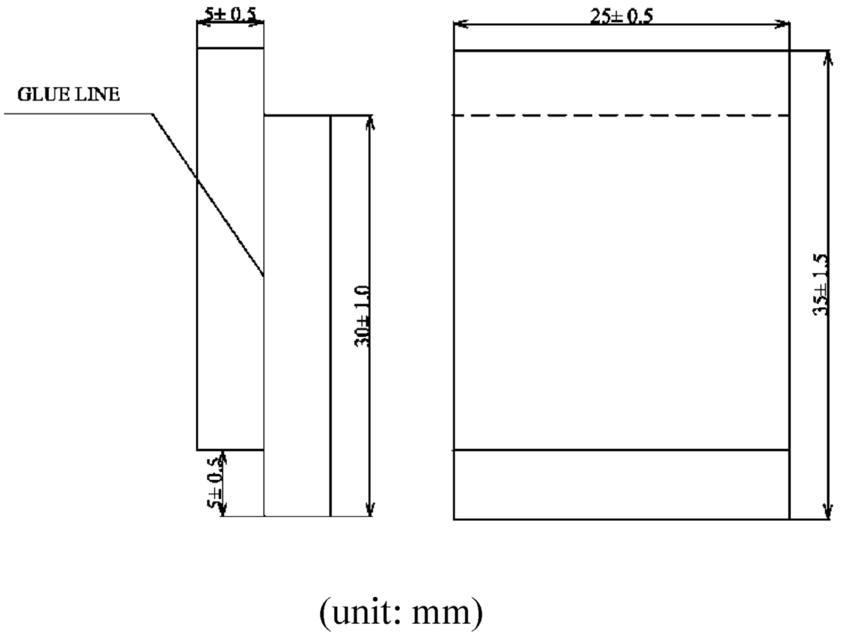
The RVA parameters were calculated using the RVA-4 (Newport Scientific Pvt. Ltd., Australia). The method standard 2 was used according to the American Association of Cereal Chemistry. Distilled water was added to all samples to prepare a 6% suspension (on a dry weight basis, w/w). Each sample was maintained at 50 °C for 1 min and then heated to 95 °C at 6 °C/min for 5 min. Finally, each sample was cooled to 50 °C at 6 °C/min for 2 min.

2.6. Viscosity test

Viscosities were determined and expressed in Pa.s. The viscosities of the starch-based wood adhesive with different durations of acid hydrolysis were measured in triplicate at 30 °C.

2.7. Shear strength test

The shear strength of the samples was tested on the basis of the Chinese industry standard HG/T 2727-2010. Freshly cut wood pieces in the size of 25 mm × 25 mm × 5 mm were smoothened with rough sandpaper (Scheme 1). Prior to the tests, these wood



Scheme 1. Shape and dimension of shear test specimen (HG/T 2727-2010).