



Effects of heat pretreatment of starch on graft copolymerization reaction and performance of resulting starch-based wood adhesive

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ABSTRACT

In this study, effects of starch heat pretreatment at 70, 80 and 90 °C on graft copolymerization reaction with vinyl acetate (VAc) and the performance of the resulting starch-based wood adhesive (SWA) were investigated. It was shown that SWA pretreated at 90 °C achieved the best performance. At this temperature, the bonding capacity improved by 17.84% compared to the adhesive synthesized without heat pretreatment and the viscosity increased by 18.16% after 7 free-thaw cycles, much better than other samples. Scanning electron microscopy (SEM) and polarizing microscopy demonstrated that structures of starch granules were fully damaged after heat pretreatment at 90 °C. The reaction took place not only on the surface of starch granules, but also internally, leading to improvement in the grafting amounts and grafting efficiency by 42.86% and 39.03%, respectively. This was further confirmed by Fourier transform infrared spectroscopy (FT-IR), Confocal Raman microscopy (CRM) and X-ray photoelectron spectroscopy (XPS), which also showed better reaction homogeneity both between different starch granules and from granule surface to its internal structure.

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1. Introduction

In recent years, the transformation of bio-based polymers, such as polysaccharide, lignin-derivatives and xylan into adhesives have received strong interest [1–3]. This is not only due to their abundance and low cost, but also to the growing environmental awareness. A number of reports have demonstrated that the grafting of vinyl monomers onto starch is a very promising alternative method for petrochemical-based adhesives [4,5]. As a result, tremendous efforts have been made to improve the performance of starch-based wood adhesive (SWA) [6,7]. However, SWA still exhibits several drawbacks for industrial use, including the low initial viscosity, poor storage stability and mobility, and insufficient bonding capacity. Therefore, improving the properties of SWA is desirable for practical industrial use.

Several factors, such as reaction temperature, reaction time, ratio of starch to monomer and additives have been studied to figure out their influence on the graft copolymerization of starch with monomers [8–10]. In particular, gelatinized and ungelatinized starch has both been applied in its grafting modification [11–13]. The modification of starch involve gelatinization processes can break the inter-chains hydrogen bonding, which may have an impact on the group exposure of granules and mass transfer in the system [14]. Since starch is one of the major materials in SWA that takes almost half of the total solid content, its status could have an important influence on the reaction with VAc, as well as the performance of the resulting product. Although gelatinized starch was used in some studies as graft copolymerization with monomers [15,16], how they might affect the reaction is not thoroughly examined. To our knowledge, no investigation has been conducted so far that would involve the mechanism of the effect of starch heat pretreatment on its grafting copolymerization. Therefore, it's important to investigate the influence of starch heat pretreatment on the copolymerization process with VAc.

In this experiment, SWA was synthesized from starch at different heat pretreatment temperatures. Due to the reason that heat pretreatment of starch will result in high viscosity of the

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system and lead to low reaction efficiency, adjustments on acid hydrolysis pretreatment and conditions for polymerization have been made correspondingly. Several techniques, including scanning electron microscopy (SEM), polarizing microscopy, Fourier transform infrared (FT-IR) spectroscopy, Confocal Raman microscopic (CRM) and X-ray photoelectron spectroscopy (XPS) were utilized in hope to elucidate the relationship between the starch granules status and the grafting extent. The homogeneity from granules to granules and from the surface to the internal structure, as well as the performances of the resulting product were also examined. The final goal is to obtain SWA with relevant storage stability, high bonding strength and appropriate initial viscosity, which could better meet the needs of industrial applications.

2. Experimental

2.1. Materials

Native corn starch (NCS, food grade) was purchased from Dazong Starch Co. (Shandong, China). Vinyl acetate (VAc), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), acetone, hydrochloric acid and urea were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). All other reagents were of analytical grade.

2.2. Synthesis of SWA

To obtain SWA with a suitable initial viscosity of industrial use, different reaction time of acidic hydrolysis were optimized in the previous study, and the recorded values for non-heat pretreated were 70 min and those for 70 °C, 80 °C, 90 °C heat pretreated were 80 min, 80 min and 90 min, respectively. The SWA with heat pretreatment was synthesized as follows: dried corn starch (100 g) and hydrochloric acid (200 mL, 0.5 M) were put in a four-necked round-bottomed flask and stirred at 60 °C for some time. After the acid hydrolysis reaction, the pH of the mixture was adjusted to 4.0 and the temperature was raised respectively to 70, 80 and 90 °C, where it was kept for 0.5 h. The temperature was then adjusted to 70 °C, followed by addition of SDS (1.3 g) and APS (0.6 g). Afterward, VAc (70 g) was dropped into the solution at a constant speed for a period of 3.5 h, followed by addition of APS (0.3 g) for supplement and the temperature was kept for another 1 h. To remove residual monomers, the temperature was raised to 80 °C and kept for 0.5 h, then the mixture was cooled to 60 °C and urea (15 g) was added and stirred for another 0.5 h. Finally, the mixture was cooled to 30 °C and the pH value was adjusted to 6.0 using 1 M sodium hydroxide. The resulting SWA were named as 70SWA, 80SWA, 90SWA, where the numbers before SWA correspond to heat pretreatment temperature.

For comparison, a conventional SWA was prepared, following the above process but without heat pretreatment and was named as NSWA.

2.3. Shear strength test

The shear strength of SWA was tested using the method described in the literature [17]. All tests were replicated ten times, and the results were presented as the average repeats with a standard deviation of <2.5 MPa.

2.4. Free-thaw stability test

The stability of SWA was determined by F/T recycling, which was analyzed by the method reported in the literature [18]. The F/T cycle was repeated 7 times for each sample. The viscosity was

measured using an NDJ-8S rotational viscometer (Ning Run, Shanghai Scientific Co., China) at 12 rpm using spindle number 4, and the viscosity was measured in triplicate mode at 25 ± 1 °C.

2.5. Measurements of grafting amounts (G) and grafting efficiency (GE)

For all the starch-based adhesives, both G and GE values were measured using previously reported methods [19]. The grafted starch samples were acquired by Soxhlet extraction method of solid adhesives with acetone for 48 h at 75 °C to remove the homopolymers of VAc. The grafted starch with non-heat pretreatment was denoted as NHGS, whereas the grafted starch with heat pretreatment was named as 70HGS, 80HGS and 90HGS, respectively (the number before HGS denotes the heating temperature).

2.6. Scanning electron microscopy (SEM) and polarizing microscopy

The native, heated and grafted starch samples were frozen at -75 °C for 24 h and then lyophilized using a Scientz-10N apparatus (Ningbo, China). The surfaces of all the samples were then coated with a gold thin layer under vacuum before SEM (Quanta 200, Holland) studies at an accelerating voltage of 5 kV.

The polarized light micrographs of starch granules were acquired by uniformly disperse the heated starch pastes and the non-heated starch granules in deionized water then place a drop of the starch suspension on a glass slide, followed by cover up with a cover glass plate before being subjected to microscopy observations. An Olympus BX41 polarized optical microscope (Olympus, Japan) equipped with a Micro Publisher 5.0RTV camera was used at the magnification set of 400 (40×10).

2.7. Fourier transform infrared (FT-IR) spectroscopy

The powder of NCS and grafted starch was mixed and ground with KBr at weight ratios of 1:100, then 60 mg of the mixture was pressed to form a tablet. The spectra were acquired using a Nexus 470 FT-IR spectrometer (Nicolet Corp., USA). For each sample, the absorbance spectra were collected with 32 scans between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} . The baseline correction was performed for every sample using Omnic software. The vertical distance from the peak top to the baseline was the peak height. For grafted starch, the relative amount of grafting was determined by the peak height at the 1741 cm^{-1} characteristic of ester groups to that located at 576 cm^{-1} characteristic of C–H vibration of corn starch, and the ratio was denoted as I_{1741}/I_{576} [20].

2.8. Confocal Raman microscopic (CRM)

The CRM was conducted by previously described method [21]. For each grafted starch sample, one hundred starch granules were studied, and the relative carbonyl content for every granule was determined by the absorption area ratio of the carbonyl ($1708\text{--}1766 \text{ cm}^{-1}$) band to the carbohydrate band ($460\text{--}510 \text{ cm}^{-1}$) $\times 100$ [22,23].

2.9. X-ray photoelectron spectroscopy (XPS)

The XPS spectra were collected using Escalab 250Xi XPS system (Thermo Scientific, USA) with Al K α X-ray source. The sample surface was etched for 30 s by argon gas before the XPS analysis. The energy of the entire spectrum was spanned from 1350 to 0 eV with a scanning step of 1 eV. The high-resolution spectrum of the C1 s in the region from 278 to 296 eV was collected at intervals of 0.05 eV.

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