

## Effects of urea on freeze–thaw stability of starch-based wood adhesive



Zhenjiong Wang<sup>a,b</sup>, Zhengbiao Gu<sup>a,\*</sup>, Zhaofeng Li<sup>a</sup>, Yan Hong<sup>a</sup>, Li Cheng<sup>a</sup>

<sup>a</sup> State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, 214122 Wuxi, Jiangsu, People's Republic of China

<sup>b</sup> School of Biochemical and Environmental Engineering, Nanjing Xiaozhuang University, 3601 Hongjing Road, 211171 Nanjing, Jiangsu, People's Republic of China

### ARTICLE INFO

#### Article history:

Received 16 September 2012

Received in revised form 7 February 2013

Accepted 10 February 2013

Available online 18 February 2013

#### Keywords:

Waxy corn starch

Wood adhesive

Urea

Freeze–thaw stability

### ABSTRACT

Urea was used to improve the freeze–thaw (F/T) stability of a renewable starch-based wood adhesive (SWA). The improved stability was supported by the enhanced viscosity stability and bonding performance stability after repeated F/T cycling. The results of dynamic time sweep experiments, differential scanning calorimetry (DSC) and pulsed nuclear magnetic resonance (PNMR) showed that the improved stability can be due to the ability of urea to inhibit the retrogradation of starch molecules in the starch-based wood adhesive system. Urea can be used as an effective additive for improving storage properties of starch-based wood adhesive in low temperature environment. Approximately 15% (w/w) urea was the determined optimal dosage.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

With the worsening of the global energy crisis, commonly used non-renewable raw materials of wood adhesives, namely, petroleum and natural gas (Imam, Gordon, Mao, & Chen, 2001), are being gradually replaced with renewable biopolymers, such as animal protein glue produced from bone (Konnerth, Hahn, & Gindl, 2009), soybean protein (Ciannamea, Stefani, & Ruseckaite, 2010; Liu et al., 2010), natural tannin (Kim & Kim, 2003), and starch (Imam, Mao, Chen, & Greene, 1999; Imam et al., 2001).

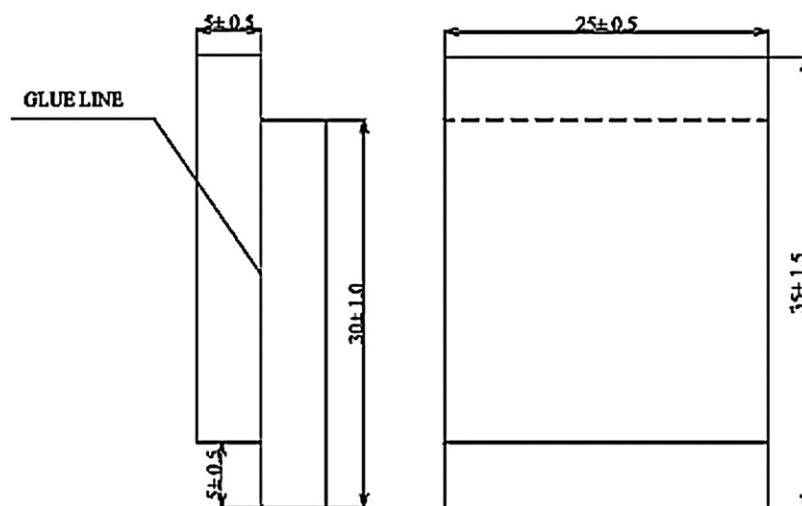
Starch is a relatively inexpensive and renewable product that can be obtained from multiple plant sources and that has been extensively used as wet-end additive, coating binder, sizing agent, adhesive, and textile size (BeMiller & Whistler, 2009). A few studies have been conducted on the potential of utilizing starch as wood adhesive. Recent studies have focused on formaldehyde-free wood adhesives, which are obtained through the reaction between a cross-linker and a blend of starch with other polymers, such as starch/PVA (Imam et al., 1999, 2001), starch/tannin (Moubarik, Pizzi, Allal, Charrier, & Charrier, 2009; Moubarik, Charrier, Allal, Charrier, & Pizzi, 2010; Moubarik et al., 2011) and starch/isocyanates (Tan, Zhang, & Weng, 2011). However, such wood adhesives cannot be used at room temperature because the required curing temperature is usually over 100 °C. Previously, our

group reported a renewable starch-based wood adhesive (SWA) that can be used at room temperature (Wang, Gu, Hong, Cheng, & Li, 2011; Wang, Li, Gu, Hong, & Cheng, 2012). The bonding performance of the SWA meets the requirements for use as a wood bond. However, this SWA is not freeze–thaw (F/T)-stable and prone to losing its bonding capacity and flow properties during transportation or storage in a cold environment, or when subjected to multiple F/T cycles.

Urea is an organic compound widely used as a solid nitrogen fertilizer, as a constituent of cattle feeds and animal feedstock, and as a raw material for manufacturing resins and other products for various industrial applications. Urea is often used in starch sizes system to bring about considerable viscosity changes (Chiou, Fellows, Gilbert, & Fitzgerald, 2005; Hebeish, El-Thalouth, & Kashouti, 1981; Kuo & Wang, 2006; Li, Vasanthan, & Bressler, 2012). In particular, it is well known that the addition of urea influences the gelatinization and retrogradation characteristics of starch (Tamaki, Konishi, & Tako, 2011). In aqueous suspensions, urea facilitates starch gelatinization and solubilization (Chiou et al., 2005; Hebeish et al., 1981; Kuo & Wang, 2006; Li et al., 2012). Furthermore, urea can also effectively suppress the retrogradation of starch gel (Ogawa et al., 2000; Tako et al., 2008). During storage in a cold environment or when subjected to multiple F/T cycles, the viscosity of starch solution increases to form a gel, thereby losing its flow properties. Urea can reduce the gel strength by decreasing the intermolecular network formation between water and amylose (McGrane, Mainwaring, Cornell, & Rix, 2004). Therefore, urea can likely be used to improve the F/T resistance of SWA. However, the effect of urea on the stability of SWA has not yet been investigated.

\* Corresponding author. Tel.: +86 510 85329237; fax: +86 510 85329237.

E-mail addresses: [wangzhenjiong@gmail.com](mailto:wangzhenjiong@gmail.com) (Z. Wang), [zhengbiaogu@yahoo.com.cn](mailto:zhengbiaogu@yahoo.com.cn) (Z. Gu).



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

In the present study, urea was added to SWA to produce urea/SWA, consequently improving the quality of renewable SWA. The bonding strength and viscosity variation after F/T cycles of SWA were evaluated to confirm the effect of adding urea to the adhesive system. The adhesive characteristic was analyzed to determine the interaction between starch and urea. Furthermore, the thermal and rheological properties, as well as the mobility and distribution of water in the SWA system, were examined to verify the quality improvement of SWA with the addition of urea.

## 2. Materials and methods

### 2.1. Materials

Waxy corn starch was supplied by Qinhuangdao Lihua Starch Co. (China). VAc, ammonium persulfate (APS), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium dodecyl sulfate (SDS), urea and hydrochloric acid were provided by Sinopharm Chemical Reagent Co. (China). The chemical agents used were of analytical grade, and used without further purification.

### 2.2. Synthesis of urea/starch-based wood adhesive

The SWA sample was synthesized as follows: about 50 g dried waxy corn starch and 100 mL hydrochloric acid (0.5 M) were mixed in a four-necked, round-bottom flask and stirred at 60 °C for 30 min. The pH of the mixture was adjusted to 6.0 with  $\text{NaHCO}_3$ , and the temperature was increased to 95 °C. After 30 min of starch gelatinization, the reaction temperature was allowed to cool to 60 °C, followed by the addition of 0.7 g SDS, 15 mL VAc, and 0.2 g APS under nitrogen protection. After 30 min of pre-polymerization, the reaction temperature was increased to 70 °C. Subsequently, 35 mL VAc and 0.3 g APS were added to the mixture over a period of 3 h. After polymerization, the temperature was increased to 80 °C, and the mixture was stored for 30 min.  $\text{NaHCO}_3$  was used to adjust the pH to 6.0 after cooling to room temperature.

The urea/SWA samples were prepared as follows: urea (5 wt.%–20 wt.%) were homogenized in SWA sample using an Ultra Turrax basic homogenizer (IKA T18 Basic, IKA Labortechnik, Staufen, Germany) for 30 s, respectively. The mixture was re-circulated through a lab-scale high-pressure homogenizer (NS1001L-PANDA 2K, Niro Soavi S.p.A., Parma, Italy) for several minutes at a pressure of 250 bar to achieve multiple passes through

the valves. The adhesive samples were kept stable at room temperature for 24 h.

### 2.3. Evaluation of adhesive properties

#### 2.3.1. Effect of freezing–thawing on the adhesive stability

The effect of F/T cycles was studied by placing adhesive samples (30 ml) in plastic containers, freezing for 22 h at 4 °C, and thawing for 2 h at 25 °C for analysis. This F/T cycle was repeated 0 times to 10 times, and its influence on the sample viscosities was determined after each cycle. The viscosity was measured using a Brookfield viscometer (Model DV-II+Pro, USA) at 50 r/min using spindle number 29 and expressed in Pa s. All measurements were performed in triplicate at 25 °C  $\pm$  1 °C.

#### 2.3.2. Effect of freezing–thawing on the adhesive bonding stability

Shear strength of the adhesive samples before and after F/T cycling was tested according to Chinese industry standard HG/T 2727-2010 (China, 2010). Freshly cut pieces of wood (*Betula platyphylla*) with dimensions of 25 mm  $\times$  25 mm  $\times$  10 mm were glued with adhesives under static pressures of 0.5–1.0 MPa at 25 °C for 24 h (Scheme 1). Before the shear strength tests, the glued specimens were stored in the laboratory at 23 °C  $\pm$  2 °C and 50%  $\pm$  5% humidity for 48 h. The shear strength of the glued samples in the dry state was determined using a WDT-10 shear strength analyzer (KQL Corp., China). The shear strength was calculated as follows:  $\sigma_M = F_{\max}/A$ , where  $\sigma_M$  (MPa) is the shear strength,  $F_{\max}$  (N) is the observed maximum failing load, and  $A$  ( $\text{mm}^2$ ) is the bonding surface of the sample. The testing speed was 2 mm/min. All tests were replicated six times, and the results are presented as averages.

### 2.4. Rheological analysis

The dynamic viscoelastic properties of the adhesive samples were analyzed using an AR1000 rheometer (TA Corp., UK) with a parallel plate (diameter = 40 mm) placed at a gap of 0.5 mm. The sample was placed in the rheometer, and the edge of the plate was covered with a thin layer of silicon oil to prevent water evaporation. The evolution of storage modulus ( $G'$ ) and loss tangent ( $\tan\delta$ ,  $\tan\delta = G''/G'$ ) was recorded as a function of time for 4 h at 25 °C in order to describe the gelling process of the mixture. The strain and frequency were set at 2.0% and 1 Hz, respectively.

Download English Version:

<https://daneshyari.com/en/article/10603619>

Download Persian Version:

<https://daneshyari.com/article/10603619>

[Daneshyari.com](https://daneshyari.com)