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

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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.

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.

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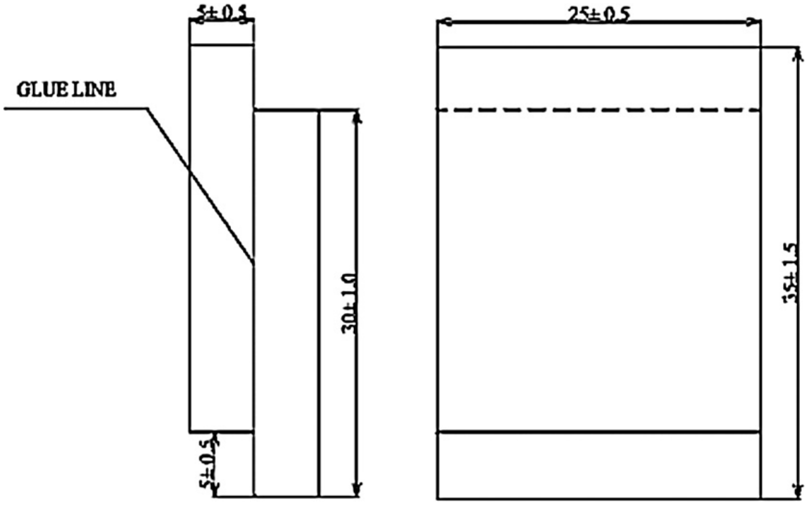

Scheme 1. Shape and dimension of the shear test specimen (HG 2727-2010).

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 ($NaHCO_3$), 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 $NaHCO_3$, 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. $NaHCO_3$ 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 ± 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 × 25 mm × 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 ± 2 °C and 50% ± 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 σ_M (MPa) is the shear strength, F_{max} (N) is the observed maximum failing load, and A (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 (tanδ, $\tan\delta = G''/G'$) 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.

Table 1
Variation in the apparent viscosity of starch-based wood adhesives with different urea contents at different freeze–thaw cycles.

Sample	0 cycle	1 cycle	2 cycles	3 cycles	4 cycles	5 cycles	6 cycles	7 cycles	8 cycles	9 cycles	10 cycles
	Viscosity (Pa s)										
Control	5.40 ± 0.38	6.73 ± 0.47	8.12 ± 0.72	10.55 ± 0.90	19.28 ± 1.73	26.4 ± 2.32	Too high	Too high	Too high	Too high	Too high
SWA + 5% urea	3.52 ± 0.34	3.75 ± 0.36	4.23 ± 0.39	4.94 ± 0.42	5.56 ± 0.43	6.06 ± 0.51	7.18 ± 0.73	9.57 ± 0.95	12.49 ± 1.38	16.10 ± 1.56	Too high
SWA + 10% urea	2.50 ± 0.12	2.71 ± 0.13	3.25 ± 0.21	3.25 ± 0.23	3.42 ± 0.22	3.45 ± 0.25	3.60 ± 0.27	4.75 ± 0.33	5.93 ± 0.28	7.87 ± 0.28	9.59 ± 0.46
SWA + 15% urea	2.35 ± 0.10	2.50 ± 0.11	2.50 ± 0.11	2.52 ± 0.13	2.72 ± 0.11	2.75 ± 0.14	3.00 ± 0.16	3.01 ± 0.18	3.04 ± 0.21	3.25 ± 0.21	3.28 ± 0.22
SWA + 20% urea	2.00 ± 0.07	2.00 ± 0.07	2.00 ± 0.08	2.02 ± 0.10	2.25 ± 0.12	2.30 ± 0.11	2.32 ± 0.19	2.35 ± 0.20	2.47 ± 0.22	2.50 ± 0.22	2.50 ± 0.28

2.5. Differential scanning calorimetry (DSC) analysis

The thermal properties of adhesive samples were determined from DSC curves obtained using Pyris 1-DSC (PerkinElmer Corp., Norwalk, CT, USA). These adhesive samples (about 6 mg) were accurately weighed in aluminum DSC pans, sealed, and equilibrated at room temperature for 24 h before analysis. Scans were performed from 25 °C to 90 °C at a constant rate of 10 °C/min. The retrogradation enthalpy (ΔH_r) was evaluated based on the area occupied by the main endothermic peak and expressed in terms of J/g of dry starch using equipment software. A sealed, empty crucible was used as a reference, and indium was used for temperature calibration. All measurements were performed in triplicate.

2.6. PNMR analysis

The adhesive samples were transferred into NMR tubes (ID = 0.5 cm, L = 20 cm). A Teflon plug was inserted, and the tube was sealed with parafilm to prevent water evaporation. Proton relaxation measurements were recorded using an NMR spectrometer (Oxford Instruments, Bucks, UK) operating at 25 °C at a resonance frequency of 22.9 MHz. Eight scans were accumulated, and the number of echoes for Carr–Purcell–Meiboom–Gill (CPMG) decays applied was 1024. A recycle delay of 3 s was inserted between scans to allow full spin relaxation. The transverse relaxation time (T_2) was measured using the CPMG decays and recorded using a pulse spacing of 200 μs between the 90° and 180° pulses. The transverse relaxation time curves were analyzed using an exponential model as described by Eq. (1) using 1stopt software (v.1.5, 7D-Soft High Technology Inc., Beijing, China):

$$A = A_O e^{(t/T_2)} \tag{1}$$

where A_0 is the relative measure of the amount of water fractions corresponding to T_2. T_2 represents more mobile fractions of water in the mixture (Provencher, 1982). The tube with samples was frozen at 4 °C for 22 h and thawed at 25 °C for 2 h for the same analysis. This cycling was repeated 10 times. Transverse (T_2) relaxation curves were recorded after each cycle.

2.7. Statistical analysis

Statistical analysis was performed using DPS 7.05 software (Zhengjiang University, Hangzhou, China). Significant differences ($p < 0.05$) between treatment means were determined using Duncan's multiple range tests.

3. Results and discussion

3.1. Effects of urea on the performance of SWA after F/T cycling

The beneficial effect of adding urea to the SWA system was directly verified by the improved F/T stability and bonding performance stability of the urea/SWA, which underwent a series of F/T cycles.

The viscosity profiles of SWA with different urea contents after a series of F/T cycles are shown in Table 1. The apparent viscosity of the adhesive samples depended on the urea concentration. Compared with the control sample, the apparent viscosity of SWA with 20% urea decreased from 5.40 Pa s to 2.00 Pa s. The apparent viscosity changes caused by urea may be hypothesized that urea diminishes the hydrogen bonding among the SWA molecules, because urea is a hydrogen bond-breaking agent.

In addition, the apparent viscosity of the adhesive samples increased with increasing periods of freezing and thawing. After 5 F/T cycles, the apparent viscosity of the SWA increased from 5.40 Pa s to 26.4 Pa s. Thus, the adhesive sample almost lost its flow properties. These results suggest that the reorganization of starch molecules may affect functional properties such as viscosity or gel behavior during cold storage.

However, compared with control, the apparent viscosity of urea/SWA showed higher F/T resistance with increasing urea content (5%–20%). The samples with more than 5% urea passed 1–10 cycles. After 10 F/T cycles, the apparent viscosity of the adhesive with 15% urea increased by 0.93 Pa s. The adhesive with 20% urea content increased by only 0.5 Pa s or less. Apparently, under low temperature conditions, the apparent viscosity stability of SWA is significantly improved with the addition of urea to the adhesive system. Thus, hypothetically, the presence of urea hinders the starch molecules in SWA from forming a gel structure.

The stability of the bonding characteristics of the urea/SWA before and after F/T cycling was also evaluated. As shown in Table 2, after 10 F/T cycles, the shear strengths of the adhesives with or without urea evidently decreased, possibly due to the rapid increase in the apparent viscosity of the control after a series of F/T periods. The exorbitant apparent viscosity of the adhesive emulsion hindered the permeation of the emulsion into the wood surface. Hence, the shear strength of the control evidently decreased after a series of F/T cycles. However, the loss ratio of the bonding strength decreased from 73.3% to 32.1% with increasing urea content from 0% to 20%. The presence of urea makes it possible to limit the bonding performance loss during the freeze–thaw process. This finding can be attributed to the reorganization of starch molecules that affected the stability of the SWA and led to the loss of bonding characteristics. In terms of the balance between performance and the addition amount of urea, 15% (w/w) urea may be considered the appropriate dosage under the current conditions.

Table 2
Effect of urea on the bond characteristics[a] of starch-based wood adhesives before and after 10 freeze–thaw cycles.

Sample	Shear strength (MPa)	Shear strength after 10 F/T cycles (MPa)	Loss rate (%)
Control	5.88 ± 0.06^{b}	1.57 ± 0.07^{d}	73.3
SWA + 5% urea	5.98 ± 0.08^{ab}	2.65 ± 0.05^{c}	55.7
SWA + 10% urea	6.04 ± 0.07^{a}	3.52 ± 0.06^{b}	41.7
SWA + 15% urea	6.07 ± 0.06^{a}	4.09 ± 0.08^{a}	32.6
SWA + 20% urea	6.05 ± 0.05^{a}	4.11 ± 0.07^{a}	32.1

[a] Mean ± SD values followed by the same column followed by different superscripts are significantly different ($p \leq 0.05$).

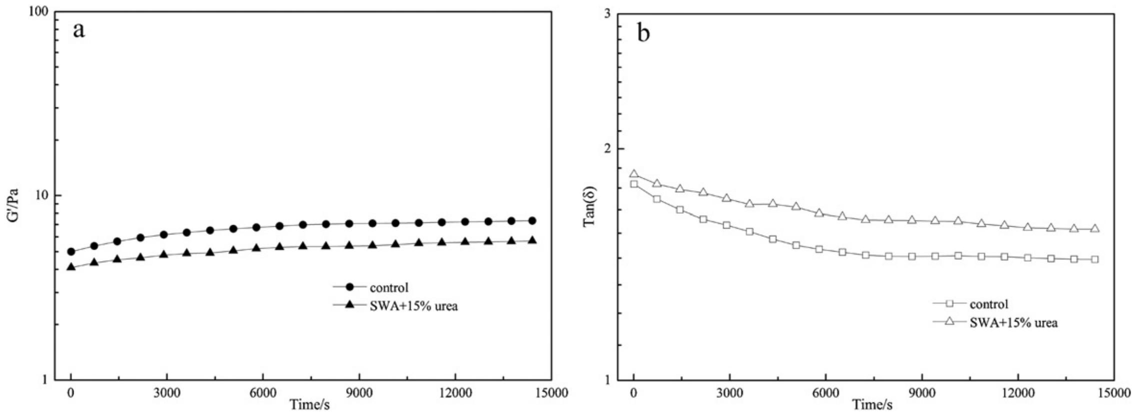

Fig. 1. Evolution of the storage modulus (G') and the loss tangent (tanδ) versus time for urea/SWA at 25 °C: (●, ○) control, (▲, △) SWA with 15% urea.

The improved performance stability produced by the addition of urea to the SWA suggests that urea affects the adhesive properties related to the bonding strength stability and viscosity variation of the adhesives. Thus, the rheological properties and thermal stability of SWA, as well as the mobility and distribution of water in the SWA system, were further analyzed.

3.2. Rheological properties of the urea/SWA

3.2.1. Dynamic viscoelastic properties of urea/SWA at room temperature

Changes in the storage modulus (G') as a function of time at 25 °C for 4 h were measured for SWA without or with 15% urea (Fig. 1a). The behavior pattern of the G' values of the control showed an initial rapid rise in modulus, followed by a constant stage, whereas the G' values of SWA with 15% urea increased more steadily at the initial period and then remained constant thereafter. In addition, during the entire process, the G' values of the control were higher than those of SWA with 15% urea. In order to illustrating the differences in the viscoelastic behavior, the loss tangent "tanδ" which states directly the G''/G' ratio, can be described as a characteristic parameter. The changes in the loss tangent (tanδ) with time are shown in Fig. 1b. The tanδ values decreased with aging time, and the value of the tanδ of the control was lower than that of SWA with 15% urea (Fig. 1b). Therefore, all the samples presumably became more elastic during the time sweep process, and the SWA with 15% urea was more viscous than the control. The increase of the viscous component of the adhesive emulsion also confirmed that the presence of urea inhibited the gelation behavior through diminishing the hydrogen bonding among the SWA molecules. Therefore, urea can increase the emulsion stability of SWA at room temperature.

3.2.2. Dynamic viscoelastic properties of urea/SWA after F/T cycling

Fig. 2a shows changes in the storage modulus (G') as a function of time for SWA without and with 15% urea after repeated F/T cycling. The G′ values of the control continued to increase without the plateau region even after 4 h whether after 2 or 5 F/T cycles. Furthermore, the variation of tanδ with time is shown in Fig. 2b. For the control after 2 F/T cycles, it can be observed that the beginning of the process was dominated by the viscous behavior of the system (tan$\delta > 1$). The gel point (tan$\delta = 1$) was then observed, and the elastic behavior (tan$\delta < 1$) dominated after the gel point which is characteristic of liquid-like to solid-like transition. This phase transition behavior is presumably due to the slow formation and rearrangement of the molecular chains of SWA. At low temperatures, the starch molecules in pastes or gels are known to associate by retrogradation, resulting in precipitation, gelation, as well as changes in consistency and opacity. Crystallites eventually begin to form, accompanied by gradual increases in rigidity and phase separation between the polymer and water (Karim, Norziah, & Seow, 2000). Therefore, the liquid-like to solid-like transition of SWA can be due to the retrogradation of the starch molecules in SWA. For the control after 5 F/T cycles, the final G' value was significantly higher than after 2 F/T cycles (Fig. 2a). In addition, the magnitudes of tanδ were within the range 0.44–0.65, indicating that the sample was more elastic than viscous (Fig. 2b). It indicated that the SWA after 5 F/T cycles could be thought as a weak gel (Oh, Kim, &

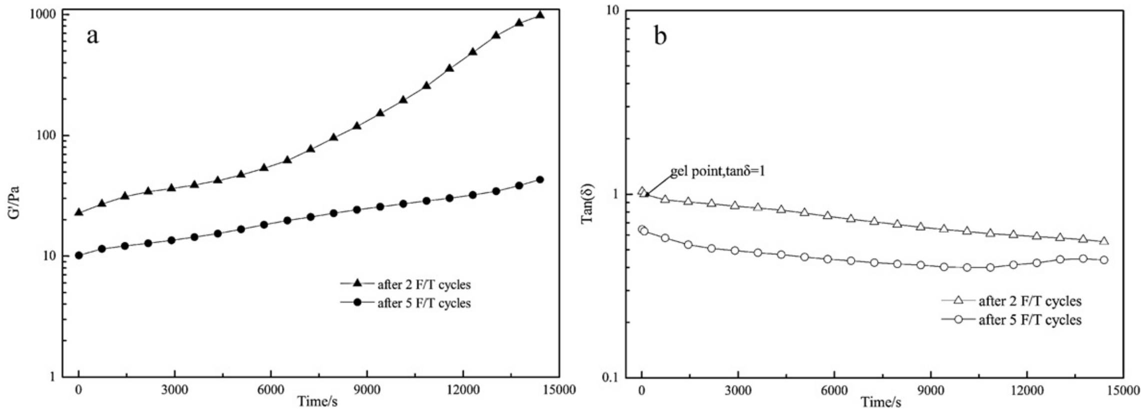

Fig. 2. Evolution of the storage modulus (G', solid symbols) and the loss tangent (tanδ, open symbols) versus time for starch-based wood adhesive after different freeze–thaw cycles: (▲, △) after 2 freeze–thaw cycles, (●, ○) after 5 freeze–thaw cycles.

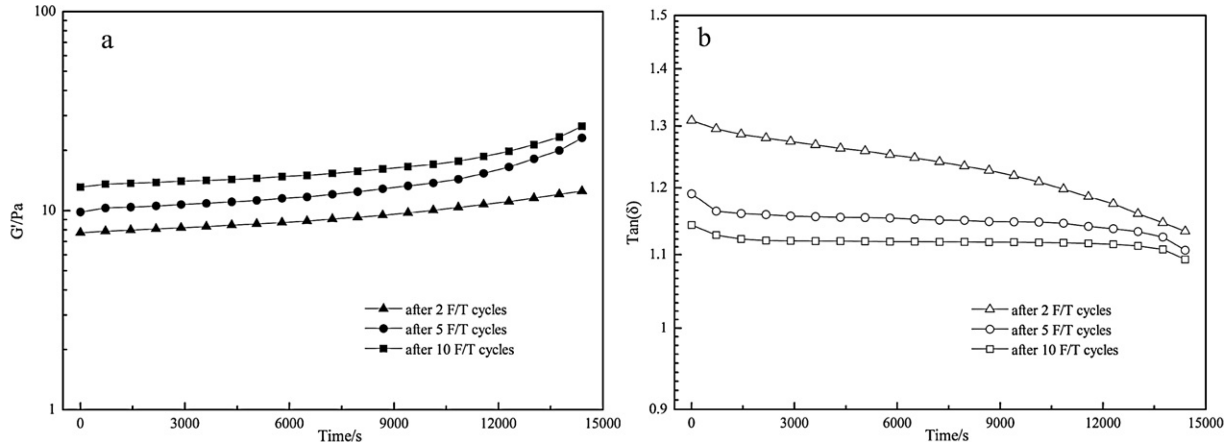

Fig. 3. Evolution of the storage (G′, solid symbols) and the loss tangent (tanδ, open symbols) versus time for starch-based wood adhesive with 15% urea after different freeze–thaw cycles: (▲, △) after 2 freeze–thaw cycles, (●, ○) after 5 freeze–thaw cycles, (■, □) after 10 freeze–thaw cycles.

Yoo, 2010). The results are also consistent with the results of the apparent viscosity variation in the control sample after F/T cycling.

The changes in the G' and tanδ as a function of time for SWA with 15% urea after repeated F/T cycling are shown in Fig. 3a and b, respectively. It can be observed that the final G' value after 10 F/T cycles was apparently higher than those of other samples, while the final tanδ value showed the opposite trend. It indicated that SWA became more elastic during the process of repeated F/T cycles. In addition, all final tanδ value is higher than 1 (Fig. 3b). The result implies the SWA with 15% urea can maintain a viscous behavior despite undergoing all the F/T cycles. It is suggested that urea can hinder the starch molecules from forming a gel structure by disrupting the intermolecular hydrogen bonds (McGrane et al., 2004). The results again confirm the improved freeze–thaw stability of urea contributed by urea to SWA

3.3. DSC measurements

Differential scanning calorimetry (DSC) is used to study not only the disordering behavior of starch during gelatinization, but also its reordering behavior during the aging of the formed gel (Russell, 1987). It has been proven the most useful in providing basic information on starch retrogradation (Karim et al., 2000). In the case of retrograded starch, the enthalpy values of the retrograded starch reflected the melting of crystallites formed by the association between adjacent double helices during gel storage (Hoover & Senanayake, 1996; Karim et al., 2000).

The results of the dynamic time sweep experiments had been proven that the starch molecules in SWA rearranged into an ordered structure (retrogradation) after undergoing a series of F/T cycles. Therefore, the changes in the retrogradation enthalpy of SWA with different urea concentrations during a series of F/T cycles would be further evaluated by DSC (Table 3). In the absence of urea, the ΔH_r for the control significantly increased with the storage time from 2.97 J/g (5 F/T cycles) to 4.83 J/g (10 F/T cycles). It could reflect that retrograded starch form a strong hydrogen bond between the molecules and complete a cement structure in amorphous regions. However, the ability of urea to prevent retrogradation was clearly observed after addition to the SWA system. The adhesive with 10% urea did not show an evident retrogradation endotherm after 5 F/T cycles. After 10 F/T cycles, the ΔH_r value was relatively smaller compared with the control sample. Furthermore, the adhesive with 15% urea did not show an evident retrogradation endotherm on the DSC whether after 5 or 10 F/T cycles. These results suggest that urea can significantly inhibit the retrogradation of the starch molecules of SWA.

Table 3
Variation in the retrogradation enthalpy[a] of urea/starch-based wood adhesives at different freeze–thaw cycles.

Sample	ΔH_r (J/g, dry starch)	
	5 cycles	10 cycles
Control	2.97 ± 0.51^a	4.83 ± 0.46^a
SWA + 5% urea	0.56 ± 0.32^b	1.29 ± 0.31^b
SWA + 10% urea[b]	–	0.19 ± 0.22^b
SWA + 15% urea[b]	–	–

[a] Mean ± SD values followed by the same column followed by different superscripts are significantly different ($p \leq 0.05$).
[b] –, not detectable.

3.4. PNMR measurements

Water molecules play an important role in the retrogradation process of starch. Nuclear magnetic resonance spectroscopy (NMR) has been useful for investigating the molecular dynamics of water in starch systems through the use of ^{1}H, ^{2}H, and ^{17}O nuclear resonance. In addition, the resultant changes in molecular mobility during retrogradation of starch dispersions closely relate to the distribution of water molecules that can be evaluated by PNMR (Yao & Ding, 2002). The relaxation behaviors of proton could be reflected by transverse relaxation time. The constant spin–spin relaxation time namely T_2 was successfully identified from the NMR experiments using the one-pulse and the CPMG pulse sequences. Generally, T_2 indicates the fractions of water degrees of mobility.

The proton transverse (T_2) relaxation curves of the urea/SWA samples were measured by CPMG pulse sequence, as shown in Fig. 4. The mobility of the protons decreased with increasing periods of freezing and thawing, indicating an overall decrease in water mobility, which was thought to be independent of changes in moisture content (Fig. 3). In earlier study, Leung, Magnuson, and Bruinsma (1983) proposed that, as starch changes from the amorphous state to the more stable crystalline state, water molecules become immobilized as they are incorporated into the crystalline structure, resulting in a decrease in mobility of water during the storage of bread (Leung et al., 1983). When the outer short chain of the amylopectin molecules (DP = 12–16) rearranges which takes the double helix as a matrix through the hydrogen bonding, it makes bound water migration into the crystal layer. The recrystallization behavior of amylopectin involves the moving of water molecule, that means the recrystallization behavior is dependent on the water molecules which require the bound water moves into the crystal layer (Gidley & Bulpin, 1987; Ring et al.,

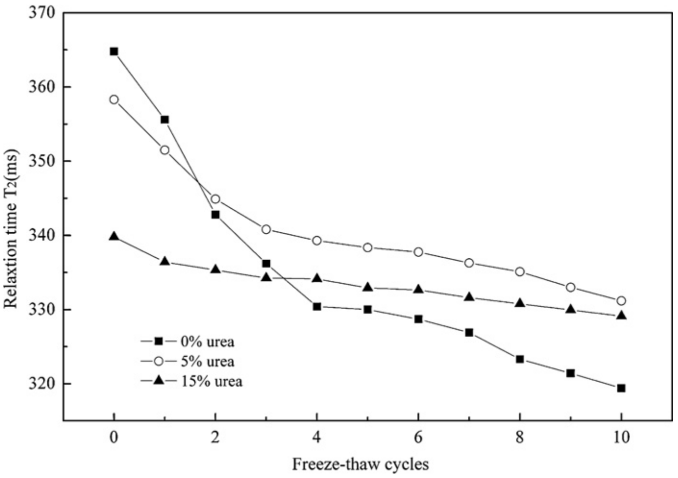

Fig. 4. Variation in T_2 of starch-based wood adhesives with different urea contents after different freeze–thaw cycles.

1987). Overall, the decrease of mobilized water during the long time storage was due to the incorporation of the water molecules to the starch crystalline structure from where part of water leaches out of the amorphous area. Hence, after F/T cycling, the retrogradation of starch molecules in the SWA decreased the water and segmental mobilities of the starch chains. The decreased T_2 of the SWA was also accompanied by the molecular aggregation of starch molecules in the starch-based polymer (Choi & Kerr, 2003; Farhat, Blanshard, Descamps, & Mitchell, 2000).

In addition, the T_2 value significantly decreased with increasing urea content. Compared with that of the control (−45 ms), the T_2 of the adhesive with 5% urea decreased by 23 ms, whereas the T_2 of the adhesive with 15% urea decreased by only 11 ms after 10 F/T cycles. It was proposed that the phenomenon was due to the interaction between starch and urea through hydrogen bonding. It could restrain the losing of water molecules and inhibit the retrogradation behavior of amylopectin. Combined with the results of the dynamic time sweeps and DSC, urea could inhibit the retrogradation of starch molecules in the SWA while maintaining the mobility of water molecules in the starch adhesive emulsion to some extent during periods of freezing and thawing.

4. Conclusions

This work clarified that the functions of urea on the freeze–thaw stability of starch-based wood adhesive varied depending on the different ratios of urea/SWA through a variety of determination methods. The results demonstrated that the addition of urea to starch-based wood adhesive could significantly improve the viscosity stability and bonding performance stability after repeated F/T cycling. Based on the results of the dynamic time sweep experiments, DSC and PNMR, the mechanisms can be attributed to the ability of urea to retard the retrogradation of starch molecules in the SWA system, particularly with repeated F/T cycling. Urea should hinder the starch molecules from forming a gel structure and maintain the mobility of water molecules in the starch adhesive emulsion, leading to the retardation of retrogradation and it must be confirmed whether this is due to urea acting with SWA to disrupt hydrogen bond that prevents the association of starch chains. There is a need for further investigation to determine the retrogradation mechanism between starch and urea. These studies were important for the development of starch-based wood adhesive with longer shelf lives to make them compete more effectively in wood industry.

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