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Improving the performance of starch-based wood adhesive by using sodium dodecyl sulfate

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ABSTRACT

Sodium dodecyl sulfate (SDS) was used to improve the performance of starch-based wood adhesive. The effects of SDS on shear strength, viscosity and storage stability were investigated. It was shown that, although the addition of 1.5–2% (dry starch basis) SDS resulted in a slight decrease in shear strength, the mobility and storage stability of adhesive were significantly enhanced. Possible mechanisms regarding specific action of SDS were discussed. It was proved, using blue value or differential scanning calorimetry (DSC) analysis, that the amylose–SDS complexes were formed in the adhesive. The complex formation or simple adsorption of SDS with starch molecules might hinder the aggregation of latex particles, as shown by scanning electron microscopy images, and inhibit starch retrogradation, as observed by DSC analysis. As a result, in the presence of SDS, the adhesive had higher mobility and storage stability, indicating that SDS could be used to prepare starch-based wood adhesives with high performance.

1. Introduction

With the increasing use of wood composite products, the applications of wood adhesives have grown tremendously (Kaboorani & Riedl, 2011). At present, formaldehyde-based adhesives, such as phenol-formaldehyde and urea-formaldehyde, are predominantly used in the wood-based composite industry. However, they are petrochemical-based and cannot be sustained in the long term due to a limited reserve of oil and natural gas (Jang, Huang, & Li, 2011). Moreover, during the production or use of wood composite products, these adhesives emit carcinogenic formaldehyde into the environment, thus reducing indoor air quality and posing a health risk to humans. Increasing concerns about the heavy dependence on petroleum and the harm of emissive formaldehyde to human health promote the need for a formaldehyde-free wood adhesive based on renewable resources (Li, Geng, Simonsen, & Karchesy, 2004). Starch is one of the most abundant natural, renewable, and biodegradable polymers, which is produced by many plants as a source of stored energy (Imam, Mao, Chen, & Greene, 1999; Le Corre, Bras, & Dufresne, 2010). It has been used as an adhesive in a wide range of products (Imam, Gordon, Mao, & Chen, 2001). However, the bonding properties of normal starch do not show the substantial strength required to glue constructional wood material (Imam et al., 1999). It is neccesary to improve the performance of starch-based wood adhesives to allow them to compete with petrochemical-based adhesives.

In our previous studies, a starch-based wood adhesive was prepared by the grafting of vinyl acetate onto starch, using ammonium persulfate as the initiator (Wang, Gu, Hong, Cheng, & Li, 2011; Wang, Li, Gu, Hong, & Cheng, 2012). However, the starch-based wood adhesive was shown to have relatively poor mobility and storage stability, probably due to starch retrogradation, which resulted in low performance as a wood adhesive. Some studies have indicated that the surfactants could effectively retard retrogradation of starch by forming starch–surfactant complexing (Eliasson, 1994; Gudmundsson, 1992; Kim & Robinson, 1979; Richardson, Kidman, Langton, & Hermansson, 2004). However, the effect of the surfactants on the mobility and storage stability of starch-based wood adhesives has not been investigated.

Sodium dodecyl sulfate (SDS) is a widely commercialized anionic surfactant, and is an organosulfate consisting of a 12-carbon tail attached to a sulfate group. In this study, before graft copolymerization of vinyl acetate onto starch, SDS was added to improve the performance of the starch-based wood adhesive. Mobility and

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storage stability of the starch-based wood adhesive were examined to confirm the positive effect of SDS.

2. Materials and methods

2.1. Materials

Normal corn starch was supplied by Shandong Zhucheng Starch Co. (Shangdong, China). Vinyl acetate, ammonium persulfate, and SDS were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All other reagents were of analytical grade.

2.2. Synthesis of the starch-based wood adhesive with SDS

About 50 g of dried corn starch and 100 mL of hydrochloric acid (0.5 M) were put into a four-necked round-bottomed flask and stirred at 60 °C for 60 min. The pH of the starch solution was adjusted to 4.0. Then, 0.5–2% (dry starch basis) SDS was added to the solution, followed by the addition of 0.4 g of ammonium persulfate under nitrogen protection. The reaction temperature was increased to 70 °C, and 43 mL of vinyl acetate was dropped into the solution over a period of 1.5 h. Following this, the temperature was increased to 85 °C and maintained for 0.5 h. Finally, after the temperature of the reaction mixture was cooled to 30 °C, the pH value was adjusted to 6.0.

For comparison purposes, a conventional starch-based wood adhesive was prepared, following the above process but without the addition of SDS.

2.3. Shear strength test

The shear strength of the starch-based wood adhesive samples was tested, as described by Wang et al. (2011, 2012). All tests were replicated ten times, and the results were repeatable within the deviation of ±2.5 MPa.

2.4. Measurement of viscosity

The viscosity of the starch-based wood adhesive samples was determined using a NDJ-1 rotational viscometer (JK Corp., China). The sample was transferred into the holder of the viscometer, and rotation at 30 rpm for 10 min was chosen to determine the adhesive viscosity.

2.5. Measurement of blue value

SDS (0.02 g) was added to 40 mL of 0.5% gelatinized corn starch solution, and kept at 50 °C for 30 min. After shaking, 2.5 mL of the solution and 1 mL of 0.02 mol/L iodine–potassium iodide solution were mixed, followed by dilution to 100 mL. The mixture was kept at 32 °C for 15 min. The blue value was obtained from the absorbance at 660 nm. For comparison purposes, the control solution was prepared following the above process but excluding SDS.

2.6. Differential scanning calorimetry (DSC) analysis

The formation of the amylose–SDS complexes was analyzed using a differential scanning calorimeter (Q200 DSC, TA Instruments-Waters LLC, USA). The starch-based wood adhesives, without SDS or with 1.5% SDS, were put into aluminum DSC sample pans. During scan testing, the temperature was increased from 40 °C to 120 °C at a heating rate of 5 °C/min. An empty pan was used as a reference sample.

Starch retrogradation was also analyzed using the DSC. The starch-based wood adhesives, without SDS or with 1.5% SDS, were stored in a refrigerator at 4 °C for 10 or 25 days, then put into aluminum DSC sample pans. During scan testing, the temperature was increased from 30 °C to 90 °C, at a heating rate of 5 °C/min, with an empty pan as a reference sample. The peak temperature and enthalpy (ΔH, J/g) were calculated, and were used to indicate the degree of starch retrogradation in the starch-based wood adhesives.

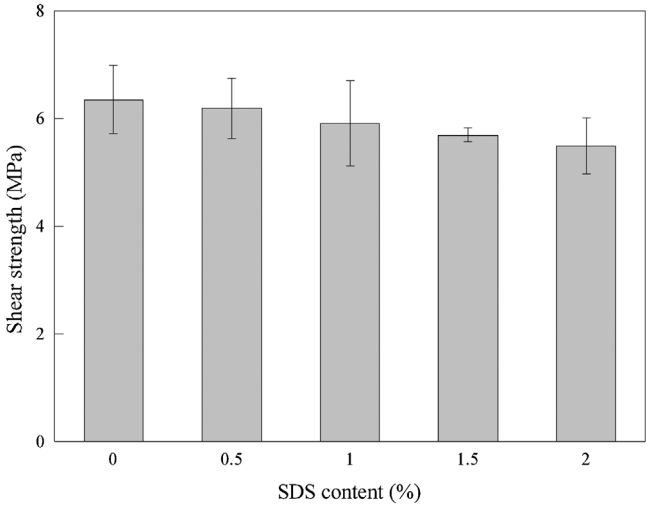

Fig. 1. Effect of SDS on shear strength of starch-based wood adhesive.

2.7. Scanning electron microscopy (SEM) analysis

The starch-based wood adhesives, without SDS or with 1.5% SDS, were freeze-dried and cut into small pieces, and then all specimens were observed using a scanning electron microscope (Hitachi S-4800, Japan).

2.8. Statistical analysis

Data were statistically analyzed using DPS 7.05 (Zhejiang 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. Effect of SDS on shear strength of starch-based wood adhesive

The shear strengths of the starch-based wood adhesives containing different amounts of SDS are shown in Fig. 1.

It was found that the addition of 0.5–2% (dry starch basis) SDS resulted in a slight decrease in the shear strength of the wood adhesive, which may be related to the micelles produced by the SDS during the polymerization (Kuramoto & Geniès, 1995). When SDS was added, the micelles were formed in the adhesive. These micelles accumulated and led to the formation of weak layers on the boundary between the adhesive and the wood fiber (Veselovskiĭ & Kestelman, 2002). The presence of weak layers may have negative effects on bond formation and adhesion strength (Acda, Devera, Cabangon, & Ramos, 2012; Gardner, 2008). Nevertheless, compared to the adhesive without SDS, there was no significant decrease ($p < 0.05$) in the shear strength of the adhesives with 0.5–2% SDS, which still had high bonding capacities for the production of wood-based composites.

Table 1
Effect of SDS on viscosity of starch-based wood adhesive.

SDS content (%)	0%	0.5%	1%	1.5%	2%
Viscosity (Pa s)	–	–	11.1 ± 0.3	8.2 ± 0.3	4.9 ± 0.3

–, mean beyond the range of the NDJ-1 rotational viscometer.

Table 2
Shear strength of starch-based wood adhesives during storage, with different SDS content.[a]

SDS content (%)	Shear strength (MPa)				
	1 day	5 days	10 days	20 days	30 days
0	6.3 ± 1.1	5.6 ± 0.4	5.1 ± 1.3	4.2 ± 0.8	3.9 ± 0.5
0.5	6.2 ± 1.0	5.5 ± 0.7	5.0 ± 0.9	4.7 ± 1.1	4.4 ± 0.7
1	5.9 ± 1.4	5.4 ± 0.7	5.2 ± 0.48	4.6 ± 1.4	4.4 ± 0.6
1.5	5.7 ± 0.6	5.4 ± 0.6	5.0 ± 0.7	4.9 ± 0.3	4.9 ± 1.0
2	5.5 ± 0.5	5.5 ± 0.5	5.4 ± 0.6	5.1 ± 1.2	4.9 ± 0.7

[a] The adhesive was stored at 25 °C and 70% RH.

3.2. Effect of SDS on mobility of starch-based wood adhesive

Viscosity is an important physical property that largely governs the mobility of wood adhesives (Qi & Sun, 2010). For the starch-based wood adhesive, high viscosity usually leads to poor mobility and storage stability. The viscosities of the adhesives with different SDS contents are shown in Table 1.

The adhesive without SDS had a viscosity above 100 Pa s, and was in a gel state. It could not be used as wood adhesive due its poor mobility. The addition of 0.5% SDS did not result in an obvious decrease in the viscosity of the adhesive, which still remained in the gel state. With the SDS content increasing to 1% or above, a significant decrease in the viscosity of the adhesive was achieved, which would allow easy handling, smooth spreading, and sufficient penetration of the adhesive into the wood surface.

3.3. Effect of SDS on storage stability of starch-based wood adhesive

For starch-based wood adhesives, storage stability is one of the most important properties. It can be evaluated by observing shear strength and viscosity changes during storage. As shown in Tables 2 and 3, with increasing storage time, the shear strength of the starch-based wood adhesives gradually decreased (Table 2), while the viscosity exhibited an increasing trend (Table 3).

For the adhesive without SDS, storage resulted in a significant decrease in shear strength. After being stored for 30 days, its shear strength was only 62% of that which was stored for 1 day. Furthermore, after being stored for 1 day, the adhesive without SDS had a viscosity that was too high to be determined by the NDJ-1 rotational viscometer, and formed a non-flowing gel, which became harder during storage over a longer period. Thus, the adhesive without SDS had poor storage stability.

An obvious improvement in storage stability of the adhesive was observed following the addition of SDS (Tables 2 and 3). After being stored for 30 days, the shear strength of the adhesives with 1.5% or 2% SDS decreased by only 14% or 11%, respectively, compared with those stored for 1 day. In addition, although the adhesive with 0.5% SDS was in a non-flowing gel state, a higher proportion of SDS could improve the viscosity stability. After being stored for 30 days, the viscosity of the adhesives with 1% SDS was 2.3-fold that of the adhesives stored for 1 day. For the adhesives with 1.5% or 2% SDS, the same storage resulted in 50% or 29% increase in the viscosity, respectively. Good storage stability would be conducive to the application of starch-based wood adhesives.

3.4. Mechanism analysis of the specific action of SDS

3.4.1. The formation of amylose–SDS complexes in starch-based wood adhesives

The reaction of iodine with starch to form starch–iodine complexes has been studied by many investigators (Eliasson, 1994; Gudmundsson, 1992; Kim & Robinson, 1979; Krog, 1971; Murdoch, 1992; Stawski, 2008). The spectrophotometric measurements of the blue value intensity can reflect the amount of amylose–iodine complexes present (Stawski, 2008). When the alkyl chains of the emulsifier enter the amylose helix, the amylose–iodine complexes cannot be formed, and, therefore, the blue value decreases. As a result, the blue value can reflect the formation of amylose–SDS complexes. We found that the addition of SDS into a corn starch solution caused a 63.8% decrease in the blue value, and a change in the color from blue to purple, which indicated that the amylose–SDS complexes were formed.

In order to confirm the formation of the amylose–SDS complexes in starch-based wood adhesive, DSC was used to determine the helical transition. The result showed that the adhesive without SDS had no phase transition (Fig. 2a) which proved there were no internal lipids and pre-existing amylose-inclusion complexes. For the adhesive with 1.5% SDS, an endothermic phase transition was observed at 95.36 °C (Fig. 2b), which might be attributed to the melting of the amylase–SDS complexes. Our observation was in agreement with the previous report (Jonhed & Järnström, 2006), which showed that a reversible helical conversion occurred at 95 °C in amylose–SDS complexes. A schematic of the amylose–SDS complexes in the starch-based wood adhesives containing SDS is illustrated in Fig. 3.

In addition, besides the formation of amylose–SDS complexes, part of the SDS might be adsorbed onto amylose or amylopectin molecules.

Table 3
Viscosity of starch-based wood adhesives with different content of SDS during storage.[a]

SDS content (%)	Viscosity (Pa s)						
	1 day	5 days	10 days	15 days	20 days	25 days	30 days
0	–	–	–	–	–	–	–
0.5	–	–	–	–	–	–	–
1	11.1 ± 0.3	13.0 ± 0.4	13.4 ± 0.2	15.3 ± 0.2	21.1 ± 0.4	22.9 ± 0.1	25.6 ± 0.1
1.5	8.2 ± 0.3	10.3 ± 0.1	11.9 ± 0.3	11.9 ± 0.1	12.0 ± 0.5	12.3 ± 0.1	12.3 ± 0.2
2	4.9 ± 0.3	5.3 ± 0.1	5.8 ± 0.3	6.0 ± 0.2	6.2 ± 0.1	6.2 ± 0.3	6.3 ± 0.4

–, mean beyond the range of the NDJ-1 rotational viscometer.
[a] The adhesive was stored at 25 °C and 70% RH.

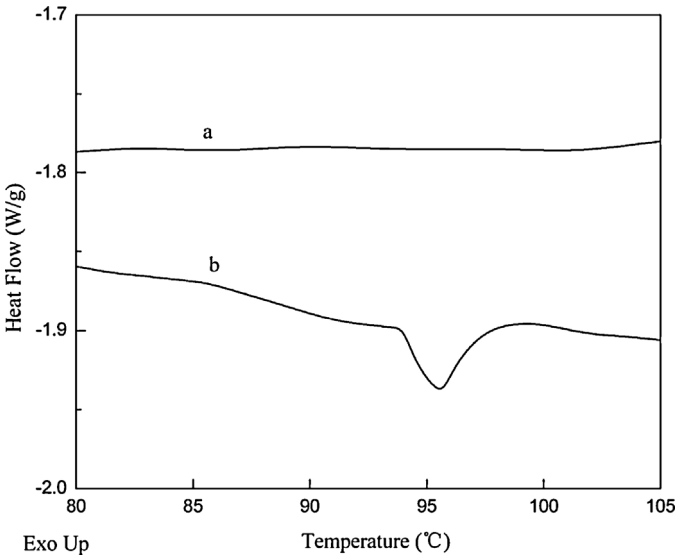

Fig. 2. The DSC thermograms of starch-based wood adhesives: (a) the adhesive without SDS; (b) the adhesive with 1.5% SDS.

3.4.2. SDS-hindered aggregation of latex particles in starch-based wood adhesive

As shown by the SEM images in Fig. 4, after the starch-based wood adhesive without SDS was freeze-dried, the holes in the surface were non-uniform, suggesting that particles in the adhesive may have gathered together. In contrast, relatively uniform holes were formed in the surface of the freeze-dried adhesive with 1.5% SDS, suggesting that the latex particles were well dispersed, which is one of the important indicators of good mobility and storage stability of the adhesive with SDS. We inferred that the formation of amylose–SDS complexes or simple adsorption of SDS with the starch molecules may result in charging the latex particles, and, thus, the aggregation of latex particles in the starch-based wood adhesive is hindered.

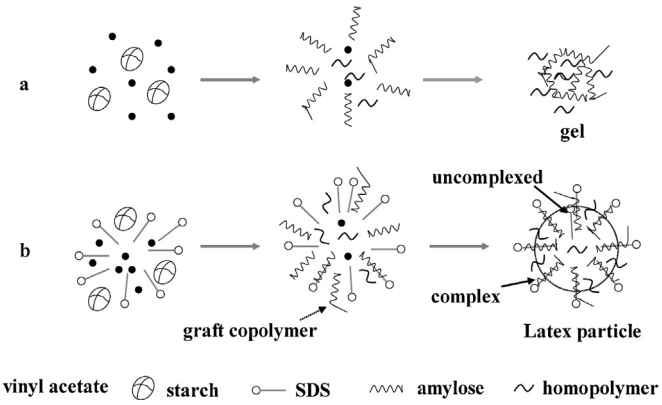

Fig. 3. Schematic diagram of the amylose–SDS complexes in the starch-based wood adhesive: (a) without SDS; (b) with SDS.

3.4.3. SDS-inhibited retrogradation of starch in starch-based wood adhesive

DSC has been widely used to study the thermal behavior of starch retrogradation. The DSC melting endotherm of starch provides the enthalpy as well as the melting temperatures of the crystalline structure in starch, which reflects the degree and perfection of the crystallinity (Durrani & Donald, 1995). As starch retrogradation was one of the major factors for the poor storage stability of the adhesive, DSC was used to analyze the effect of SDS on starch retrogradation in the starch-based wood adhesive.

The melting temperatures and enthalpies of starch-based wood adhesives are summarized in Table 4. After being stored for 10 days, the ΔH value of the adhesive without SDS was 2.46 J/g, which was much higher than that of the adhesive with 1.5% SDS. Although, after being stored for 25 days, the ΔH value of the adhesive with 1.5% SDS was higher than that which was stored for 10 days, it was still much lower than that of the adhesive without SDS. These phenomena suggest that SDS effectively inhibited starch retrogradation in the adhesive, which may also be a major factor contributing to the good storage stability of the adhesive with SDS.

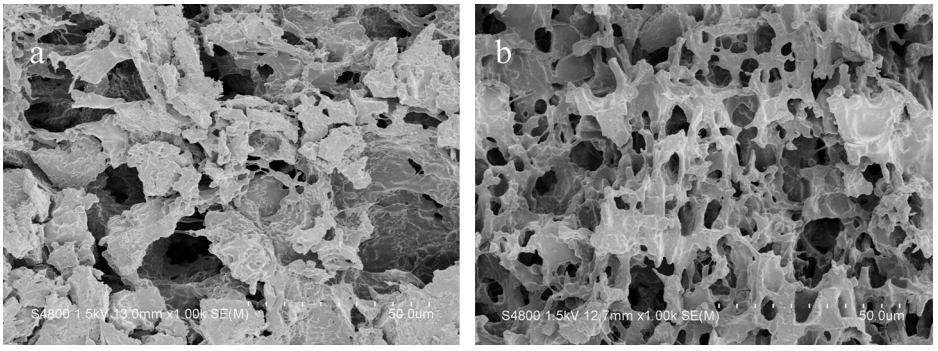

Fig. 4. SEM images of freeze-dried starch-based wood adhesives: (a) the adhesive without SDS; (b) the adhesive with 1.5% SDS.

Table 4
DSC parameters of starch-based wood adhesives during storage.[a]

Samples	10 days				25 days			
	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Adhesive without SDS	41.9	53.4	65.4	2.46	44.6	55.3	66.4	5.61
Adhesive with 1.5% SDS	46.0	50.6	52.8	0.16	45.7	57.8	67.4	1.26

[a] The adhesive was stored at 4 °C and 70% RH.

It is worthwhile to note that SDS may mainly hinder the retrogradation caused by the amylose, due to the formation of amylose–SDS complexes.

4. Conclusion

Compared with the starch-based wood adhesive without SDS, both the mobility and storage stability of the adhesives were significantly enhanced by the presence of 1.5–2% (dry starch basis) SDS. Possible reasons may be the formation of the amylose–SDS complexes or simple adsorption of SDS with the starch molecules, which hinder the aggregation of the latex particles and inhibit the retrogradation of starch in the starch-based wood adhesive.

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