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Cross-linked soy-based wood adhesives for plywood

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ABSTRACT

To improve the water resistance of soy-based adhesive for wood panels, three kinds of cross-linkers, namely, epoxy resin (EPR), melamine–formaldehyde (MF) and their mixture EPR+MF were used in this paper. The results indicated that all the three cross-linkers improved the water resistance of soy-based adhesive and the hybrid cross-linker EPR+MF, was the best. With press temperature 160 °C and press time 8 min, type II and even type I plywood could be prepared when 6.4%EPR+6.4%MF is used as cross-linker of soy-based adhesive. FT-IR indicated that the great improvement of water resistance of soy-based adhesive modified with EPR and MF might be caused by the reaction between epoxy and –OH, and that between MF and –NH.

1. Introduction

Formaldehyde-based adhesives, such as urea–formaldehyde (UF), melamine–formaldehyde (MF), phenol–formaldehyde (PF), are widely used for the preparation of wood panels. But formaldehyde emission caused by these resin adhesives has confused wood industry and has been a topic of concern for many years. Some standards or requirements were given to define the acceptable formaldehyde emission levels. The newest requirement on formaldehyde emission comes from California Air Resources Board (CARB) formaldehyde emissions regulation of U.S. It was passed in 2008 and got effective in 2009. Today, the mounting interest in formaldehyde emission is still driving major changes in wood panel industry as well as the resin industry that supplies the wood panel industry. In response to the need on environment-friendly adhesives, great attention has been given to adhesives from natural materials, such as starch [1,2], soy-based adhesives [3–5], and so on, although most of these adhesives have almost been pushed out of market in wood panel industry during the past 30 years.

Soy-based adhesive was once a major adhesive for preparation of plywood. But it has been replaced by synthetic resins since the 1960s. Till the 1990s, it returned to the study area as a wood adhesive. It is reported that one of the soy-based formaldehyde-free adhesives has been used for production of interior plywood panels since 2004 [6]. However, the application of soy-based adhesives is rather limited. Now, most of the efforts on soy-based adhesive are given to the improvement of its bad water resistance. To resolve this problem, some methods could be employed to modify the soy adhesive, such as hydrolysis, chemical denaturation, cross-linking, enzyme modification, and so on.

Cross-linking modification is a comparatively acceptable method for the modification of soy-based adhesive. Cross-linkers can be either mixed with soy adhesive directly before its application or added during the preparation of soy adhesive. For the latter method, acrylates [7,8], maleic anhydride [9], etc. are used and in most cases graft polymerization will occur. Commonly, some complex preparation procedures are involved in this method. Therefore, it is much easier in handling to mix cross-linkers directly with soy adhesive. An effective cross-linker is the key for this method. Since there are many reactive groups in soy proteins, such as –OH, –SH, –COOH, and $-NH_2$, many chemicals could be used for the cross-linking of soy adhesive. Epoxy [6], aldehyde and its deratives [10] have already been proved effective cross-linkers for soy-based adhesive. With different cross-linkers, the mechanism for the improvement of performance of soy adhesive is different. Epoxy groups are thought to react with all of the aforementioned functional groups in soy proteins [11]. Huang J et al. proposed the possible curing mechanisms of the soy–polyepoxide adhesives [12]. For cross-linker aldehyde and its derivatives, such as urea–formaldehyde, hydroxymethyl phenol, the main reaction group, comes from $-NH_2$ in soy protein.

Besides choosing a suitable cross-linker, its addition amount is very important for the application of soy adhesive. Because of the usage of some expensive cross-linkers, such as epoxy, the cost of soy-based adhesive is greatly dependent on the addition amount of cross-linker. Wood composites bonded with soy protein isolate and Kymene are reported to show shear strengths comparable to or higher than those of composites bonded with phenol–formaldehyde [13]. As a wet-strength agent for paper, Kymene is an aqueous solution of cationic polyamidoamine–epichlorohydrin

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(PAE). However, because of the high dry weight ratio SPI/Kymene 1.33:1, cross-linker Kymene is the most expensive component of the soy-based adhesive. A new curing agent was developed by the same research group from epichlorohydrin and ammonium hydroxide to decrease the cost of soy-based adhesive. But there was still about 14% on dry soy flour weight of this curing agent needed for the preparation of soy-based adhesive and interior plywood [6]. When melamine–urea–formaldehyde (MUF) resin is added to soy-adhesive as a cross-linker, the addition amount of solid MUF is about 40% on solid soy flour or even higher [14,15]. For phenol–formaldehyde, the weight ratio of phenol–formaldehyde to soy adhesive was 30:70 in public reports [16]. In this formulation phenol–formaldehyde had a solid content of 55% and soy solution of 42%.

In this paper, the effects of different cross-linkers on the water resistance of soy-based adhesive were studied. In order to transfer all of the possible hydrophilic groups of soy protein to hydrophobic ones, a hybrid cross-linker was used for the modification of soy-based adhesive. The objectives of this work were as follows: (1) to optimize the proportion of components of hybrid cross-linker; (2) to decrease the addition amount of cross-linker; and (3) to prepare plywood with good water resistance.

2. Materials and methods

2.1. Materials

Defatted soy flour (53.4% protein content) was obtained from Yuxin Soybean Protein Co., Ltd, China. Poplar veneer with a thickness of 1.5 mm and moisture content of 8–10% was purchased for the preparation of plywood. Epoxy resin (EPR) was a commercial product with the name of E-44, whose epoxide number was 0.41–0.47 and softening point was 12–20 °C. All other chemicals mentioned in this work were all of reagent grade.

2.2. Preparation of soy-based adhesive

Soy-based adhesive was prepared according to a method already reported [17]. A three-neck round-bottom flask equipped with a mechanical stirrer, a thermometer and a condenser was charged with water (187 g), sodium dodecyl benzene sulfonate (0.8 g), CaO(1.9 g) and NaOH (3.7 g) to 70 °C. Soy flour (80 g) was then charged to the rapidly stirring solution. The mixture was heated to 90 °C over 15 min, with rapid agitation, and held between 88 °C and 92 °C for 3 h. The mixture was cooled to 35 °C in an ice bath. The solid content of the resulting soy-based adhesive was 30 ± 1%.

2.3. Preparation of melamine–formaldehyde (MF) resin

Formaldehyde 37% (150 g), melamine (80 g) and water (107 g) were charged into a three-neck flask equipped with a mechanical stirrer, thermometer and condenser and then the pH was adjusted to 9.0 with NaOH 30%. The mixture was heated to 85 °C during 20–30 min, and held the temperature for another 30 min. The mixture was cooled to room temperature and kept at pH 9.0 and room temperature.

2.4. Preparation of plywood samples bonded with soy-based adhesive

The soy-based adhesive was mixed well with different cross-linkers just before the preparation of three-layer plywood of dimensions 300 mm × 220 mm × 4 mm. The double sides glue loading was 360 g/m^2. Before sending into the press, the veneers with adhesives were allowed to rest at room temperature for 15 min and were then assembled. The plywood was pressed under pressure of 2 MPa at 160 °C for 8 min. Other press times and press temperatures were also used in this paper.

2.5. Test of dry and wet shear strength of plywood samples

After conditioning in the laboratory for 1 day, the plywood panel was then cut into shear specimens with dimension of 100 mm × 25 mm to determine its shear strength and water resistance. Each specimen has a bonded area of 25 mm × 25 mm. Both dry and wet shear strength of plywood specimens were tested on a WDS-50KN mechanical testing machine. For wet shear strength, the specimens were soaked in (63 ± 3) °C water or in boiling water for determined time. The mean result of 8–10 specimens was considered as the final shear strength. The testing method was referred to Chinese national standard GB/T 9846.3-2004. In this standard, for type II plywood, the specimens were soaked in (63 ± 3)°C water for 3 h. For type I plywood, the specimens should pass water–dry–water cycle. That is to say, the specimens were firstly soaked in boiling water for 4 h, then dried in (63 ± 3) °C for 20 h, and lastly re-applied in boiling water for another 4 h. For both type II and type I plywood, before the measuring by the testing machine, the specimens were taken out of water and left at room temperature for 10 min.

2.6. FT-IR analysis

The oven was preheated to 160 °C. Liquid soy adhesives with or without cross-linkers were put in the oven to a constant weight. The cured soy adhesives were ground into fine powder. 1 g KBr and 0.001 g soy adhesive samples were mixed well for the preparation of KBr pills. The FT-IR spectra were obtained on a Varian 1000 infrared spectrophotometer.

3. Results and discussion

3.1. Effect of cross-linker on performance of soy adhesive-based plywood

Table 1 shows the performance of plywood specimens with soy based-adhesive with or without different amounts of cross-linkers. The cross-linkers used in this work included EPR, MF and their mixture. The dry shear strength for all of the soy-based plywood specimens was good enough to satisfy the requirement of relative Chinese national standard (GB/T 9846.3-2004, ≥ 0.70 MPa). But considering that wood failure for almost all of the specimens is 100%, which meant the measured dry strengths were mainly determined by the strength of wood, it was difficult to see the effects of cross-linker on the dry shear strength of plywood. However, the water resistance of plywood specimens showed big differences with or without cross-linkers. Soy adhesive without cross-linking had no water resistance at all, which was indicated by the 100% delamination of specimens when soaked in 63 °C water for 3 h. All of the three cross-linkers in this work improved the water resistance of soy-based adhesive more or less. When cross-linked with different amounts of EPR, although the wet strength of plywood at 60 °C for 3 h could be measured, it was not enough to meet the requirement of relative standard. More than 50% of the specimens cross-linked by EPR failed the soak test in 63 °C water for 3 h and 100% of the specimens delaminated when the test condition became more severe as in boiling water cycles. With the increase of the addition amount of EPR, the percentage of number of specimens that failed in the soak test to the total number of specimens decreased from 50% to 20%, which indicated the improvement of the water resistance of soy-based adhesive, although their water resistance was not enough to meet the relative standard. Epoxy was assumed to improve the water resistance of soy adhesive because of the reaction between epoxy groups