Effects of Assembly Time on Wet Shear Strength and Formaldehyde Emission of Plywood Bonded by Urea Formaldehyde Resin

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The effects of assembly time on the properties of plywood were investigated in detail in this study. Three-layer plywood was fabricated, and its wet shear strength and formaldehyde emission were measured. The assembly time was varied to create three different assembly conditions (A, B, and C). The assembly condition A consisted of UF resin mixed with NH_4Cl and kept for 0 to 8 h before gluing; the assembly condition B consisted of glued veneer kept in the open air for 0 to 8 h; and the assembly condition C consisted of glued veneer pre-pressed for 0 to 8 h before hot-pressing. The thermal behavior of the adhesive applied through varying assembly times was tested by differential scanning calorimetry (DSC). Results showed that the plywood prepared under condition C exhibited the highest wet shear strength, which was 37% and 18% higher than those under conditions A and B, respectively. The plywood prepared under condition C exhibited the lowest formaldehyde emission, which was 32% and 16% lower than those under conditions A and B, respectively. The DSC results indicated that the curing process consisted of three sections and that the rate of the curing reaction was the fastest in the first section and was similar in the latter two sections.

Keywords: Urea-formaldehyde resin; Assembly time; Wet shear strength; Formaldehyde emission

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INTRODUCTION

Urea formaldehyde (UF) resin is a major adhesive used in the wood composite industry due to its abundance, low cost, and high dry bonding strength. It is widely used in the manufacture of wood-based panels, accounting for about 90% of the total use of wood adhesives.

Recent research has focused on improving the water resistance of the adhesive and reducing the formaldehyde emission from the resulting panels. This has been done by improving the formulation of the adhesive *via* optimization of the synthesis process (Dong *et al.* 2010; Ferra *et al.* 2010; Myers 1984), the addition of modifiers (Ye *et al.* 2012; Zhang *et al.* 2013), and the use of different curing agents (Costa *et al.* 2012; Dong *et al.* 2011). The properties of plywood bonded with UF resin are also related to the assembly process and conditions under which the hot press operates (Jiao *et al.* 2005). It is hypothesized that the wet shear strength and formaldehyde emission from the resulting plywood will be largely affected by the assembly time. It is further hypothesized that the cure characteristics of UF resin are closely related to the bonding performance of the final plywood (Gu *et al*. 2005) and that the quality of the UF resin's cure before hot-pressing will largely affect the flowability, penetrability, and ultimately the wet shear strength of the plywood. Research regarding these topics has not been previously conducted.

In this study, four types of UF resin with final molar ratios (F/U) of 0.9, 1.0, 1.1, and 1.2 were synthesized. Plywoods were bonded under three assembly conditions, and the wet shear strength of and formaldehyde emission from the plywood were tested to evaluate the effects of assembly time on the two properties. The cured adhesive, prepared under varying assembly times, was evaluated using differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Urea (industrial grade, 98%) was purchased from the Henan Zhongyuan Chemical Company. Formaldehyde (aqueous solution, industrial grade, 37%) was purchased from the Guangdong Xilong Chemical Factory. Sodium hydroxide, formic acid, and ammonium chloride (NH_4Cl, analytical grade) were obtained from the Beijing Chemical Factory. Wheat flour was obtained from the Beijing Guchuan Flour Company. Poplar veneers with 8% moisture content were purchased from Hebei province and were cut to a size of 400 × 400 × 1.5 mm.

Synthesis of UF Resins and Performance Test

Four types of UF resins with molar ratios (F/U) of 0.9, 1.0, 1.1, and 1.2 were prepared in the laboratory following the traditional "alkali-acid-alkali" three-step reaction. The resins were labeled UF-0.9, UF-1.0, UF-1.1, and UF-1.2, respectively. Formaldehyde was added once, and urea was added three times (Zhang *et al.* 2013). The physiochemical characteristics of the UF resins were determined according to the National Standard of the People's Republic of China (PRC) GB/T 14074-2006 and are shown in Table 1.

Table 1. Characteristics of UF Resins of Different Molar Ratios

Characteristic	UF-0.9	UF-1.0	UF-1.1	UF-1.2
Solids content (%)	58.4	55.7	55.0	53.9
Free formaldehyde content (%)	0.12	0.19	0.28	0.42
Curing time (s)	95	80	75	65
Viscosity (cP)	46	53	50	58

Plywood Preparation

Three-layer plywood panels were prepared. The adhesive formulation was 100 parts resin, 1 parts ammonium chloride, and 20 parts wheat flour (Zhang *et al.* 2013). The adhesive was applied to one side of a poplar veneer (of size 400 × 400 × 1.5 mm) with a spread rate of 175 g/m^2. Uncoated veneers were stacked between two adhesive-coated veneers with the grain directions of consecutive veneers perpendicular to one another. The stacked veneers were hot-pressed at 1.0 MPa and 120 °C for 6 min. Afterward, the panel was stored in an ambient environment for at least 24 h before evaluation of wet shear strength and formaldehyde emission.

Assembly Condition Arrangement

Three-layer plywood panels were prepared with UF-1.1 under three different sets of assembly conditions, as detailed in Table 2. The plywood prepared under condition A and B used the same hot press condition, following as: the hot press temperature was 120 °C, the hot press pressure was 1.0 MPa, and the hot press time was 6 min. The plywood prepared under condition C was pre-pressed at 1.0 MPa and 20 °C for 30 min before it was hot-pressed. The assembly time was no longer than 8 h because the adhesive becomes too viscous to be applied to the veneers after 8 h and the glued veneer is generally pre-pressed for 8 h in the factory.

Table 2. Assembly Conditions of UF Resins

Sample ID	Assembly conditions	Assembly time (h)				
A	UF resin mixed with NH_4Cl for 0 to 8 h before gluing	0	2	4	6	8
B	Glued veneer kept in the open air for 0 to 8 h	0	2	4	6	8
C	Glued veneer pre-pressed for 0 to 8 h before hot-pressing	0	2	4	6	8

Viscosity Measurement

A portion of the finished glue used in assembly condition A was used for viscosity measurement with a Brookfield viscometer. The spinning rate was 1 rpm, and the average of three replicate measurements taken within 2 min (at 20 °C) was determined.

Testing of the Performance of Plywood

The wet shear strength of plywood was measured in accordance with the National Standard of PRC GB/T 9846.3-2004 for Type II plywood. Six plywood specimens (Fig. 1) per panel were soaked in water at 63 ± 2 °C for 3 h and then dried at room temperature for 10 min before the bonding test was conducted. The wet shear strength was calculated as follows, according to Eq. (1), and the results from the six tested specimens from each panel were averaged.

$$\text{Wet Shear Strength (MPa)} = \frac{\text{Tension Force (N)}}{\text{Gluing Area (mm}^2\text{)}} \tag{1}$$

The formaldehyde emission from the plywood was measured by a desiccator as described in Standard GB/T 9846.3-2004. After storage in a ventilated environment (at 20 °C and 12% relative humidity) for 24 h, plywood specimens were prepared (each 50×150 mm). According to the experience of plywood manufacture in factories, it needed 24 h at least after hot pressing for the plywood cooling down to the room temperature.

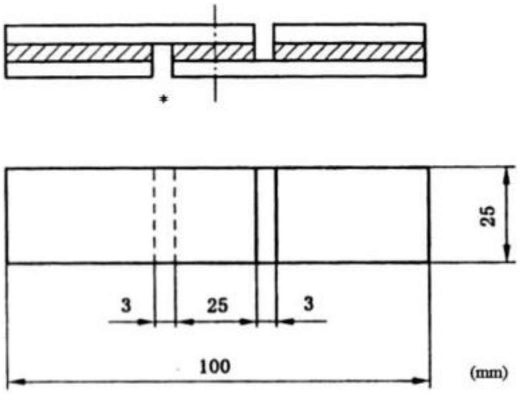

Fig. 1. Sizes of specimen for water resistance test
(* grooves cut only two-third of the way into the core veneer)

Ten specimens from the same panel were put into 9 to 11 liters of formaldehyde solution in a sealed container at 20 ± 2 °C for 24 h. The emitted formaldehyde was absorbed by 300 mL of deionized water in a container. The formaldehyde concentration in the sample solution was determined using acetyl acetone-ammonium acetate solution and the acetyl acetone method, with colorimetric detection at 415 nm. The formaldehyde emission results were the average of three times tested in parallel.

DSC Test

The reactivity change and thermal behavior of the UF resins under varying assembly times were determined using a TA Instruments model Q2000 Differential Scanning Calorimeter (New Castle, DE), which was used to evaluate the curing behavior of UF resin. The thermograms generated during the curing process were analyzed with TA universal analysis software. Resin curing was catalyzed with 1% NH_4Cl. The samples (1.0 to 3.0 mg) were pipetted into high-pressure aluminum pans and sealed with aluminum seals. The closed aluminum pans were then heated from 30 to 160 °C at a rate of 10 °C/min. The DSC results reported are the average of two samples tested in parallel.

RESULTS AND DISCUSSION

Effect of Molar Ratio of UF Resin on Properties of Plywood

The wet shear strength and formaldehyde emission of the plywood manufactured under assembly condition A are shown in Fig. 2. Both wet shear strength and formaldehyde emission decreased with decreasing urea-formaldehyde molar ratio. The plywoods prepared with UF-0.9 and UF-1.0 had low wet shear strength and only partially met the standards (represented by the dotted line at 0.7 MPa) of type II plywood according to GB/T 9846.3-2004. At low molar ratios, the amounts of reactive groups and free formaldehyde in the UF resin were comparatively low, so the curing agent (ammonium salt) reacted with free formaldehyde slowly and could not release enough acid for efficient resin curing. This resulted in lower wet shear strength and formaldehyde emission.

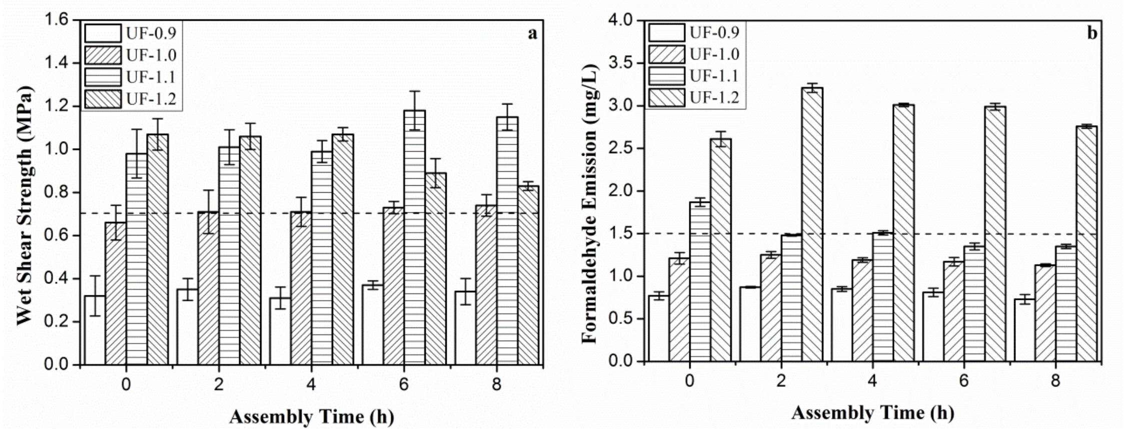

Fig. 2. Wet shear strength (a) and formaldehyde emission (b) of plywood

The plywoods prepared with UF-1.1 and UF-1.2 exceeded the standards required for type II plywood. The UF resins with molar ratios above 1.0 had many more reactive groups (*e.g.*, hydroxymethyl) and enough free formaldehyde to allow the ammonium salt to react with it to release acid, which allowed the UF resins to cure rapidly (Fan *et al*. 2006). As predicted, a high urea-formaldehyde molar ratio yielded excess free formaldehyde and ether bridges, resulting in increased formaldehyde emission from the plywood. However, the viscosity of the adhesive with molar ratio above 1.0 was too high to spread uniformly after 6 h, so they could not form adequate mechanical interlocking between wood surface and adhesive. As a result, the curing process was greatly affected and the wet shear strength decreased. In the following experiment, the UF-1.1 was used to analysis the effect of assembly conditions on the properties of plywood because the wet shear strength and formaldehyde emission of plywood bonded by the adhesive with UF-1.1 was comparable for measure the effect of assembly time on the properties of plywood.

Effect of Assembly Conditions of UF Resin on Properties of Plywood

Figure 3a shows the wet shear strength of plywood prepared under assembly condition A with UF-1.1. The wet shear strength increased by 0.2 MPa as the assembly time increased from 0 to 6 h and reached a maximum of 1.18 MPa at 6 h.

The viscosity of UF-1.1 at 6 h was 3 times higher than that at 0 h (Fig. 4), but after 6 h, the viscosity was too high to measure. Viscosity is an important physical property that controls the adhesive behaviors of wood adhesives (Gao *et al.* 2013). The coating process when using a high-viscosity adhesive became difficult because the adhesive cannot be spread uniformly across a surface. Also, an elevated viscosity of the adhesive reduced the penetration property, which led to form inadequate mechanical interlocking during the hot-pressing process. As a result, the wet shear strength decreased.

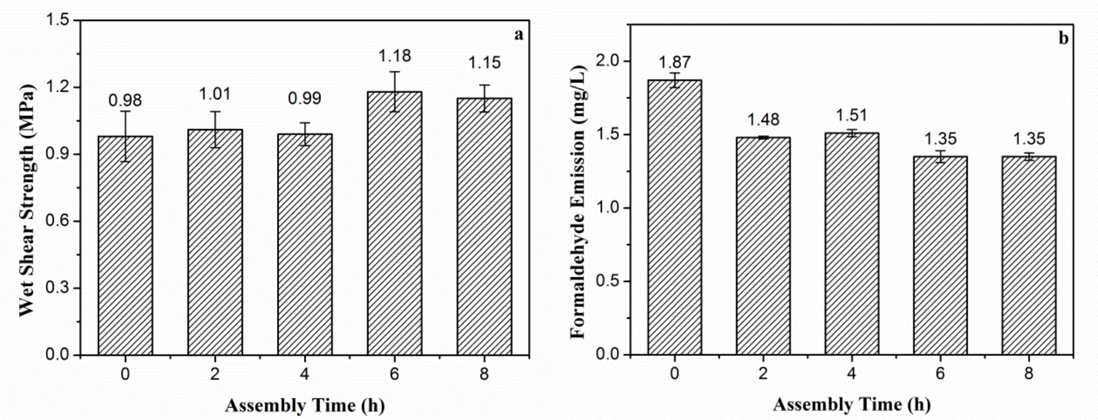

Fig. 3. Wet shear strength (a) and formaldehyde emission (b) of plywood prepared under varying assembly times

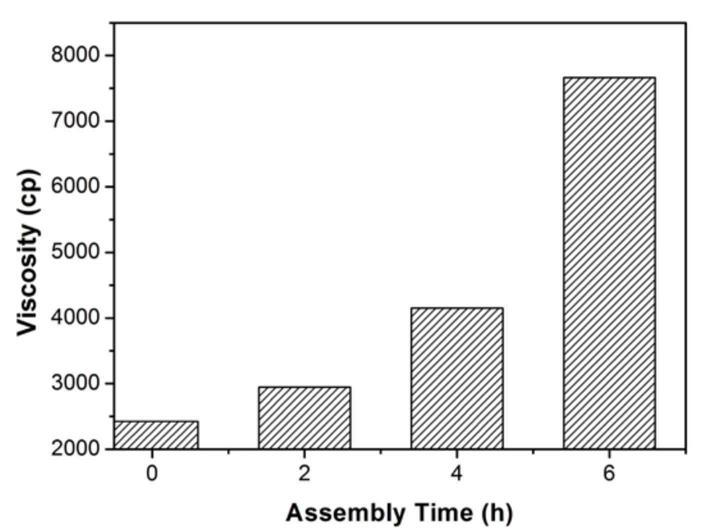

Fig. 4. Viscosity of UF-1.1 prepared under varying assembly times

As shown in Fig. 3b, the formaldehyde emission of plywood prepared under assembly condition A with UF-1.1 decreased from 1.87 to 1.35 mg/L with an increase in assembly time from 0 to 8 h. The measured formaldehyde content represents different sources of formaldehyde: unreacted formaldehyde, that produced by the hydrolysis of methylene-ether bridges, and that produced by the hydrolysis of hexamine (Pizzi and Mittal 1994). Of these sources, only the first two were considered in this study. As the elapsed time increased, some formaldehyde evaporated and more formaldehyde-generated products (*e.g.*, dimethylolurea, monomethlolurea, and hexamine) were formed in the cured adhesive. During this period, the curing reaction was promoted, which could account for the significant decrease in formaldehyde emission from the plywood (Li *et al.* 2007).

Figure 5 shows the effect of assembly time on the wet shear strength of the plywood prepared under condition B using UF-1.1. The wet shear strength improved as the assembly time increase from 0 to 8 h, reaching 1.31 MPa after 2 h. As time elapsed beyond 2 h, the wet shear strength did not noticeably change because the resin viscosity and the spread of adhesive onto the veneers were suitable. The maximum wet shear strength (1.34 MPa) and the minimum formaldehyde emission (1.09 mg/L) under condition B were 14% higher and 20% lower than those of plywood prepared under condition A, respectively. Under condition B, the UF molecules remained on the wood surface and formed a coat which was unable to over-penetrate the veneers whilst exposed to the open air. Further, condition B was conducive for the evaporation of water, which removed a portion of the formaldehyde at high temperatures. Consequently, less formaldehyde was left in the plywood. On the contrary, in the plywood prepared under condition A, excessive penetration of the UF resin into the veneers led to a starved bond line, and insufficient adhesive remained on the surface. This could account for the decrease in wet shear strength (Gu 2012).

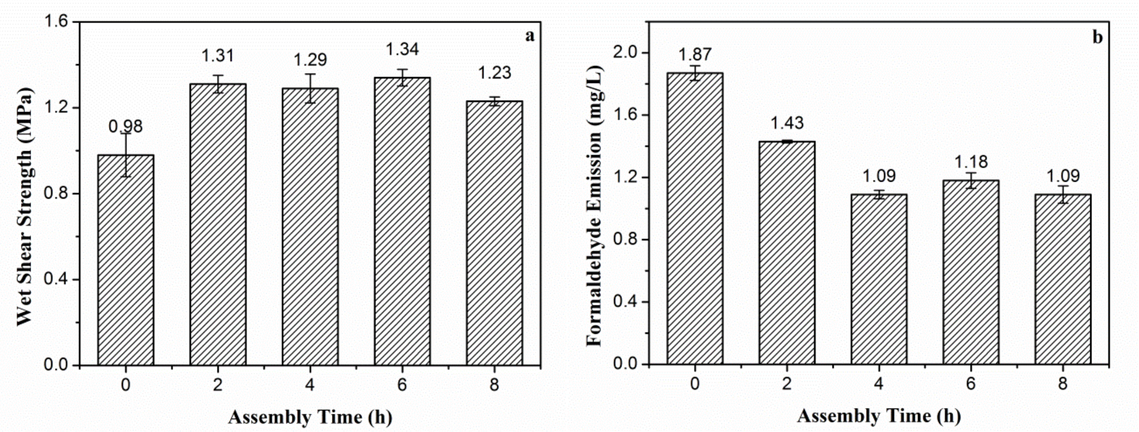

Fig. 5. The wet shear strength (a) and formaldehyde emission (b) of plywood prepared under different assembly times

As shown in Fig. 6a, the wet shear strength of the plywood prepared under condition C with UF-1.1 increased with prolonged assembly time. The wet shear strength increased by 60% from 0 to 8 h of assembly time.

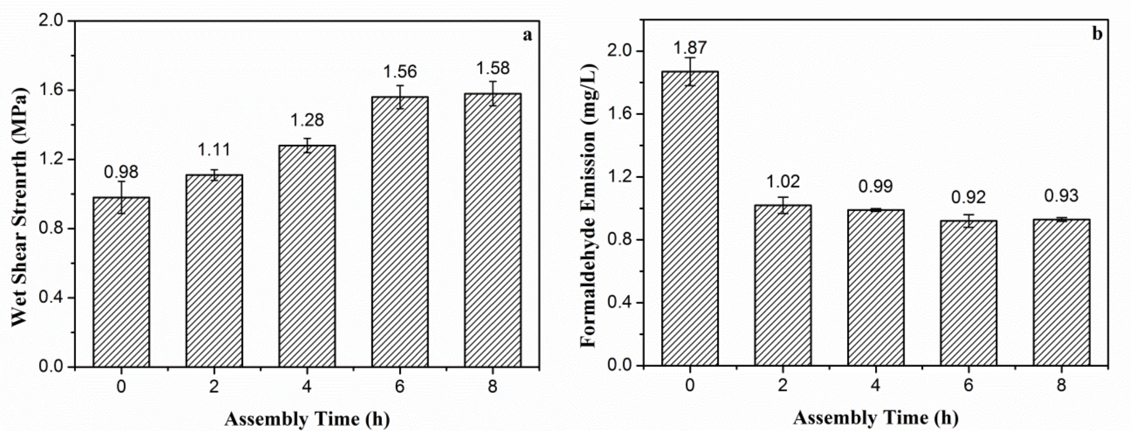

Fig. 6. The wet shear strength (a) and formaldehyde emission (b) of plywood prepared under different assembly times

The maximum value was 37% higher than that of the plywood prepared under condition A. Initially, the molecules of both water and UF were able to penetrate into the veneer easily, due to the low molecular weight and viscosity of UF (I. Gavrilovic-Grmusa *et al*. 2012). During hot-pressing, improved thermal conduction due to the increased moisture content of the veneer favored a more rapid rise in the temperature of the core layer, facilitating more complete curing. The permeability and penetration depth were high under condition C at 20 °C following cold-pressing. These parameters increased with prolonged assembly time (I. Gavrilovic-Grmusa *et al*. 2012).

A suitable assembly time allowed for more adhesive molecules to be pushed into the pores of the wood veneers and to form mechanical interlocks, thereby enhancing the wet shear strength and reducing the formaldehyde emission. As shown in Fig. 6b, the formaldehyde emission decreased from 1.87 mg/L at 0 h to 0.93 mg/L at 8 h. The minimum was 32% higher than that under condition A. As the elapsed time increased, the degree of condensation may have improved. As a consequence, the over-penetration of the adhesive and water into the plywood could be avoided, decreasing formaldehyde emission.

The maximum wet shear strength increased by 18% and the formaldehyde emission decreased by 16%, respectively, under condition C as compared to those under condition B. Under assembly condition B, the penetration depth of the adhesive into the veneer was smaller than that under condition C, and the water in the adhesive was partially volatilized into air (Gavrilovic-Grmusa *et al*. 2010). These two factors led to low moisture content in the veneer, which was the reason why the veneer's thermal conductivity was worse than that under condition C.

DSC Analysis

The dynamic DSC scans for UF-1.1 at varying assembly times are summarized in Table 3, and the DSC curves are shown in Fig. 7. The glued veneers are generally placed for 8 h at most in factory; however, the thermal behavior beyond 8 h of the UF resin also needs to be discussed in the experiment. So, 10 h and 12 h of the assembly time were also tested.

The onset temperature ranged from 69.90 to 83.23 °C and decreased with assembly time. During this process, the peak temperature also decreased from 87.01 to 77.01 °C. Exothermic peaks indicate that the UF resin was preliminarily cured. With the help of NH_4Cl, methylol aided in the synthesis of an ionic carbon intermediate *via* reaction with other methylols or hydrogens on the amide. This formed methylene and ether groups. As a result, the resin changed from a liquid to a solid with an elongated and cross-linked molecular chain, further enhancing its hardness and strength. With increasing temperature, the methylene-ether bond changed into a stable methylene group. During this process, the rearrangement of chemical bonds and the escape of small molecules led to decreased strength and hardness. Finally, with more methylene groups, the hardness and strength rose to stable levels (Wei and Gu 2004).

Table 3. Onset Temperature, Peak Temperature, and Reaction Enthalpy of the UF Resin at Varying Assembly Times

Assembly Time (h)	Onset temperature (°C)	Peak temperature (°C)	Reaction enthalpy (W/g)
0	83.23	87.01	77.4
2	81.21	85.38	63.8
4	78.92	83.62	58.6
6	76.17	81.67	58.5
8	74.51	80.17	57.6
10	71.96	78.35	56.7
12	69.90	77.01	51.6

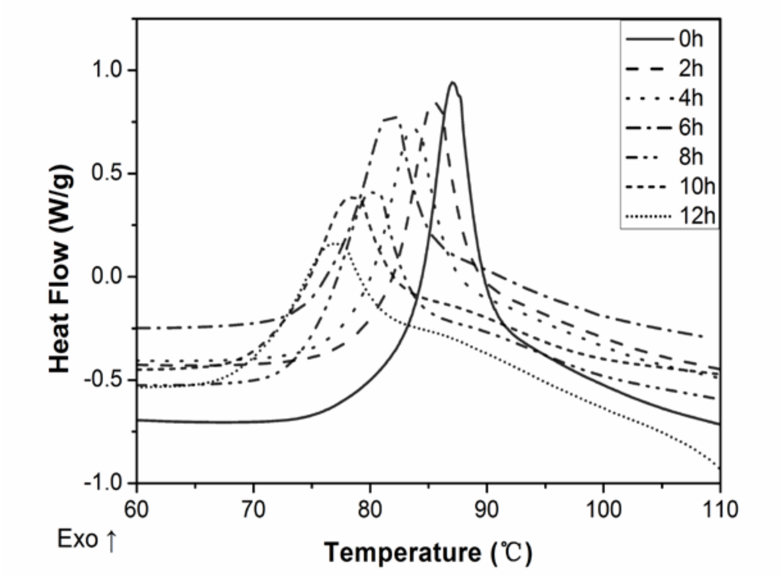

Fig. 7. DSC curve of the UF resin

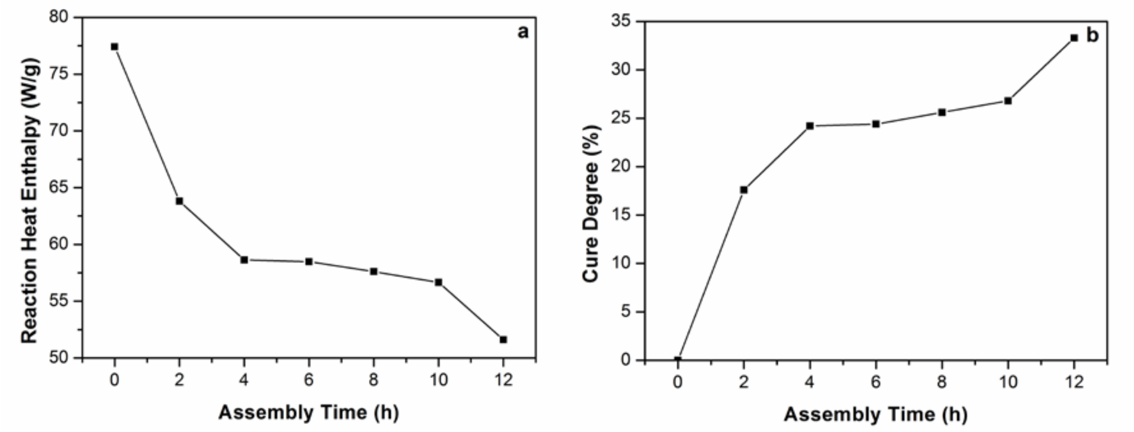

Fig. 8. Effect of assembly time on reaction enthalpy and degree of curing

The effect of assembly time on the UF resin's reaction enthalpy is shown in Fig. 8a. The effects of temperature and time on the degree of curing of UF resin were studied by measuring the amount of reactive groups present. With prolonged assembly time, the reaction enthalpy and the crosslinking cure degree of the reaction represented by the exothermic peaks decreased and the exothermic effect was weakened (Monni *et al.* 2007). The curve indicates that the curing process was composed of three stages. In the first 2 h, the rate of the curing reaction was comparable to that of section three (from 4 to 12 h), and the rate in section two (from 2 to 4 h) was lower than that in section three.

Based on the values of reaction enthalpy obtained at varying assembly times, the resin cure degree P_i (%) at elapsed time *i* (hours) after blending can be calculated as follows,

$$\mathrm{Pi}(\%)=\frac{\Delta \mathrm{H0}-\Delta \mathrm{Hi}}{\Delta \mathrm{H0}}\times 100 \qquad (2)$$

where ΔH_0 is the total reaction heat immediately after blending, ΔH_i is the total reaction heat at *i* h elapsed time after blending, and *i* is the of time elapsed after blending, in hours.

The relationship between P_i and assembly time is shown in Fig. 8b. The P_i of UF resin ranged from 0 to 33.3% and increased with assembly time. The curing reaction was composed of three sections, as previously discussed, which was due to two reasons. First, water in UF resin played a vital role as a diluter or plasticizer, as a function of water content and curing stage. The water in the UF resin also decreased the concentrations of the reactants. At the beginning of the cure, the UF resin contained too much water, which sped up the curing reaction by diluting the resin (Xing *et al*. 2004). Second, after the adhesive was allowed to cure for hours, much of the water in the UF resin evaporated and the viscosity increased. The activity of UF molecules was weakened, indicating that the rate of curing slowed down. These two reasons could explain why the rate of the resin curing reaction was fastest at the beginning of curing and decreased after 2 h. With the advancement of the curing process after 2 h, larger molecular chains were formed, which reduced the rate of the resin curing reaction.

CONCLUSIONS

1. With prolonged assembly time, the wet shear strength of plywood prepared under conditions A, B, and C (for the UF resin mixed with NH_4Cl keeping for 0 to 8 h before gluing, the glued veneer kept in the open air for 0 to 8 h, and the glued veneer pre-pressed for 0 to 8 h before hot-pressing, respectively) improved from 0.98 to 1.18, 1.34, and 1.58 MPa, respectively. The maximum wet shear strength under condition C was 37% and 18% higher than those under conditions A and B, respectively.
2. With prolonged assembly time, the formaldehyde emission of plywood prepared under conditions A, B, and C decreased from 1.87 to 1.35, 1.09, and 0.92 mg/L, respectively. The minimal formaldehyde emission under condition C was 32% and 16% higher than those under conditions A and B, respectively.

3. The DSC characterization results indicate that the curing process includes three sections. The rate of the curing reaction was the highest in the beginning of the cure, but the rates at the second and the third stages were very similar to each other.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Beijing Municipal Education Commission Science Research and Graduate Student Construction Projects - “Property and application performance of the integrated timber with fast-growing wood.”

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Article submitted: January 10, 2014; Peer review completed: March 23, 2014; Revised version received and accepted: March 28, 2014; Published: April 8, 2014.