Mechanics and Crystallinity/Thermogravimetric Investigation into the Influence of the Welding Time and CuCl₂ on Wood Dowel Welding

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Mechanical properties of wood dowel welding were studied using untreated and copper chloride (CuCl₂)-treated wood dowels. The effect of the welding time (3 s, 5 s, and 7 s) was also studied. The treated wood dowels with a welding time of 3 s had the best pullout resistance. Fibers covered with black molten material generated by the high friction temperature were found at the welding interfaces. For the untreated groups, the degree of crystallinity of the welding interfaces was higher than that of the wood dowel. For the treated groups, the degrees of crystallinity for the welding times of 5 s and 7 s were lower than that of the wood dowel. By extending the welding time, the degree of crystallinity decreased. A thermogravimetric (TG) analysis was used to detect changes in the wood components. The hydrolysis of cellulose and hemicellulose occurred during immersion. The analyses illustrated that pyrogenic decomposition of the wood components occurred during the wood dowel welding process. For the treated groups, the degree of pyrolysis was higher than that of the untreated groups for the same welding time. An increased welding time also promoted pyrolysis during the welding process.

Keywords: Wood dowel welding; Pullout resistance; Welding time; CuCl₂; Pyrolysis

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INTRODUCTION

Wood dowel welding creates a new bonding interface layer through the friction between the wood dowels and substrate holes. During this process, some wood components are softened, fused, and eventually become solidified until the friction stops (Sandberg *et al.* 2013; Zhou *et al.* 2014).

With a slow inserting speed, the welding time increases and more friction occurs between the wood dowels and substrate holes, which results in more molten materials being generated and increased frictional weight loss of the wood dowels. In the study by Belleville *et al.* (2013b), the optimum inserting speeds for maple and birch were 25 mm/s and 16.7 mm/s, respectively. No obvious difference was found between the inserting speeds of 16.7 mm/s and 25 mm/s for birch. However, specimens could not be prepared at a rotation speed of 1000 rpm and inserting speed of 25 mm/s. The welding process generated a lot of smoke and carbonization at a rotation speed of 2500 rpm and inserting speed of 12.5 mm/s. These phenomena illustrated that the inserting speed is an important factor. For wood dowel welding, the inserting speed is referred to as the welding time (Belleville *et al.* 2013b).

The friction generated between the wood dowels and substrate holes can cause the temperature to rapidly increase. Using the theoretical formula from Zoulalian and Pizzi (2007), it was found that the highest temperature at the welding interface could reach 183 °C using the optimum parameters for beech. However, Rodriguez *et al.* (2010) found that the highest temperatures for birch and maple were over 300 °C. Another study showed that the temperature could be influenced by the rotation speed. For both birch and maple, the temperature could reach 244.1 °C and 282.6 °C at 1000 rpm, 281.1 °C and 297.4 °C at 1500 rpm, and 328.6 °C and 327.3 °C at 2500 rpm, respectively. Meanwhile, both birch and maple specimens showed the best pullout resistance at temperatures of 244.1 °C and 282.6 °C, respectively, and a rotation speed of 1000 rpm (Belleville *et al.* 2013b). According to this analysis, with an increased rotation speed, the temperature at the welding interface could reach 300 °C and the pullout resistance could be affected by the temperature.

Under the action of high friction temperature, pyrolysis occurs at the welding interface. This is considered to be a non-volatilization conversion of materials into volatile mixtures (Sun et al. 2010). Because of the high crystallinity, cellulose is relatively stable at high temperatures. It can be pyrolyzed at approximately 300 °C to 340 °C. However, the amorphous region of cellulose is similar to hemicellulose, which can be depolymerized and pyrolyzed at approximately 225 °C (Fengel and Wegener 1984). Lignin is affected over a wide temperature range. When the temperature is between 50 °C and 200 °C, endothermic reactions with lignin occur, and exothermic reactions can happen above 200 °C (Sun et al. 2010). Based on the summary above, the highest temperature that can be reached at the welding interface is 300 °C. At this temperature, lignin, hemicellulose, and other amorphous materials can be pyrolyzed into flowing materials (Stamm et al. 2006; Delmotte et al. 2008; Rodriguez et al. 2010; Belleville et al. 2013a). Most of the flowing materials are composed of xylans and lignin. Recrystallized xylans and furanic compounds are generated from the pyrolysis of carbohydrates (Pizzi et al. 2006). The smoke generated from the welding process is composed of water vapor, carbon dioxide, and other nontoxic volatile degradation compounds (Omrani et al. 2008).

Welded joints can be successfully manufactured, but the bonding strength is lower than that of structural adhesives. Therefore, many studies have been conducted to improve the pullout resistance of welded joints. Smaller diameters for the substrate hole and dry wood dowel, and non-vertical welding could improve the pullout resistance (Pizzi *et al.* 2004; Kanazawa *et al.* 2005). In addition to the physical enhancement methods mentioned above, chemical enhancement methods have been performed in several studies. Wood dowels immersed in ethylene glycol can potentially decrease the glass transition temperature, but the liquid decreased the friction between the wood dowel and substrate hole, which resulted in poor welding with a worse pullout resistance (Pizzi *et al.* 2004). Welding joints pretreated with citric acid, a lignin additive, and wood extractives additive could improve the pullout and water resistances (Pizzi *et al.* 2011, 2013; Peña *et al.* 2015, 2016; Amirou *et al.* 2017).

CuCl₂ solution is weakly acid. It performed in a similar role to citric acid, which was used in the study of Amirou *et al.* (2017). The surface layer of wood dowel could be softened by acid corrosion during immersing in CuCl₂ solution. And then the surface layer of wood dowel could provide more molten materials to form a welding interface. So in this study, 0.1 mol/L CuCl₂ solution was used to chemically enhance properties of wood dowel welding. In previous studies, for welding depths of 30 mm, 12-mm diameter wood dowels with a 2% moisture content (MC) immersed in CuCl₂ for 7 d improved the

pullout resistance 23.86%, but the tensile strength of the wood dowels decreased 50%. This was difficult to manufacture specimens with 12-mm diameter wood dowels (Stamm *et al.* 2011; Zhu *et al.* 2017a). Therefore, 10-mm diameter wood dowels with a 2% MC immersed in CuCl₂ for 30 min were used in this study. The tensile strength of the wood dowels did not remarkably decrease. In addition, the presence of Cu²⁺ could improve the insect resistance ability of welded joints. Meanwhile, the temperature at the welding interface was measured and analyzed.

Based on the method of treating with CuCl₂ and using different welding times, the pullout resistance of the welded joints was tested. The Weibull distribution was applied to study the pullout resistance and 0.05 fractile of the pullout resistance, which are widely used in the construction field. The degree of crystallinity was measured using X-ray diffraction (XRD) analysis to study the variety of the amorphous materials during the immersing and welding process. The chemical changes were determined using TG analysis. These analyses were used to assess the performance of the wood dowel welding (Delmotte *et al.* 2008; Segovia *et al.* 2009; Belleville *et al.* 2013a; Zhu *et al.* 2017b).

EXPERIMENTAL

Materials

Wood dowels, 10 mm in diameter and 100 mm in length, were fabricated from birch wood (*Betula pendula*; Crownhomes, Jiangsu, China). The air dried density at 12% MC of the birch dowel was 557 kg/m³. Chinese larch (*Larix gmelinii*; Crownhomes, Jiangsu, China) slats with the dimensions of 40 mm (Tangential, T) × 50 mm (Radial, R) × 500 mm (Longitudinal, L) were used as substrates. The air dried density at 12% MC of the larch was 680 kg/m³.

All of the wood dowels were placed in an oven at 63 °C until a 2% MC was reached. The tensile strength of the wood dowels was 4864 N. Half of the wood dowels were immersed in 500 mL of 0.1 mol/L CuCl₂ solution for 30 min at 20 °C and 60% relative humidity (RH). After immersion, the wood dowels were placed in an oven until the MC was 2% again. The tensile strength of the wood dowels treated with CuCl₂ was 4791 N. The decision to use the temperature of 63 °C was based on preliminary experiments. It was found that the wood dowels could achieve the desired MC over 2 d at that temperature with minimal warping or cracking. All of the substrates were exposed to a temperature of 20 °C and RH of 60% until reaching a 12% equilibrium MC.

Specimen preparation

The wood substrates were pre-drilled with holes 8 mm in diameter and 30 mm in depth using a drilling machine (Proxxon TBH Typ 28 124, Proxxon, Stuttgart, Germany). Next, the wood dowels were welded into the pre-drilled holes in the substrates to create bonded joints at a high-speed rotation of 2400 rpm (Leban *et al.* 2008). The inserted part of the dowel became conical in shape (Fig. 1). Black molten material spilled out of the welding interfaces (Fig. 2) because of the different abrasion levels during the welding process. Rotation of the wood dowel stopped when fusion and bonding was achieved after 3 s, 5 s, and 7 s (Belleville *et al.* 2013). Thirty specimens were prepared for each group, but several specimens were broken during welding or the testing process. Groups A, B, and C were manufactured from the untreated wood dowels (untreated groups), and

groups D, E, and F were manufactured from the CuCl₂-immersed wood dowels (treated groups).



Fig. 1. Conical shape of the welding interfaces after different welding times: a) 3 s; b) 5 s; and c) 7 s



Fig. 2. Black molten material that spilled out of the welding interface for the untreated groups

Methods

Pullout resistance test

After welding, the wood slats were cut into 10 parts that were even in length, so that every welded dowel was 40 mm (T) \times 50 mm (R) \times 50 mm (L) in size. The specimens were conditioned at 20 °C and 60% RH for 7 d before the tests were conducted.



Fig. 3. WDW-300E universal testing equipment

The pullout resistance of the specimens was tested using a universal testing machine (Fig. 3, WDW-300E; Jinan Popwil, Jinan, China) that pulled the welded wood

dowels out of the substrate at a speed of 2 mm/min (O'Loinsigh *et al.* 2012). The specimens were fixed by clamping the dowel into the jaw of a fixed beam, while the substrate block was fixed to a mobile beam *via* a metal framework.

Weibull distribution analysis

The reliability and 0.05 fractile analysis of data have been widely used in the construction filed. In this study, the Weibull distribution was applied to study the reliability of pullout resistance, and the 0.05 fractile of pullout resistance was calculated. The Weibull distribution function (F(x)) was determined according to Eq. 1, and the probability density function (f(x)) was calculated according to Eq. 2, which was transformed by a differential of Eq. 1,

$$F(x) = 1 - e^{-\left(\frac{x - a_0}{\beta}\right)^{\alpha}} \tag{1}$$

$$f(x) = \frac{\alpha}{\beta} \times \left(\frac{x - a_0}{\beta}\right)^{\alpha - 1} \times e^{-\left(\frac{x - a_0}{\beta}\right)^{\alpha}}$$
(2)

where α , β , and a_0 are the shape, scale, and location parameters, respectively. The reliability of the data was shown with α . The variable *x* is the pullout resistance, and $\left(\frac{x-a_0}{a}\right)^{\alpha}$

 $e^{-\left(\frac{x-a_0}{\beta}\right)^{\alpha}}$ is the probability of the random pullout resistance being bigger than *x*.

Sample preparation for XRD and TG analyses

The XRD analysis, used to determine the degree of crystallinity, was performed on a TWIST-TUBE X-ray diffractometer (Bruker D8 ADVANCE, Bruker, Karlsruhe, Germany) using Cu K α radiation (40 kV, 200 mA), from 5° to 40° with a step size of 8°/min. The samples prepared for the XRD analysis included the wood dowels and welding interfaces. Each sample was prepared by scraping and mixing the powders from all of the relative tested specimens in a uniform manner. The powders were collected by scraping the black welding material, especially for the welding interfaces. All of the powder from each sample was uniformly stirred and blended. Then, the powders were dried to a 0% MC at 100 °C before testing.

The programmed heating pyrolysis of the wood dowels and welding interfaces was performed on a NETZSCH STA 449F3 simultaneous thermal analyzer (Netzsch, Selb, Germany). The samples in the crucible for the TG analysis were heated from 50 °C to 600 °C at a heating rate of 10 °C/min. Purified nitrogen was used as the carrier gas to provide an inert atmosphere. The samples were similarly prepared for the XRD analysis. The TG analysis was performed using 10 mg of powder for each test (Hu *et al.* 1998; Tan *et al.* 2006).

RESULTS AND DISCUSSION

Pullout Resistance and Interface Morphology

The pullout resistances of the welded specimens are summarized in Table 1. Group D with the $CuCl_2$ -immersed wood dowels and a welding time of 3 s showed the highest pullout resistance. Group C with the untreated wood dowels and a welding time of 7 s showed the lowest pullout resistance.

A welding phenomenon was observed for the untreated groups. A little amount of black molten material spilled out of the welding interfaces for group A, and lots of molten material spilled out of the welding interfaces for groups B and C, along with smoke and a scorched smell (Fig. 2). Because of the spilled molten material, the pullout resistance of group A was 28.33% and 87.12% higher than that of groups B and C, respectively. All of the specimens for each group were cut into two pieces down the middle (Fig. 1). The size of the welded dowels at the middle was measured (Fig. 1). Group A had the largest size, and group C had the smallest, which could have been why group A had the highest pullout resistance. Meanwhile, cracks were found in the welding interfaces of group C, which resulted in the worst pullout resistance. Based on these analyses, it was concluded that a welding time of 3 s was the best welding time for the untreated groups. With an extended welding time, more molten material spilled out, and cracks were generated at the welding interface, which decreased the bonding strength.

The pullout resistance of the treated groups was 68.28%, 34.08%, and 36.62% higher than that of the untreated groups at the welding times of 3 s, 5 s, and 7 s, respectively. Figures 2 and 4 show that different phenomena were seen with the black molten material that spilled out of the welding interfaces. From Fig. 2, the black material was a disperse powder for the untreated groups. However, the material was observed to be a continuous sheet in Fig. 4. This resulted in a better bonding strength for the treated groups. According to the pullout resistance analysis and welding phenomena, the treatment method of immersing the wood dowels in CuCl₂ could improve the bonding strength of the welding interface between the wood dowel and substrate hole.

Croup	Treated	Welding	Maximum	Minimum	Mean Value	COV ²	Number of
Gloup	with CuCl ₂	Time (s)	Value (N)	Value (N)	(N)	(%)	Specimens
Α	No	3	3602	2072	2790 (444) ¹	15.92	25
В	No	5	3024	1056	2174 (553)	25.45	20
С	No	7	2434	722	1491 (509)	34.15	17
D	Yes	3	6094	3006	4695 (714)	15.21	26
E	Yes	5	3836	1584	2915 (709)	24.34	19
F	Yes	7	2614	1208	2037 (428)	21.01	17

Table 1. Pullout Resistance of the Welded Specimens for Each Group

¹ - Values in parentheses are the standard deviation; ² – coefficient of variation

For the treated groups, the welding time was an important influencing factor. From Table 1, the pullout resistance of group D was 61.06% and 130.49% higher than that of groups E and F, respectively. Figure 4 shows that the molten material had different performances. Similar to the untreated groups, a little molten material spilled out of the welding interface at a welding time of 3 s, and a lot of molten material spilled out at welding times of 5 s and 7 s, which resulted in a better bonding strength for group D. For groups D and E, continuous sheets of black material were found at the welding interfaces, especially for group E. However, for group F, more molten material spilled out of the welding interface as threads and sheets, which resulted in the lowest bonding strength of the treated groups.

Figure 5a shows the transversal arrangement of the long fibers caused by tearing and pulling vertical fibers from the wood dowel and substrates during the welding process; these fibers were covered with molten material. During the testing process, excellent tensile fiber strengths did not affect the pullout resistance. The bonding strength of the molten material was the main source of the pullout resistance. The interface shown in Fig. 5b showed a similar phenomenon to the one seen in Fig. 5a, except for two differences. First, the length of the fiber for group B was shorter than that of group A because of the longer friction welding time. Second, the failure mode of the welding interface was different. The molten material in the group A interface was broken with the whole block, but a laminated fracture occurred in group B due to weaker bonding at the interface. Almost no obvious fiber could be seen at the interface in Fig. 5c, and the molten material was broken into many small pieces, which resulted in the weakest bonding strength.

For the treated groups (Figs. 5d to 5f), vertical and long fibers covered by molten material could be found at the welding interfaces. During the testing process, the tensile strength of the fiber contributed to the pullout resistance, which resulted in the highest pullout resistance observed in this study. In Fig. 5e, group E showed the same interface morphology as group A. Therefore, the pullout resistance of group E was comparable to that of group A. Meanwhile, group F showed the same interface morphology as group B. According to these results, immersing the wood dowels in CuCl₂ improved the bonding strength of the welding interface. Thirty replicate specimens were initially manufactured for each group, but several specimens were broken during welding or the testing process. With longer welding time, the number of broken specimens increased for both the untreated and treated groups, especially for the welding time of 7 s. It was concluded that a welding time of 3 s was the best time for both the untreated and treated groups in this study.



Fig. 4. Black molten material that spilled out of the welding interfaces for the treated groups: a) group D; b) group E; and c) group F



Fig. 5. Microcosmic morphology of each group: a) group A; b) group B; c) group C; d) group D; e) group E; and f) group F

Weibull Distribution of the Pullout Resistance

All of the specimens were broken during the resistance tests by 120 s. In this study, an a_0 of 0 was reflected. The Weibull distribution function was then rewritten as follows:

$$1 - F(x) = e^{-\left(\frac{x}{\beta}\right)^{\alpha}}$$
(3)

Once the logarithm of both sides was taken, Eq. 3 became:

$$\ln\left[-\ln\left(1-F(x)\right)\right] = \alpha \ln x - \alpha \ln \beta \tag{4}$$

In the regression inspection graph of the Weibull distribution (Fig. 6), $\ln x$ and $\ln[-\ln(1-F(x))]$ were set as the X- and Y-coordinates, respectively. Equation 4 was rewritten into the linear form given in Eq. 5,

$$Y = bX + a \tag{5}$$

where *b* is α , and *a* is $-\alpha \ln \beta$.



Fig. 6. Regression inspection of the Weibull distribution for each group

For the six welded groups, six equations were obtained from Fig. 6. All of the correlation coefficients for the six linear equations were more than 90%. Therefore, the pullout resistances for all six welded groups complied with the Weibull distribution.

Y = 6.8061X - 54.4453	(Group A)	(6)
Y = 3.8422X - 29.9128	(Group B)	(7)
Y = 2.8949X - 21.5019	(Group C)	(8)
Y = 6.9013X - 58.7951	(Group D)	(9)
Y = 3.8481X - 31.0933	(Group E)	(10)
Y = 4.6501X - 35.8406	(Group F)	(11)

Table 2. Parameters α , β , and 0.05 Fractile of the Pullout Resistance for Each Welded Group

Group	α	β	0.05 Fractile of the Pullout Resistance (N)
A	6.8061	2979.29	1926
В	3.8422	2405.19	1110
С	2.8949	1681.67	603
D	6.9013	5011.09	3259
E	3.8481	3229.53	1493
F	4.6501	2225.14	1175

With Eqs. 6 through 11, the α and β parameters were calculated and are shown in Table 2. From Table 2, the α of the 3-s welding time was bigger than for the welding times of 5 s and 7 s for both the untreated and treated groups. According to this, the pullout resistance of the 3-s welding time groups showed the best reliability, which was also certified by the coefficient of variation given in Table 1.

The Weibull distribution function (F(x)) and probability density function (f(x)) could be calculated by inputting the α and β parameters for each group, as shown with Eqs. 12 through 23. Using the design code for wood science and construction, design values were applied. For the test data, the design value meant a 0.05 fractile value, which could be calculated with Eqs. 12 through 23 for each group. The 0.05 fractile values are shown in Table 2. For the untreated and treated groups, groups A and D with the 3-s welding time showed the highest 0.05 fractile values, respectively. For the same welding time, the 0.05 fractile values for the treated groups were higher than for the untreated groups. Therefore, the regularities of the 0.05 fractile value distribution were similar to the mean values.

Group A:

$$F(x) = 1 - e^{-\left(\frac{x}{2979.29}\right)^{6.8061}}$$
(12)

$$f(x) = 2.28447 \times 10^{-3} \times \left(\frac{x}{2279.29}\right)^{5.8061} \times e^{-\left(\frac{x}{2279.29}\right)^{6.8061}}$$
(13)

Group B:

$$F(x) = 1 - e^{-\left(\frac{x}{2405.19}\right)^{3.8422}}$$
(14)

$$f(x) = 1.597 \times 10^{-3} \times \left(\frac{x}{2405.19}\right)^{2.8422} \times e^{-\left(\frac{x}{2405.19}\right)^{3.8422}}$$
(15)

Group C:

$$F(x) = 1 - e^{-\left(\frac{x}{1681.67}\right)^{2.8949}}$$
(16)

$$f(x) = 1.721 \times 10^{-3} \times \left(\frac{x}{1681.67}\right)^{1.8949} \times e^{-\left(\frac{x}{1681.67}\right)^{2.8949}}$$
(17)

Group D:

$$F(x) = 1 - e^{-\left(\frac{x}{5011.09}\right)^{6.9013}}$$
(18)

$$f(x) = 1.377 \times 10^{-3} \times \left(\frac{x}{5011.09}\right)^{5.9013} \times e^{-\left(\frac{x}{5011.09}\right)^{6.9013}}$$
(19)

Group E:

$$F(x) = 1 - e^{-\left(\frac{x}{3229.53}\right)^{3.8481}}$$
(20)

$$f(x) = 1.192 \times 10^{-3} \times \left(\frac{x}{3229.53}\right)^{2.8481} \times e^{-\left(\frac{x}{3229.53}\right)^{3.8481}}$$
(21)

Group F:

$$F(x) = 1 - e^{-\left(\frac{x}{2225.14}\right)^{4.6501}}$$
(22)

$$f(x) = 2.09 \times 10^{-3} \times \left(\frac{x}{2225.14}\right)^{3.6501} \times e^{-\left(\frac{x}{2225.14}\right)^{4.6501}}$$
(23)

XRD Analysis

Figures 7 and 8 show a peak near a 2θ value of 22° and a minimum near a 2θ value of 18° . The degree of crystallinity was measured by the index of crystallinity, which was calculated by the occupancy extent of the crystalline region of the specimen (Isogai and Usuda 1990). This study used the method from Segal *et al.* (1959) (Eq. 24) to calculate the degree of crystallinity ($C_{\rm rI}$) of the wood dowel and welding interfaces,

$$C_{rI} = \frac{(I_{002} - I_{am})}{I_{002}} \times 100\%$$
(24)

where I_{002} is the maximum intensity of the crystal diffraction angle near a 2θ of 22° and I_{am} is the minimum intensity of the amorphous diffraction angle near a 2θ of 18° .

The degree of crystallinity for each group is shown in Table 3. The test diffraction curves of the untreated and treated groups are shown in Figs. 7 and 8, respectively, and some noticeable areas that indicated chemical changes were labelled.

From Fig. 7, all four samples showed three obvious diffraction peaks at 15.5° , 22° , and 34.5° . From Table 3, the degrees of crystallinity for the wood dowel, group A, group B, and group C were 24.5, 33.6, 31.1, and 30.5, respectively. Compared with the calculated data, all of the degrees of crystallinity increased after the wood dowel welding process. Both thermal pyrolysis and structural rearrangement played an important role in determining the content of the crystalline region. The ruptured cellulose chain caused by the high temperatures resulted in a decreased crystallinity. However, some reactions resulted in improved degrees of crystallinity. The -OH group between the cellulose chains was dehydrated by a crosslinking reaction that caused the microfibril to be arranged in an orderly fashion. Additionally, the amorphous region of the cellulose crystallized because of a rearrangement of the molecular chain.

For group A, the intensities of the diffraction peaks at 15.5° and 22° were more obvious and narrow than for the wood dowel. This may have been caused by the

pyrolysis of hemicellulose and other amorphous materials, which resulted in an increased relative amount of crystal cellulose. The diffraction peak curve at 30° may have been caused by the formation of other crystal materials. A transition layer was found at the peak at 20.5° due to the pyrolysis of crystal cellulose at high temperatures. During the welding process, the highest temperature reached was 344 °C, and the pyrolysis temperature of cellulose is 325 °C. Therefore, crystal cellulose was pyrolyzed during the welding process. However, the welding temperature was above 325 °C for less than 1 s, which resulted in only a small amount of crystalline cellulose being pyrolyzed. For groups B and C, the XRD curves were similar to that of group A. By extending the welding time, the temperature was kept above 325 °C at the welding interfaces for 5 s and 6 s for groups B and C, respectively. Based on this temperature distribution for groups B and C, the diffraction peaks at 15.5° and 22° were weaker than those of group A because of the increased pyrolysis of crystal materials. Therefore, increasing the welding time decreased the degree of crystallinity because of the pyrolysis of crystal cellulose. However, the molten material that spilled out of the welding interfaces could not be pyrolyzed further at high temperatures, and this caused the degree of crystallinity to only slightly decrease.



Fig. 7. XRD curves of the wood dowel and welding interfaces for the untreated groups



Fig. 8. XRD curves of the wood dowel and welding interfaces for the treated groups

All of the samples also showed three obvious diffraction peaks at 15.5° , 22° , and 34.5° in Fig. 8. Another diffraction peak was found at 28.5°, which indicated the presence of CuCl₂ in the wood dowel and welding interfaces after immersion. As given in Table 3, the degrees of crystallinity for the wood dowel, wood dowel immersed in CuCl₂, group D, group E, and group F were 24.5, 27.6, 29.0, 20.5, and 18.5, respectively. Compared with the calculated data, the degree of crystallinity of the wood dowel increased after immersion. The hemicellulose and other amorphous materials of the wood dowel were hydrolyzed in the acidic CuCl₂ solution, and this resulted in the relative amount of crystal cellulose. For group D, the degree of crystallinity was slightly higher than that of the wood dowel immersed in CuCl₂. The reasons for this phenomenon were similar to those for the phenomenon seen for the untreated groups. By extending the welding time, the degrees of crystallinity of groups E and F were smaller than that of the wood dowel immersed in CuCl₂. From Table 3, the degrees of crystallinity for the untreated groups were higher than those of the treated groups. The highest temperature at the welding interfaces for the untreated groups was 344 °C, and that of the treated groups was 290 °C. The long cellulose chains were broken into short chains, and the hemicellulose was hydrolyzed into polysaccharose substances. Meanwhile, the cleavage of ether bonds between the lignin and polysaccharose occurred during immersion. Therefore, the wood components of the treated groups were hydrolyzed during the CuCl₂ immersion process and resulted in a decreased pyrolysis temperature. The temperature of the welding interfaces for the treated groups was lower than for the untreated groups during the welding process, but the pyrolysis degree of the treated groups was higher than for the untreated groups.

Based on the discussion above, the pyrolysis degree of the treated groups was much higher than for the untreated groups, especially for the crystal materials. From Fig. 5, the pullout resistance was determined by the bonding strength of the molten material. From Figs. 2 and 4, it was determined that the bonding strength of the treated groups was higher than that of the untreated groups. Therefore, the higher pyrolysis degree caused by acid hydrolysis could have improved the pullout resistance in this study.

Group	Wood Dowel	Wood Dowel- CuCl ₂	А	В	С	D	Е	F
Relative Crystallinity (%)	24.5	27.6	33.6	31.1	30.5	29.0	20.5	18.5

Table 3. Relative Crystallinity of the Wood Dowel and Welding Interfaces

TG/Differential Thermogravimetric Analysis

From the TG curves in Fig. 9a, it was determined that the thermal events occurred in three stages: (1) slow weight loss below 225 °C due to moisture evaporation and pyrolysis of the wood extractives; (2) major weight loss from 225 °C to 390 °C due to the pyrolysis of cellulose, hemicellulose, and lignin; and (3) slow and continuous weight loss above 390 °C due to the decomposition of small lignin and wood extractives. During the major weight loss process, hemicellulose decomposed over the temperature range of 225 °C to 325 °C, and the temperature for the fastest pyrolysis rate was approximately 265 °C. Over the range of 325 °C to 390 °C, the pyrolysis of cellulose occurred, with the fastest pyrolysis rate occurring at 350 °C. For the lignin and wood extractives, pyrolysis occurred from 200 °C to 500 °C and 150 °C to 600 °C, respectively. After the TG analysis, the products from the pyrolysis of cellulose and hemicellulose were mainly volatile compounds. In the case of lignin, pyrolysis primarily resulted in

carbonization. Most of the lignin and wood extractives were turned into solid compounds by high aromatization and carbonization (Lu *et al.* 2004).

Figure 9a shows that the TG curves of the welding interfaces for each group were similar to that of the wood dowel, except for the final weight loss. From Table 4, the final weight loss of the wood dowel was higher than that of the wood dowel immersed in CuCl₂. This difference may have been caused by the hydrolysis of hemicellulose and cellulose in the wood dowel during immersion. Meanwhile, the hydrolysis of hemicellulose also caused the lower weight loss in the second stage.

The final weight losses for each group were lower than for the wood dowels. This phenomenon could have been caused by the pyrolysis of cellulose and hemicellulose during the welding process, which resulted in a higher relative content of lignin in the welding interfaces than in the wood dowel. Based on this phenomenon, the welding interfaces produced more solid compounds than the wood dowel during the TG analysis. In the second stage, the weight loss of the wood dowel was higher than for any of the other groups because the amount of hemicellulose and cellulose in the welding interfaces was lower than in the wood dowel. By increasing the welding time, more hemicellulose and cellulose were pyrolyzed during the welding process, which resulted in a decreased weight loss during the second stage.

For the untreated groups, from the differential thermogravimetric (DTG) curves (Fig. 9b), two main pyrolysis stages were observed for the wood dowel. Hemicellulose decomposed from 225 °C to 325 °C, and cellulose was pyrolyzed from 325 °C to 390 °C. Only a single peak was found around 360 °C in the DTG curves of the welding interfaces for the untreated groups. This could have been caused by the pyrolysis of hemicellulose during the welding process. Meanwhile, the highest temperature of the welding interface was approximately 350 °C, which was almost as high as the temperature of the fastest pyrolysis rate for the welding interfaces. Therefore, during the TG analysis, almost no pyrolysis of hemicellulose occurred, which was unlike the fast pyrolysis of hemicellulose in the wood dowels. The fastest pyrolysis rate of the welding interface was lower than that of the wood dowel. Comparing groups A and B, the DTG curves showed similar processes, but the fastest pyrolysis rates and corresponding temperatures were different. For group A, the fastest pyrolysis rate and corresponding temperature were 0.91 mg/min and 358.9 °C, while they were 0.89 mg/min and 354.6 °C for group B, respectively. These differences could have been caused by the increased pyrolysis of cellulose and short chains generated from long broken chains with the increased welding time. This conclusion was the same as the one reached for the decreased degree of crystallinity from the XRD analysis. For group C, the pyrolysis rate was lower than for groups A and B below 325 °C. However, the pyrolysis rate increased rapidly after 325 °C, and the fastest pyrolysis rate was 0.91 mg/min when the temperature was 356 °C. According to these results, more hemicellulose, cellulose, and amorphous materials were pyrolyzed during welding with an extended time, which caused the decrease in the degree of crystallinity and rapid pyrolysis from 325 °C to 356 °C.

For the treated groups, two main peaks were found at around 310 °C and 352 °C in the DTG curves (Fig. 9b) because of the decreased pyrolysis temperature of the wood components, which could have been caused by the effect of CuCl₂, including the hydrolysis of hemicellulose and cellulose and the catalysis action (Liao 2003). By extending the welding time, the peak at 352 °C showed a decreasing trend, and for group F, the peak at 352 °C disappeared. This phenomenon could have been because of a greater degree of hemicellulose and cellulose pyrolysis. For group D, the pyrolysis degree

of hemicellulose and cellulose was the lowest during the welding process, which resulted in the strongest peak intensity at approximately 310 °C. The peak intensity for group F was between that of groups D and E. It was lower than that of group D because of a higher pyrolysis of hemicellulose and cellulose during the welding process. It was higher than that of group E because almost all of the components were pyrolyzed at 310 °C for group F and only some of the components were pyrolyzed at 352 °C for group E.

For the treated groups, the placement of the pyrolysis weight loss shoulder shifted to the left (Fig. 9a), which corresponded to the new peak around 310 °C in the DTG curves. The increased pyrolysis rate at the beginning could have been the reason for this shift. The cellulose depolymerization and glass transition process occurred before 250 °C, and generated active cellulose.



Fig. 9. TG (a) and DTG (b) curves of the wood dowel and welding interfaces for each group

Croup	We	Residual Ratio (%)		
Gloup	First Stage Second Stage Third Stage			
Wood Dowel	3.65799	66.74592	8.05038	21.54571
A	3.06799	63.46327	8.13236	25.33638
В	2.42874	59.54275	10.00001	28.02850
C	1.40249	57.14046	10.63715	30.81990
Wood Dowel-CuCl ₂	3.85123	59.29514	10.20196	26.65167
D	4.90359	56.68447	12.34098	26.07096
E	5.38449	48.83664	13.53382	32.24505
F	6.28214	47.57793	13.87300	32.26693

Table 4. TG Weight Loss Percent and Residual Ratio of the Wood Dowel andWelding Interfaces for Each Group

The welding interfaces of the treated samples contained CuCl₂, which could also be proven by X-ray photoelectron spectroscopy. Because of the presence of CuCl₂, the pyrolysis of cellulose was catalyzed, which resulted in the pyrolysis weight loss shoulder shifting to the left and increased reaction velocity. However, with the increased reaction temperature, the pyrolysis rate of the treated groups was lower than that of the untreated groups, and this phenomenon was the same one observed in the studies by Liao (2003) and Tan *et al.* (2006). The addition of CuCl₂ could have caused the obvious decrease in the pyrolysis weight loss of cellulose and slow occurrence of a carbide phase, which resulted in the weight loss ratio of the treated groups being lower than that of the untreated groups. The temperature of the welding interface reached 250 °C, and the pyrolysis of cellulose with the catalysis of CuCl₂ in the treated groups was faster than that in the untreated groups. Thus, the degrees of crystallinity of the treated groups were lower than those of the untreated groups, which was in accordance with the conclusions of the XRD analysis.

According to the above analysis, an increased welding time decreased the pullout resistance because of the loose bonding connection. Due to the catalysis of CuCl₂, the pyrolysis degree of the treated groups was higher than that of the untreated groups, which resulted in better molten bonding. Based on this reaction, the pullout resistance of the treated groups was higher than that of the untreated groups.

CONCLUSIONS

- 1. Rotation welding enabled the joining of wood dowels and substrates with considerable strength. The samples manufactured with the dowels immersed $CuCl_2$ that were welded for 3 s showed the highest pullout resistance and data reliability.
- 2. The pullout resistance of the wood dowel welding complied with the Weibull distribution. For both untreated and treated groups, the pullout resistance of welding time 3 s showed the highest reliability. And 0.05 fractile of the pullout resistance of welding time 3 s was larger than that of welding time 5s and 7s.
- 3. The degree of crystallinity increased because of the pyrolysis of amorphous materials after welding. By extending the welding time and using CuCl₂ treated dowels, more crystal materials were pyrolyzed, which decreased the degree of crystallinity.

4. From the TG/DTG analysis, the pyrolysis of cellulose and hemicellulose occurred during the welding process. A longer welding time caused more cellulose to be pyrolyzed and the addition of CuCl₂ promoted the pyrolysis of cellulose.

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