

The Effect of Layer Moisture Content Distribution on Lumber Surface and Bonding Interface Properties

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This study investigated the effect of drying on moisture content (MC) distribution through ash lumber thickness, as well as the effect on wood surface and bonding at the interface. After the drying of lumber, the wood surface contact angles and free energy were collected over 6 days, and the MC difference (between surface and core) was measured. At the same time, the isocyanate adhesive strength, as well as the elemental composition of carbon (C_{1s}), nitrogen (N_{1s}), and oxygen (O_{1s}) on the lumber surface and at the bonding interface, were tested daily. Both the wood surface contact angle and free energy changed with a change in MC difference. The O_{1s} concentration at the bond interface decreased with increased MC difference, and the adhesive strength declined accordingly. To attain the best bond interface, the MC difference between the surface and core should be controlled within the range of 0.5 to 1%.

Keywords: Ash lumber; MC distribution; Surface free energy; Surface function group; Bonding interface

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INTRODUCTION

There are differences in wood moisture content between the core and surface layers after drying. The active groups on the wood surfaces change with moisture movement from the core to surface until the piece reaches equilibrium. This process is known as wood surface passivation. The wood surface contact angle, free energy, and bonding strength may be influenced by the active groups changing during the storage period when moisture is not in equilibrium. If the moisture difference between the core and surface layers is high, the internal force (stress) in wood increases and this leads to drying defects and influences wood glue properties (Bergman 2010).

Understanding and improving the bond interface between wood and adhesive is very important for the wood products industry. The bond interface is one of the most important factors and accounts for 70% of all wood product applications (Collett 1972; Gardner *et al.* 1991; Gu and Cheng 2003; Kamke and Lee 2007; Custodio *et al.* 2009). Furthermore, the quality of the glueline depends on adhesive type, manufacturing process, and bond quality (Gu 2003). The adhesive quality is affected by other factors such as the contact angles and surface free energy (Qian 1999).

The wettability measurement is a useful method for determining the thermodynamic behavior of the surface substrate and the physical processing of wood such as drying and aging impacts on wettability (Gardner *et al.* 1991; Shi and Gardner 2001; Tang *et al.* 2012; Yang *et al.* 2014). The lumber surface functional groups (such as OH-)

are important factors in determining adhesive quality. The free energy at the substrate surface is defined as the energy that is required to produce one unit of surface area without putting more stress upon the surface (Qin 2003). Furthermore, these wood surface properties change during drying and can be classified into three inactivation mechanisms: (a) exudation of extractives to the surface, which lowers the wettability or hides the surface, (b) reorientation of wood surface molecules, which reduces wettability or places for bonding, and (c) irreversible closure of large micro-scale pores in cell walls (Christiansen 1990; Shupe *et al.* 1998).

The solid surface free energy is very close to the liquid critical surface tension according to the Zisman theory. Therefore, the solid surface free energy can be estimated by measuring the critical surface tension as a numerical value (Stamm 1959). The change in lumber surface moisture content (MC) influences both surface radicals and the MC difference through the thickness and also depends on the lumber surface MC. The moisture content difference is defined as the difference between the MC of the middle and average of the top and bottom layers of the lumber.

To provide information regarding both the energy and chemistry of the wood surface, wettability studies and surface analysis for chemical composition by X-ray photoelectron spectroscopy (XPS) can be used (Gardner *et al.* 1991). The XPS method, also called electron spectroscopy for chemical analysis (ESCA), can be used for elemental analysis (Li 2003a). During XPS analysis, the excitation source energy of the X-ray is high. XPS analysis not only can stimulate the valence electrons located in the atomic orbitals, but also stimulate the inner orbital electrons in the core level as well. The outgoing photoelectron energy is directly related to both the ingoing photon energy and the binding energy of the atomic orbitals. Therefore, for certain monochromatic excitation sources and the related atomic orbitals, the photoelectron energy is specific. For example, when the excitation source of the energy is fixed, the photoelectron energy is related only to the type of element and the atomic orbit level of the ionized excitation ion. Therefore, the types of elements can be analyzed qualitatively according to photoelectron binding energy. The change in MC difference between the core and surface is very important because the elemental composition of carbon (C1s), nitrogen (N1s), and oxygen (O1s) in the lumber (as well as the bonding interface) will differ according to the MC difference changes (Li 2003a). This is important because a change in these values may have a negative effect on wood bonding and finishing (Christiansen 1990; Gardner *et al.* 1991)

The purpose of this study was to investigate the effect of the lumber surface and the bonding interface functional groups by MC differential through the lumber thickness during six consecutive storage days after drying, to investigate the interaction between MC difference and the presence of functional groups on the bond surface, and to provide evidence for the theory of the glue strength of lumber.

EXPERIMENTAL

Materials

The ash lumber (*Fraxinus* spp.) used in this study originated in Pennsylvania, USA. The nominal thickness was 25.4 mm (4/4"), and the average thickness was 23.8 mm. The lumber was bought and donated by the Innovation and Practice Base of North East Forest University and the International Famous Furniture Design Research Institute in Dongguan, China. Flat sawn and quartersawn lumber were cut from the same tree at the same height

because the cutting directions can affect the water conduction direction, which could influence liquid wettability due to wood extractives migrating to the wood surface with moisture flow during drying (Christiansen 1990).

Aqueous polymer isocyanate (API) glue was prepared in the authors' laboratory. The main components of the API were polyvinyl acetate emulsion (PVAC) and styrene butadiene rubber (SBR), with the ratio of (PVAC:SBR=85:15 wt%). Fine calcium carbonate (CaCO_3) was used as filler (20 wt%). Some properties of the API included pH=6.8, solids content=41.77%, and viscosity=170 mps at 30 °C. Also, isocyanate was used as hardener (API:isocyanate=100:12.5 wt%). All the components were added in a wide neck flask and stirred before use. The isocyanate (purity: 98%, grade: reagent), glycerin (purity: >98%, grade: reagent), and amino-formaldehyde (purity: 98%, grade: reagent) were purchased from Shanghai Rocky Adhesives Co., Ltd. (Shanghai, China).

Methods

The method of testing for MC differences through the thickness of the lumber was in accordance with the drying quality standard (State Forestry Administration 2009). When the lumber thickness was less than 50 mm, it was divided into three even layers (two surface and one core). The method used to make the layered MC specimens is shown in Fig. 1, and the ash lumber drying curve is shown in Fig. 2. The ending surface MC was 7.56% (average of three samples), and all lumber was dried using the same wood drying schedule (Fig. 2). Considering that wood is isomeric in every direction, all specimens were selected from the same tested lumber piece in order to lower the variation in measurements. But even within a piece of lumber, variation can be considerable. For example, contact angles tend to be slightly greater on latewood than earlywood (Shupe *et al.* 1998).

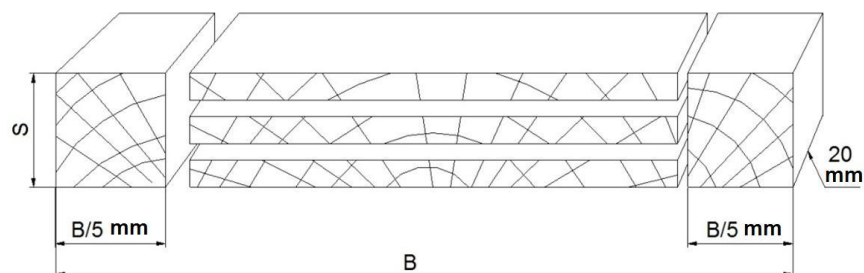


Fig. 1. The method of cutting the MC specimens into three layers. B: width, S: thickness

Specimens were divided into three equal sized layers. The MC of each layer was tested using the weight method. The MC difference through the thickness of the piece was calculated using the following equation,

$$\Delta W = W_2 - (W_1 + W_3)/2 \quad (1)$$

where ΔW is MC difference and W_1 , W_2 , and W_3 represent the top, middle, and lower layer MC, respectively. Three pieces of lumber were selected and placed into a chamber with consistent temperature (25 °C) and humidity (60%) to investigate the wood surface property changes when the MC changed with time. Two pieces of wood were cut from each lumber every day for the MC difference determination. Thus, the change in MC of each layer was measured daily. Then, the MC difference between the surface and core was calculated.

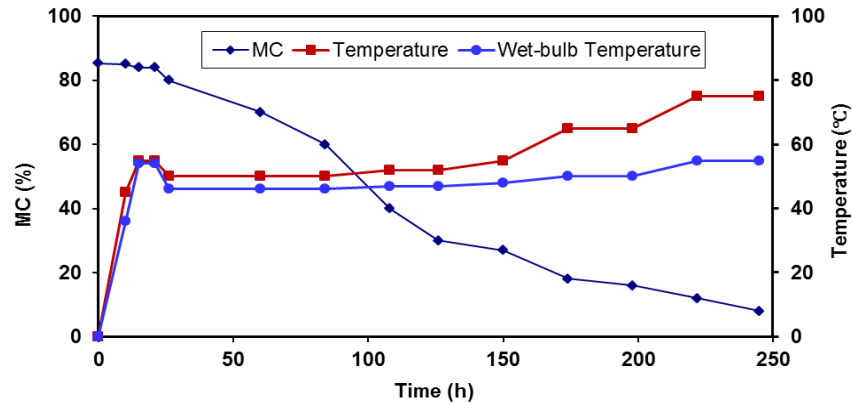


Fig. 2. Ash lumber drying curve

The surface wetting ability was evaluated by measuring the contact angle. The contact angles of different surface tension liquids were used on the wood surfaces and were measured with a JC2000A contact angle/surface tension apparatus (Shanghai Zhongchen Digital Technology Equipment Co., Ltd., Shanghai, China). Four different liquids, *i.e.*, aqueous polymer isocyanate (API) glue, distilled water, glycerin, and amino-formaldehyde, were used. The liquid drop volume was 0.001 mL. According to the W. A. Zisman theory (Stamm 1959), the free energy of a solid surface is equivalent to the critical liquid surface tension. The cosine of a solid contact angle ($\cos\theta$) can be calculated using the following equation (Stamm 1959),

$$\cos\theta = 1 + K(r_C + r_{LA}) \quad (2)$$

where r_C is the critical surface tension, K is a constant, and r_{LA} is the liquid surface tension. When $\theta = 0^\circ$, $\cos\theta = 1$, and then $r_C = r_{LA}$. After the contact angles were obtained, a straight line was drawn showing the relationship of r_{LA} vs. $\cos\theta$. The solid surface free energy can be calculated from the figure when $\theta = 0^\circ$.

Three groups of testing lumber were selected. The changes of the surface contact angles were tested every day while the lumber was being conditioned in the chamber for 6 days. As wood naturally possesses porosity, the surface is not smooth and liquid osmosis penetrability is very high. In order to decrease measurement error, 10 pictures were taken from each piece of lumber and 30 pictures were taken daily for each liquid treatment to calculate the average contact angles. The pictures were taken immediately after the liquid was dropped on the wood surface and the angle measured.

To observe the bonding interface, aqueous polymer isocyanate (API) was used to glue the wood samples together. The specimens for the normal compression shear strength tests were cut from the lumber in the radial direction. The specimen length, width, and thickness were 30, 25, and 10 mm, respectively. The bonding area was 25 mm \times 25 mm, and the glue loading was 125 ± 5 g/m². The samples were pressed with pressure of 1.5 MPa for 24 h at room temperature. Then, the specimens were tested with a testing rate of 2 mm/min and the compression shear strength was calculated using Eq. 3,

$$\sigma = \frac{P_{\max}}{b \times l} \quad (3)$$

where σ is the normal compressing shear strength (MPa), P_{\max} is the maximum failure load (N), b is the width of the shear section (mm), and l is the length of the shear section (mm).

At the same time, the wood stress was also measured. The stress was calculated using Eq. 4,

$$Y = \frac{S - S1}{2L} \times 100\% \quad (4)$$

where Y is the stress (%), S is the width of the specimen before it was cut to tooth shape (mm), $S1$ is the tooth width of the specimen after its MC reaches equilibrium (mm), and L is the tooth length (mm). The sample cutting diagram is shown in Fig. 3. The normal compression shear strengths of the specimens that changed with MC, MC differences, and stress were analyzed daily for six days.

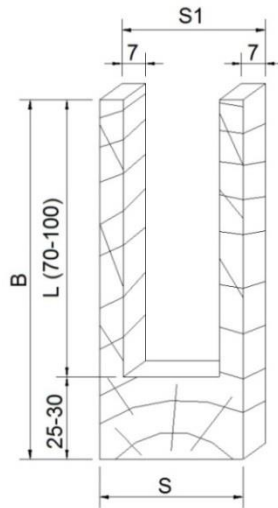


Fig. 3. The cutting diagram of the stress samples (unit: mm)

The C1s, N1s, and O1s contents on both the lumber surface and bonding interface were tested daily for six days during the MC difference measurements, using X-ray photoelectron spectroscopy (XPS) (ESCA-750, Shimadzu; Kyoto, Japan). Small specimens were mounted onto a holder with double-sided adhesive tape. The C1s, N1s, and O1s spectra bands were collected daily (Liu *et al.* 2010).

RESULTS AND DISCUSSION

Lumber Surface Wetting Ability

The surface wetting ability was evaluated using the surface contact angle. The lumber surface contact angle and free energy is shown in Table 1. The dried wood surface MC was 7.56% (Fig. 2), and it increased to 9.80% after 6 days. The surface free energy exhibited a downward trend during the six day period. From day one to day three, the average decline was 2.00 mJ/m²/d. After the 4th day, the rate dropped to 1.53 mJ/m²/d. The MC increased after the wood had been conditioned for three days. The surface free energy declined quickly after the third day. This can be attributed to the lumber's ability to absorb water, which caused a reaction between the functional groups on the lumber surface and the hydroxide radicals from the water, allowing the surface free energy to decline.

Table 1. Contact Angle and Free Energy of Ash Lumber Surface

Time (day)	API glue 63.3 (mN/m)	Water 72.8 (mN/m)	Glycerin 74.9 (mN/m)	Amino-formaldehyde 80.5 (mN/m)	Surface free energy (mJ/m ²)
	Contact Angle θ (°)	Contact Angle θ (°)	Contact Angle θ (°)	Contact Angle θ (°)	
1	53.3 (0.32 [*])	55.1 (0.21)	57.3 (0.78)	62.5 (1.04)	29.8
2	55.4 (0.79)	56.8 (0.10)	59.5 (0.95)	64.2 (0.90)	26.9
3	56.2 (0.42)	57.7 (0.46)	60.7 (0.90)	65.7 (0.85)	25.8
4	57.8 (0.45)	59.1 (0.49)	61.5 (0.85)	66.3 (0.46)	24.2
5	59.7 (0.25)	60.7 (1.00)	63.2 (0.26)	67.6 (0.67)	21.7
6	60.1 (1.20)	61.6 (0.70)	62.9 (0.45)	68.8 (1.61)	20.6

* The data in the parentheses are the standard deviations.

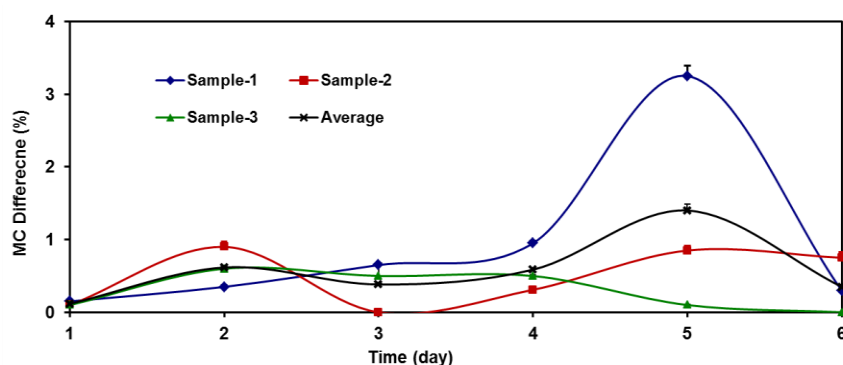


Fig. 4. The MC differences through the thickness changing with time (the bars are standard deviations)

MC Difference and Effects

The MC differences showed fluctuating tendencies under the same storage conditions, as shown in Fig. 4. From day 1 to 2, MC differences increased slowly. After the second day, they exhibited a downtrend, meaning that the difference of the MC between the core and the surface was decreasing. The lumber surface absorbed the water from the atmosphere. On the third day, the MC differences reached their minimum, and then began to increase gradually. However, throughout the process, the intensity change was slow. The MC differences increased to their largest peak and then decreased, exhibiting an oscillating trend.

C1s, N1s, and O1s Content on the Lumber Surface and the Bonding Interface

The C1s, N1s, and O1s contents on the lumber surface layers and the bonding interfaces were measured using an XPS, while the MC core to surface differences were simultaneously measured during the 6 day testing period. The results of the XPS wide scan spectra for the three elements, which were measured 6 times in 6 days, are shown in Fig. 5. The C1s, N1s, and O1s content percentages of the lumber surfaces and bonding interfaces are summarized in Table 2.

The element contents changed considerably with exposure to time and conditioning to the new equilibrium MC%. However, the peak values were not maintained for the complete storage duration (Fig. 5). The C and O contents did not change significantly in the first 3 days, as shown in Table 2. However, the contents began to change considerably on the 4th day. They increased 3% on the 4th day, then decreased about 1% on the 5th day

and increased 5% on the 6th day. The C1s change with time on the surface was unstable. The main reason for the instability was probably that the specimens were heavily affected by the drying schedule and the MC was asymmetric, allowing greater change in the C1s. At the same time, the O1s content changed irregularly. Generally, the C1s, O1s, and N1s contents changed significantly as more storage time passed. This testifies that the MC difference through the lumber thickness affected the contents heavily due to the migration of water to the surface layer. This water movement also acted to transport low molecular weight extractives to the surface region resulting in surface active groups changes.

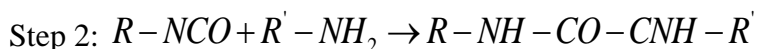
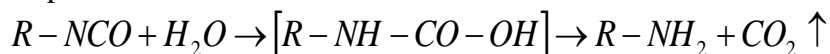
Table 2. The C1s, N1s, and O1s Content Percentages of Lumber Surface and Bonding Interface

Atom	Content on lumber surface (%)						Content on bonding surface (%)					
	1d	2d	3d	4d	5d	6d	1d	2d	3d	4d	5d	6d
C1s	68.99	67.6	68.47	72.3	71.00	75.26	73.04	72.15	72.51	76.42	75.07	78.43
N1s	0.89	0.66	0.37	0.90	1.32	0.78	2.78	2.59	2.36	2.80	3.42	2.86
O1s	30.12	31.74	31.16	26.8	27.68	23.96	24.18	25.26	25.13	20.78	21.51	18.71

C, H, O and N elements exist in high concentrations both in wood and in the adhesive used in this study. In the chemistry characterization of the adhesive and wood (Li 2003b), it is very important to analyze the state change for the element C in order to define the peak of absorption. The goal of such an analysis is to determine the C combinations as well as estimate the lumber surface chemistry component and its change. For the elemental changes on the bonding interface, C1s, O1s, and N1s changed substantially. Compared with those located on the lumber surface, C1s and N1s inside of the piece increased, but the O1s content decreased because the glue reacted with the lumber among their functional groups (Liu *et al.* 2010).

Aqueous polymer isocyanate (API) can glue the lumber together and create a very strong crosslinked interface because of the following three reasons (Gu 2003): First, lumber is a porous material that contains a lot of the free water in the lumen and bound water in the cell wall and consists of hydroxide, carboxyl, ester, aether, and other functional groups. The hydroxyl groups from water react with API to produce strong ammonia-ester and urea bonds which is important for a strong interface (Cai and Deng 2003). The proposed reaction processes are given below.

Step 1: API reacts with water:



Step 3: API reacts with the hydroxide group:



Second, the API penetrates into the lumens of the tracheids just below the surface. When the lumber is glued together, the adhesive forms numerous nail-like bonds that enhance the glue strength effectually. Third, the polar groups in the lumber and the API react with each other to form hydrogen bonds, which helps to create a stronger bonded interface (Cheng 2004).

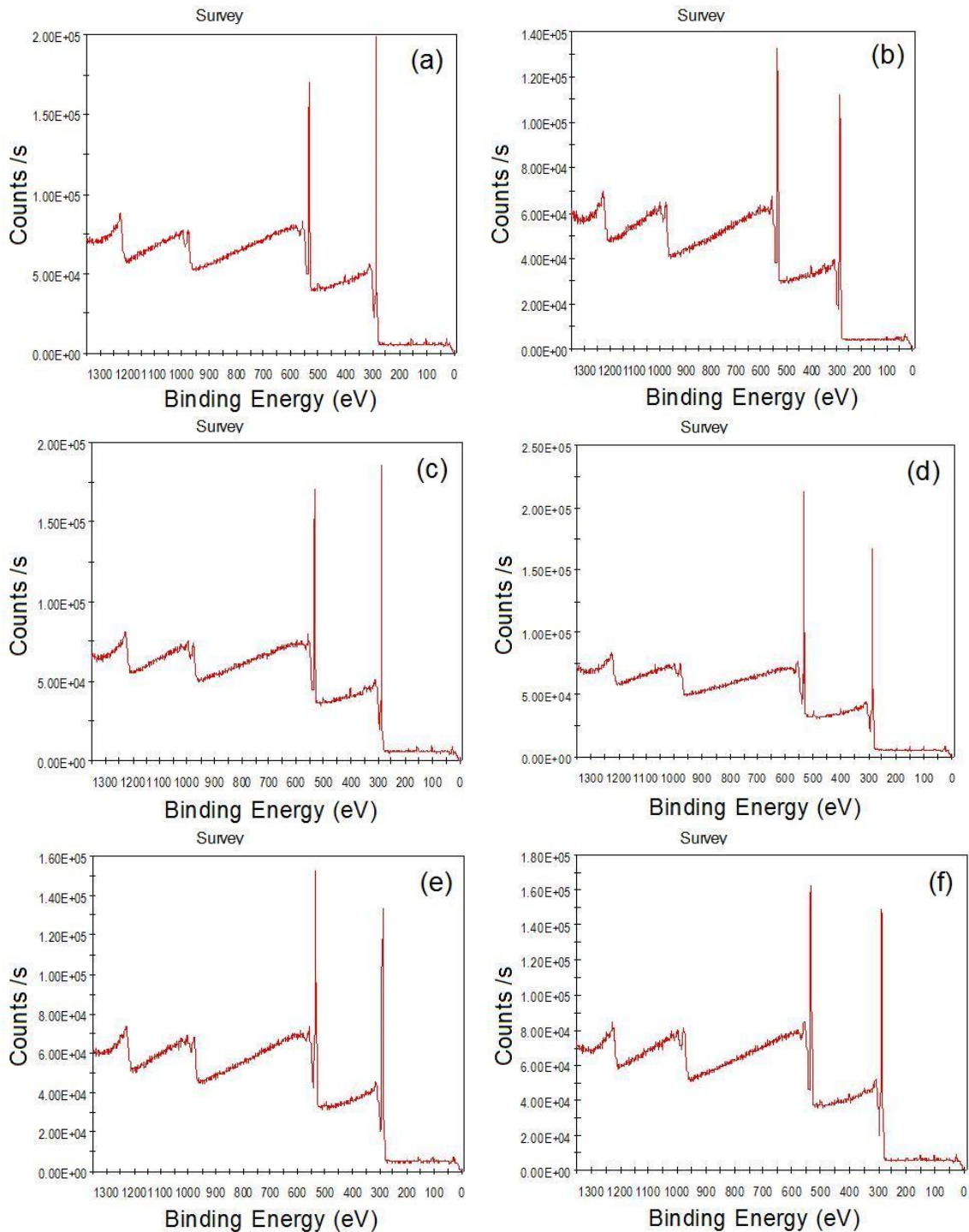


Fig. 5. XPS scan spectra of wood surface over six days (a to f for day 1 to day 6)

The normal compressing shear strength, stress, MC and MC differences between the core and surface are shown in Fig. 6. Both the MC and MC difference affected the bond quality. The internal stresses increased slightly on day 2 but then stabilized through the remaining 4 days. When the stress was consistent, the normal compression shear strength of the specimens decreased with increasing Δ MC between the surface and core. This

differential reached a maximum value after conditioning for three days. When the MC was greater than 9%, the normal compression shear strength decreased with increasing MC.

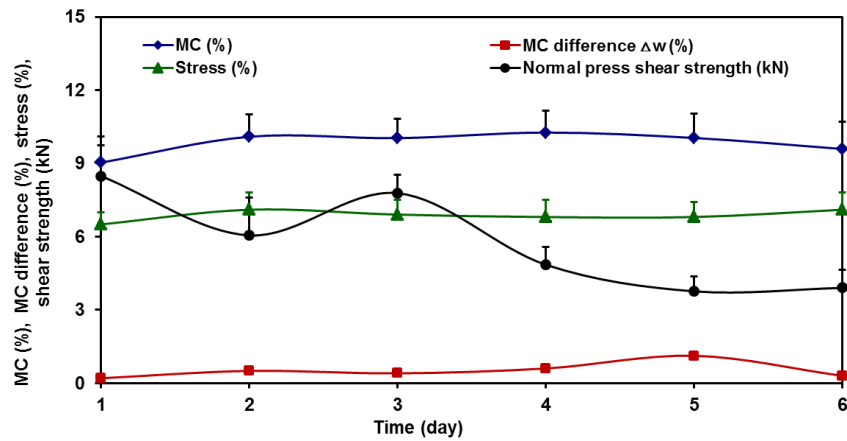


Fig. 6. MC, MC difference (surface to core), stress, and normal compressing shear strength changes with time (the bars are standard deviations)

Δ MC Effects on Functional Groups at the Bonding Interface

The MC difference effects on O1s and N1s on the bonding interface are shown in Fig. 7. O1s content at the bonding interface was highest after being conditioned for 2 to 3 days and at a MC difference of 0.6%. O1s content decreased with exposure time and as the Δ MC increased (Fig. 7a). The N1s content at the bonding interface was highest at 5 to 6 days of conditioning, during which the MC difference was near 1.4%. The N1s content increased gradually with exposure time and the MC difference increased as well (Fig. 7b).

The MC difference impacts on C1 content at the bonding interface are shown in Fig. 8. The C1s content increased to a peak at 5 to 6 days coupled with a Δ MC of approximately 0.5 to 1.0%. Furthermore, the C1s content increased gradually with the time. However, the C1s decreased if the MC differential was more than 1.0%. It is hypothesized that forces within the board exceed bondline resistance and the active groups of wood surfaces change too much at the moisture differences greater than 1%, resulting in wood drying and surface glue defects.

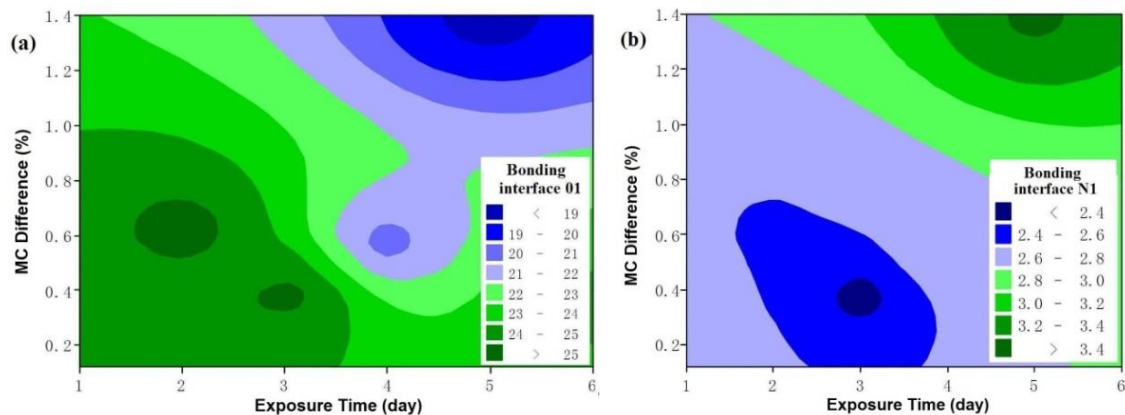


Fig. 7. The effect of MC differential and exposure time on O1s (a) and N1s (b) with respect to the bonding interface

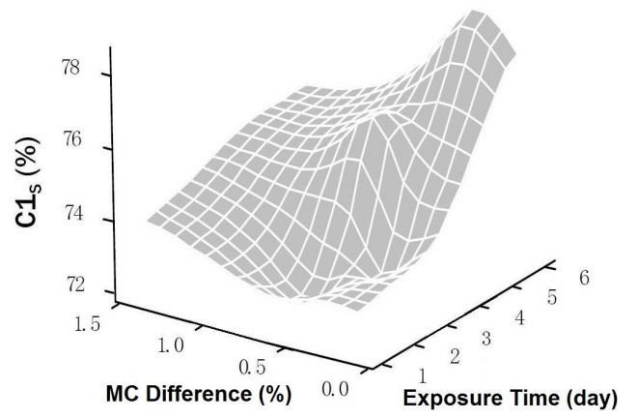


Fig. 8. The effect of MC difference and exposure time on C1 content with respect to the bonding interface

CONCLUSIONS

1. The wetting ability and free energy on the lumber surface decreased with increasing conditioning time over the course of a six-day conditioning period.
2. The OIs content percentage on the bonding interface decreased gradually as the MC difference increased.
3. The C1s content percentage on the bonding interface increased with time when the MC difference was less than 0.5 to 0.8%; however, it decreased when the MC difference was greater than 1.0%.
4. The N1s content percentage on the bonding interface was at its largest volume after the studied lumber was conditioned for 5 to 6 days. When the MC difference was less than 1%, the N1 content increased gradually as the conditioning time and MC difference increased.

ACKNOWLEDGMENTS

This research was supported by the program of Exploitation of the Lumber Drying Technology for Common Wood Species in Guangdong Province. This is a Major Science and Technology Program located in the Guangdong Province, Program Number: 2011A080404002.

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Article submitted: May 30, 2014; Peer review completed: August 28, 2014; Revised version received and accepted: November 1, 2014; Published: November 7, 2014.