Microstructure and Quantitative Micromechanical Analysis of Wood Cell-Emulsion Polymer Isocyanate and Urea-Formaldehyde Interphases

Lizhe Qin, Lanying Lin, Feng Fu, and Mizi Fan

Abstract: Emulsion polymer isocyanate (EPI) and urea-formaldehyde (UF) were selected as typical resin systems to investigate the microstructure of wood-adhesive interphases by fluorescence microscopy (FM) and confocal laser scanning microscopy (CLSM). Further, a quantitative micromechanical analysis of the interphases was conducted using nanoindentation. The FM results showed that the UF resin could penetrate the wood to a greater extent than the EPI resin, and that the average penetration depth for these two resin systems was higher in the case of latextwood. CLSM allowed visualization of the resin distribution with contrasting colors, showing that the EPI resin could not penetrate the cell wall, whereas UF resin could enter the cell walls. The micromechanical properties of the cell walls were almost unaffected by EPI penetration but were significantly affected by UF penetration, especially in the first cell wall from the glueline. This further confirmed that only cell walls with resin penetration can improve the mechanical properties of the interphase regions.

Key words: interphase microstructure, micromechanical properties, fluorescence microscope, confocal laser scanning microscope, nanoindentation

INTRODUCTION

The development of the low-carbon industry has accelerated the need for wood-based composites, wherein various resins (adhesives) are used, e.g. in the production of laminated timber, finger jointed timber, laminated veneer lumber, oriented strand board, and other engineered composites. The interaction of natural wood with the bonding agents is a decisive parameter to ensure the development of desired properties and performance of these composites, and is considered a most complex topic of research. Wood has an inherently complex anatomical structure. The major elements of wood are tracheids in softwoods, and fibers and vessels in hardwoods. The lumens and pits of cells are large enough to provide pathways for the flow of most bonding agents (Marra, 1992). Another mechanism underlying the resin penetration is diffusion of the resin into the cell walls. The above mentioned methods of resin penetration in wood can generate a complex interphase region in the composites, which is vital for load transfer across their constituents, thereby affecting the performance of the wood composites. The term “interphase” refers to the region of adhesive penetration with mixed material properties, whereas the term “interface” represents a virtual two-dimensional surface between the adhesive and the wood cells (Kamke & Lee, 2007). Studies have demonstrated that the optimum adhesive penetration would not only benefit the mechanical performance of wood composites to a great extent, but also ensure more efficient use of adhesives (White, 1977; Gindl et al., 2005; Nuryawan et al., 2014).

The penetration behavior could determine the geometry of the interphase, which is related to the wood parameters, nature of the adhesive, and the bonding process (Gavrilovic-Grmusa et al., 2012a). The penetration processes also determine the potential adhesion mechanisms (Kamke & Lee, 2007). Resin penetration can usually be classified into two levels in terms of scale: micrometer level (also called gross penetration) and nanometer level (cell wall penetration). Gross penetration results from the flow of liquid resin into the porous structure of wood, mostly filling the microscopic cell cavities; this is observed in the case of most resins having low viscosity. However, cell wall penetration occurs only when a resin is composed of small-molecular weight components such that the resin can diffuse into the cell walls or micro fissures (Tarkow et al., 1966; Marcinko et al., 1998). Although resin penetration of the cell lumens can be easily detected by light microscopy (LM), it is difficult to detect resin penetration of the cell walls (Hancock & Northcott, 1961). Different types of LM, scanning electron microscopy, fluorescence microscopy (FM), and transmission electron microscopy have been used for visualizing resin penetration in wood composites (Hare & Kutscha, 1974; Bolton et al., 1988; Johnson & Kamke, 1992; Sernek et al., 1999; Smith et al., 2002). UV-microscopy (Gindl et al., 2002), electron energy loss microscopy (Rapp et al., 1999), chemical-state X-ray microscopy (Buckley et al., 2002), confocal laser scanning microscopy (CLSM) (Xing et al., 2005;
Gavrilović-Grmuša et al., 2012a, 2012b), and scanning thermal microscopy (Konnerth et al., 2008) are used to study the resin penetration in cell walls. The relationship between adhesive penetration and macro-bond performance could also be determined by the techniques above. Recently, micro X-ray computed tomography has been used to build a model for elucidating the influence of the adhesive penetration pattern on the micro-bond performance (Kamke et al., 2014; Mckinley et al., 2016). However, understanding the effect of nanoscale adhesive penetration on the interphase performance remains a challenge.

Resin penetration in cell walls may result in a change in their chemical and mechanical properties. Understanding the micromechanical properties of the overall cell walls has recently attracted great attention and has largely been investigated by nanoindentation (NI) (Wimmer et al., 1997; Gindl et al., 2004a; Tze et al., 2007). NI is an effective and convenient method for understanding the mechanical properties of materials. This method involves loading an indenter on a sample and recording the load and displacement. The hardness and elastic modulus of the material are hence determined from the load-displacement data (Oliver & Pharr, 1992). It has been shown that resin penetration in cell walls improves the overall mechanical properties of the walls (Gindl & Gupta, 2002; Gindl et al., 2004a; Konnerth & Gindl, 2006; Stöckel et al., 2010, 2012; Liang et al., 2011; Zhang et al., 2015), and a very slight decrease in the modulus of elasticity with increasing distance from the immediate glueline has been observed. The change in the mechanical properties is attributed to the effect of adhesive penetration in the wood cell wall (Konnerth & Gindl, 2006; Konnerth et al., 2009).

Although the effect of penetration of different kinds of adhesives on the overall mechanical properties of the cell walls have been studied using NI, there are very few studies on the micromechanical properties of the interphase region after adhesive penetration. This study investigates the penetration of emulsion polymer isocyanate (EPI) and urea-formaldehyde (UF) resins within the interphase region by FM and CLSM, respectively, and the effect of resin penetration on the micromechanical properties of the cell walls in the interphase region by NI. EPI and UF resins are popular adhesives used in manufacturing structural and non-structural wood composite products, respectively. These resins have different curing and bonding mechanisms. Understanding the penetration behavior based on different curing and bonding mechanisms at the cellular level, and hence the micromechanical properties, is imperative for exploring the potential of bio-based composites, as well as for guiding innovation and production.

**MATERIALS AND METHODS**

**Sample Preparation**

A sample softwood species (*Cryptomeria fortunei* Hooibenk) was chosen as the bonded substrate. Planks with a thickness of 20 mm were collected from the stem at a height of 1.3–3.3 m (from the ground), dried in a laboratory kiln drier, and conditioned at 20±1°C/65±5% relative humidity. Smooth and fresh tangential surfaces of the planks were prepared for use. The moisture content and density of the planks were measured as 9.88% and 0.28 g/cm³, respectively.

Two commercial adhesive systems were used for the experiments, EPI (main agent/m-curing agent = 100/15; main agent: Prefere6150 with a solid content of 58%, viscosity of 8,000 mPa s at 25°C and pH of 6.8; curing agent: Prefere6653; Dynea Chemical Industry Corporation, Shanghai, China) and UF (hardener: ammonium chloride (4% sol./sol.); solid content: 65%; viscosity at 25°C: 2,640 mPa s; pH: 8.5; Shengda Flooring Corporation, Sichuan, China). The adhesives amount of 180 g/m² was first applied on the chosen planks in accordance with the procedure recommended by the manufacturers, and then two pieces of the plank were laminated. The UF-laminated planks were cured at 110°C under 0.4 MPa, whereas the EPI-laminated planks were cured at ambient temperature under 1.0 MPa.

Shear test specimens with an overlapping area of \( \sim 25 \times 25 \) mm were sampled from the laminates containing the glueline (Fig. 1a) and stored at 20±1°C/65±5% relative...
humidity for 1 week until they reached equilibrium. A total of 40 specimens for each adhesive were subjected to the shear test in accordance with the Japanese Agriculture Standard for glued laminated timber (JAS SE-8). The shear strength of the EP1 and UF-bonded laminates was 6.35 ± 0.74 and 6.97 ± 0.84 MPa, respectively, consistent with the requirement of JAS SE-8 (≥5.40 MPa).

For FM and CLSM specimens, small blocks cut from the center of the laminates with dimensions of 7 × 7 × 20 mm were infiltrated with water for 3 days, and then soaked in a 1:1 glycerin/95% alcohol mixture for 2 days. Transverse sections of 25 μm thickness were then cut from the cross-sections of the small blocks using a sliding microtome (Fig. 1b). Each section was stained with 0.5% toluidine blue O solution to suppress the autofluorescence of the wood and to trigger fluorescence of the non-absorbent adhesive. After soaking for 12 h, the sections were rinsed twice with distilled water and then dehydrated by immersion in an alcohol solution with progressively increasing concentrations (30, 50, and 70%) corresponding to various dehydrating times (30, 25, and 20 min). Finally, the dehydrated sections including the interphase regions of the wood–adhesive composites were fixed between a microscope slide and cover glass using a drop of the 1:1 glycerin/water mixture.

The specimens for indentation are normally embedded in epoxy resin. In this study, to avoid possible penetration of the epoxy resin and undesired changes in the mechanical properties of the cell wall, the specimens were prepared without embedding in epoxy resin. Instead, the specimens were directly prepared from small blocks with dimensions of 7 × 7 × 20 mm containing the glueline. A sloping apex with an angle of about 45° was created by sliding the microtome on the cross-section of the specimens. The apex covered a part of the glueline and one latewood band of the radial piece. The specimens were then mounted on an ultramicrotome. The sloping apex was cross-sectioned first with a glass knife and then smoothed with a diamond knife (Fig. 1b). A smooth surface of about 0.5 × 0.5 mm was created. The specimens were conditioned in the instrument test chamber for at least 24 h before NI test.

**FM and Image Analysis**

An Axio imager microscope (Carl Zeiss Microscopy GmbH, Jena, Germany) with a 100 W mercury burner was used to investigate the penetration of the adhesive across the interphase. A green exciter–barrier filter set (excitation wavelength 480/40 nm, emission wavelength 510 nm) was chosen to observe the sections. Adhesive penetration in the wood structure was examined quantitatively by measuring the effective penetration depth (EP) and the average penetration depth (AP) in a random area from a single glueline. EP is the total area of the adhesive detected in the interphase region divided by the width of the glueline, which can be calculated using equation (1); AP is the average depth of penetration for several column tissues within the total measurement length, which can be calculated using equation (2).

\[
\text{EP} = \frac{\sum_{i=1}^{n} A_i}{X_0}, \quad (1)
\]

\[
\text{AP} = \frac{\sum_{i=1}^{n} y_i}{N}, \quad (2)
\]

where, EP is the effective penetration depth (μm), A, the area of the adhesive object i (μm²), X, the length of the glue line in the measurement area (ten measurement areas for both earlywood and latewood. The glue line length of each area is 500 μm in this study), AP the average penetration depth (μm), y, the penetration depth of one-column tissue (μm), and N the total column number of tissues in the measurement length (μm).

The measurement parameters used in equations (1) and (2) are illustrated in Figure 2. These three parameters are usually measured using image processing and analysis software. The two parameters, X and y, could be easily measured using the Axiovision software. A was measured by circling the adhesive area with Matlab software, which provides a highly efficient and simple way of measurement (Johnson & Kamke, 1992).

**CLSM**

The sections viewed and photographed by FM were then imaged with a LSM 780 inverted confocal microscope (Carl Zeiss Microscopy GmbH) under the fluorescence mode at excitation wavelengths of 405 and 488 nm, and emission wavelengths of 401–485 nm and 493–598 nm. A Neofluar 10×/0.30 system was used to obtain the complete morphology of the wood–adhesive interphase, and then the image of the test region was magnified using an Apochromat 40×/1.20 system.

**Figure 2.** Measurement parameters in the experimental image.
The CLSM images were collected from ten replicate specimen surfaces, and the image resolutions were 0.83 and 0.35 μm per pixel side length for magnifications of 10× and 40×, respectively.

NI
All NI experiments were performed on a nanomechanical test instrument (TI 950 TribolIndenter, Hysitron Inc., Eden Prairie, MN) equipped with a three-sided pyramidal diamond Berkovich tip having a nominal radius of curvature of ~100 nm. All indentations were conducted at a temperature and relative humidity of ~22°C and 45%, respectively. Indentation was performed in a load-controlled mode using three segments: loading in 5 s to a peak force of 200 μN, holding the maximum force for 2 s, and finally unloading in 5 s. Indentation was performed at the glueline and at various distances from the glueline (Fig. 3a). The cell walls at a distance of >150 μm from the glueline, where no influence of the adhesive penetration was expected, were tested as reference.

Because of the variation in the measurements within one cell wall, at least four positions were chosen for each test region. In each test region, the space between adjacent test points was at least 20–30 times that of the maximum depth of indentation. After indentation, the test areas were examined to evaluate the position and quality of the indents. Only the indents created at the correct positions were used for the final analysis (Fig. 3c). The final data were the average of the indents on S2 in four adjacent cells for each region. The hardness (H) and the elastic modulus (E) were calculated from the load-displacement curves according to the Oliver and Pharr methodologies (1992).

The hardness is defined using the following equation:

\[ H = \frac{P_{\text{max}}}{A}, \]  

where, \( P_{\text{max}} \) is the load measured at the maximum depth of penetration (h) in an indentation cycle and A the projected contact area between the indenter and the sample at \( P_{\text{max}} \).

The reduced elastic modulus (\( E_r \)), which is the combined elastic modulus of both the tested sample and the indenter, is calculated using the following equation:

\[ E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}, \]  

where, S = \( dP/dh \) (stiffness) is the slope of the upper portion of the unloading curve in the load-displacement plot and A the projection area of the elastic content.

The elastic modulus (E) of the sample is then calculated using the following equation:

\[ \frac{1}{E_r} = \frac{1}{E} + \frac{1}{E_i} \frac{(1 - v_i^2)}{(1 - v^2)}, \]  

where, v and \( v_i \) (0.07) are Poisson’s ratios of the specimen and indenter, respectively, and \( E_i \) is the modulus of the diamond indenter (1,140 GPa). In all the calculations, v is assumed to be 0.422 (Gibson & Ashby, 2001) for the wood cell walls.

RESULTS AND DISCUSSION

Microstructure of the Overall Interphase Region

An example of EPI and UF resin penetration forming an interphase is given in Figure 4. Toluidine blue staining suppressed the autofluorescence of wood effectively, so that the adhesives show green fluorescence. The penetration of EPI and UF resins into the lumens of the tracheids for both earlywood and latewood has been calculated (Table 1).

It is apparent that the resin–wood interphase is complicated by the presence of the resin and wood, and the resin penetration in the wood rays and tracheids. In the earlywood region, the maximum penetration depth for the EPI resin was measured at the rays and was approximately four times the diameter of earlywood lumen (in the radial direction), whereas the maximum penetration depth in the tracheids was approximately twice the diameter of earlywood lumen. In the latewood region, the maximum penetration depth for the EPI resin was also measured at the rays and was approximately three times the diameter of the latewood lumen, and the maximum penetration depth in the latewood tracheids was...
not more than twice the diameter of the latewood lumen. Moreover, the AP and EP in the earlywood, irrespective of penetration in the rays or tracheids, were higher than those in latewood for the EPI resin (Table 1). The UF resin penetrated the wood significantly deeper than the EPI resin. For the UF resin, the AP and EP in earlywood were higher than those in latewood. In earlywood, the maximum penetration depth was about nine times the diameter of the earlywood lumen, whereas the maximum penetration depth in the tracheids was three times the diameter of the earlywood lumen. In latewood, the maximum penetration depth was also measured at the rays, which was about nine times the diameter of the latewood lumen, and the maximum penetration depth in the latewood tracheids was less than three times the diameter of the latewood lumen.

Gross penetration of adhesives is the main parameter related to the adhesive interphase formulation, and a difference in the penetration characteristics between the adhesives implies different interphases and bonding performance. The penetration is determined by wood-related parameters (such as the lumen diameter and a certain grain slope on the wood surface), properties of the resin and adhesive mix (such as adhesive mix composition, viscosity, amount of adhesive spread, hardening time, and rate of resin curing), and bonding processing parameters (such as assembly time, press temperature, and pressure). Table 1 shows that the AP in earlywood tracheids for the EPI and UF resins were around 56 and 108 μm, respectively, and roughly one-third of that into the rays. The AP in latewood tracheids were around 27 and 77 μm, respectively, nearly one-quarter of that into the rays. After excluding the non-penetration areas (cell walls and unfilled lumen area) of the interphase region, the EP values were lower than the AP values. However, similar to the results for the AP, the EP in earlywood was more than twice that in latewood, and penetration for the UF resin was more than twice that for the EPI resin. The former may be due to the smaller lumen diameter and greater deposition of extractives in the latewood compared with that in the earlywood, and the latter may be due to the difference in the viscosity, and pressing parameters between the EPI and UF resins. Although the UF interphase was formed under lower pressure (0.4 MPa), a much higher curing temperature (110°C) and lower viscosity (2640 mPa s) would lead to a UF resin with better mobility, indicating that the permeability of UF was greater than that of EPI. UF samples having a better bonding interphase would be formed because of the greater penetration depth.

Gross penetration of adhesives is the main parameter related to the adhesive interphase formulation, and a difference in the penetration characteristics between the adhesives implies different interphases and bonding performance. The penetration is determined by wood-related parameters (such as the lumen diameter and a certain grain slope on the wood surface), properties of the resin and adhesive mix (such as adhesive mix composition, viscosity, amount of adhesive spread, hardening time, and rate of resin curing), and bonding processing parameters (such as assembly time, press temperature, and pressure). Table 1 shows that the AP in earlywood tracheids for the EPI and UF resins were around 56 and 108 μm, respectively, and roughly one-third of that into the rays. The AP in latewood tracheids were around 27 and 77 μm, respectively, nearly one-quarter of that into the rays. After excluding the non-penetration areas (cell walls and unfilled lumen area) of the interphase region, the EP values were lower than the AP values. However, similar to the results for the AP, the EP in earlywood was more than twice that in latewood, and penetration for the UF resin was more than twice that for the EPI resin. The former may be due to the smaller lumen diameter and greater deposition of extractives in the latewood compared with that in the earlywood, and the latter may be due to the difference in the viscosity, and pressing parameters between the EPI and UF resins. Although the UF interphase was formed under lower pressure (0.4 MPa), a much higher curing temperature (110°C) and lower viscosity (2640 mPa s) would lead to a UF resin with better mobility, indicating that the permeability of UF was greater than that of EPI. UF samples having a better bonding interphase would be formed because of the greater penetration depth.

### Table 1. Thickness of Glueline, and Penetration of Emulsion Polymer Isocyanate (EPI) and Urea–Formaldehyde (UF) Resins.

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>Thickness of Glueline (μm)</th>
<th>Position</th>
<th>AP (μm)</th>
<th>EP (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPI</td>
<td>29.39 ± 6.95</td>
<td>Earlywood</td>
<td>56.34 ± 11.46</td>
<td>22.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Latewood</td>
<td>26.97 ± 3.24</td>
<td>10.67</td>
</tr>
<tr>
<td>UF</td>
<td>26.78 ± 7.46</td>
<td>Earlywood</td>
<td>107.65 ± 38.62</td>
<td>47.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Latewood</td>
<td>76.50 ± 9.65</td>
<td>21.53</td>
</tr>
</tbody>
</table>

AP only refers to the penetration in the tracheids and excludes penetration in the rays.

AP, average penetration depth; EP, effective penetration depth.

**Figure 4.** Penetration of (a) emulsion polymer isocyanate and (b) urea-formaldehyde in earlywood and latewood. The upper parts of the slices show penetration in earlywood, the lower parts show penetration in latewood, and the middle layers denote the glueline.

**Microstructure of Penetrated Cell Wall with Adhesives**

FM could be used to acquire fluorescence images of the interphase with strong contrast between the adhesive and the wood cell walls. FM in combination with the image analysis software could be a suitable tool for quantitative analysis of the gross penetration. However, because of its lower image resolution, FM could not be used to observe the microstructures of wood tissues such as cracks and deformations in the cell walls. CLSM can sharply differentiate the adhesive from the wood cell walls based on the bright contrasting color, and help in visualizing the adhesive distributions and micro-cracks in the wood tissues (Fig. 5). It is evident that
the tracheid walls at the outermost layer of the bonding surface were fractured and deformed during planning and bonding. Microscopic cracks, including the fissures in the cell wall, either between the adjacent tracheids or between the ray and the tracheid, were illustrated clearly. This indicates that during bonding, the adhesives may move primarily along the least resistant path, especially under an external compression force; that is, the EPI and UF resins penetrate the lumens of the axial tracheid and ray tissue, as well as the microscopic cracks presented at the exposed bonding surface. Moreover, the UF resin was observed not only in lumens exposed to the bonded surface but also in adjacent lumens, which indicates that UF resin could pass from the exposed lumens to the adjacent lumens through the pits in the cell walls. Horizontal flow might occur through bordered pits on the radial side of the tracheids, whereas vertical flow might occur from one tracheid to another through the bordered pits on the endings of the tracheids or simple pits between ray cells and tracheids. It has been reported that the bordered pits on the cell walls could prevent the adhesive from flowing through the adjacent tracheids, but simple pits show little hindrance to adhesive penetration (Gindl, 2001).

The results presented here also indicate that the UF resin may have penetrated the lumens adjacent to the exposed lumens primarily by passing through the cross-field pits.

In Figure 5a, a small degree of penetration in the cell wall was detected. The EPI resin was observed only in the lumens exposed to the bonded surface, and the penetration depth depended on the size of the tracheid lumens exposed on the bonded surface. EPI resin is a pre-polymerized adhesive that cannot pass through the cell cavities and pits easily. During bonding, water in the EPI resin was absorbed by the wood cell wall. On the other hand, the high-molecular-weight polymer molecules were merely attached to the inner walls of the tracheid and ray tissue exposed to the bonded surface, or/and the pit membrane; this led to poor permeability in the cell wall. There is a considerable difference in cell wall penetration between the EPI and UF resins. The cell wall penetration of the UF resin was also observable. The UF resin was observed not only in the cell walls exposed to the bonded surface, but also in the adjacent cell walls (Fig. 5b). The UF resin is an in situ polymerized adhesive with low molecular weight. Some small molecules could enter the cell walls from the voids between the microfibrils.
Wood tissues and resins are visualized in green and red (Figs. 5a, 5b), upon excitation with 405 and 488 nm light, respectively. The surface tissues embedded in the UF resin including the exposed cell walls and the fully filled cell walls showed a yellowish green to green color, which was different from the green color of the EPI interphase. This is interpreted as a strong indicator for the presence of UF compounds in the cell wall regions, which has been demonstrated in other studies (Stöckel et al., 2012). From Figure 5b, it was observed that in addition to the cell wall UF penetration, color variations in the interphase also reflect the amount penetrated in the cell walls. The UF resin content in the cell wall exposed to the bonded surface was the highest, showing a yellowish green color, and gradually decreased with the increase in the penetration depth, showing a yellowish green to green color.

**Micromechanical Properties of Cell Walls Due to Adhesive Penetration**

The micromechanical properties in three regions of the interphase were clearly different (Fig. 6). The significant difference between the two resins originated from the difference in their chemical structures. The cured UF resin located in the glueline showed a much lower modulus (8.43 GPa) and higher hardness (0.63 GPa) compared with the wood cell wall (15.72 and 0.51 GPa), thus reflecting the influence of the distinctly stiff and brittle nature of the UF resin because of cross-linking. The cured EPI resin located in the glueline showed a lower modulus (3.71 GPa) and hardness (0.18 GPa), with a much deeper indentation depth, because of its flexible linear polyester backbone.

Interestingly, the difference in the properties of adhesives also contributes to the performance of the penetrated cell wall in the interphase. The elastic modulus, hardness, and indentation depth of the EPI interphase cell walls were very similar to those of the unaffected cell walls. These results agree well with the CLSM results that the EPI resin cannot penetrate the wood cell walls. The elastic modulus and hardness of the UF interphase cell walls were significantly higher than those of the unaffected cell walls. It is apparent that the penetration of the UF resin may have resulted in the formation of cell-wall–adhesive composites, which gives results in higher strength. The formation of this composite could be interpreted by the interpenetrating network theory, mainly referring to the process that UF monomers penetrated into the nanovoids in the cell walls and polymerized to form interconnected networks within the wood microfibrils (Frazier & Ni, 1998).

The penetration of UF compounds in the cell wall and their content variation was highly probable from the results shown in Figure 5b. Thus, the effects of the change in regularity of this penetration on the mechanical properties of the cell walls in the interphase region are of particular interest. The effect of the UF resin in the interphase was further confirmed from the elastic modulus and hardness of the cell walls at different distances from the UF glueline (Fig. 7). The micromechanical hardness and modulus decreased with an increase in the distance from the glueline. The mechanical properties of S2 layers at the first cell wall from the glueline were the highest among those of the measured cell walls; the elastic modulus and hardness were 18.87 and 0.62 GPa, respectively, which were about 15 and 17% higher than those of the cells 150 µm from the glueline.

It is worth mentioning that the microfibril angle of the cell wall can affect the elastic modulus of the cell walls in

Figure 6. Indentation depth, reduced elastic modulus, and hardness of resins, interphase cell walls, and reference cell walls. EPI, emulsion polymer isocyanate; UF, urea-formaldehyde.

Figure 7. Reduced elastic modulus and hardness of cell walls at different distances from the urea–formaldehyde glueline.
the S2 layer. Therefore, indentation was performed on the cell walls in lateward of the same growth ring to ensure similar microfibril angles for all the measured cell walls. The difference in the mechanical properties of the cell walls resulted from the diffusion of the adhesive into the cell walls. As revealed in an earlier investigation (Gindl et al., 2004b), the elastic modulus of aminoplastic adhesives was lower than that of the cell walls, but the UF resin may diffuse into the cell walls, fill the pores in the cell walls (within the cellulose microfibrils), and increase the elastic modulus of the penetrated cell walls. The diffusion of the UF resin in the cell walls is partly due to its ability to form hydrogen bonds, which in turn results from its high reactivity. However, the gradual increase in molar volume with the high press temperatures could limit the diffusion of the resin. Slow curing of the adhesive can enhance the penetration and diffusion of the resin in the cell walls. However, hardness is independent of the microfibril angle but is dominated by the matrix properties. The hardness of the UF resin was significantly higher than that of the wood cell walls (Fig. 6), and the diffusion of the adhesive may increase the hardness of the matrix of the cell walls.

Although the diffusion of the resin in the cell walls at the interface (outermost layer of bonding surface) should be the highest, these cells have poorer mechanical properties compared with the cells adjacent to interface (first complete cell wall from glueline). This is largely because of the damage caused to the cell walls during mechanical preparation of the surface. The cells farthest from the glueline (150 μm) can be considered as reference cells. As shown in Figure 7, both the hardness and elastic modulus of the S2 layer decreased with increasing distance from the glueline, some cells showed higher variations in the data (third and fourth cell walls). Cells from the fourth cell wall onwards have almost similar mechanical properties, which are poorer than those of the cells close to the glueline, indicating minimum or no adhesive diffusion in these cells. This agree with the observation that the maximum penetration depth the tracheids is about two to three times the diameter of the lumen, as shown in Figure 4b and Table 1.

**CONCLUSION**

The characteristics of wood cell-wall–resin interphases were thoroughly investigated, and the micromechanical properties of the resin-filled cell walls were examined. Some of the specific results are listed below:

- The combination of FM, CLSM, and NI provided an effective tool to investigate the microstructure and micromechanical properties of the EPI and UF bonding interphases, and the results obtained from these three techniques corresponded with one another.
- The AP and EP for the UF resin were more than twice that for EPI, both in the earlywood band and the latewood band.
- Both EPI and UF resins could penetrate the lumens of the axial tracheid and ray tissue, as well as the microscopic cracks presented at the exposed bonding surface, but only UF could pass from the exposed lumens to the adjacent lumens through the pits.
- The micromechanical properties of the EPI interphase cell walls with little adhesive penetration were similar to that of the reference cell walls. However, cell walls within the UF resin interphase showed a significant improvement in the micromechanical properties, especially the first cell wall from the glueline.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge the financial support by the Nature Science Foundation of China (No. 31370012).

**Conflicts of Interest**

The authors declare that there are no conflicts of interest.

**REFERENCES**


