

Evaluation Of Adhesive Penetration Of Wood Fibre By Nanoindentation And Microscopy

Christopher E. Hunt¹, Joseph E. Jakes¹ and Warren Grigsby²

¹USDA Forest products Lab, 1 Gifford Pinchot Dr. Madison, WI USA

²SCION, Private Bag 3020, Rotorua, New Zealand

ABSTRACT

Adhesives used in wood products sometimes infiltrate, or diffuse into the solid material of, wood cell walls, potentially modifying their properties. These changes in cell wall properties are likely to impact the performance of adhesive bonds. While adhesive infiltration has been observed by multiple methods, the effect on cell wall properties is not well understood. We have evaluated the combination of fluorescent microscopy and nanoindentation to establish the extent of adhesive infiltration and whether the presence of adhesive in the wood fibre causes any mechanical property changes. This paper discusses the preliminary findings of this study.

INTRODUCTION

Many studies have shown that certain wood adhesives infiltrate wood cell walls with potential to change the cell wall properties. It has been proposed that adhesives such as PF, PRF, MF, MUF, and UF (phenol-phenol-resorcinol-, melamine-, melamine-urea-, and urea-formaldehyde, respectively) typically contain a low molecular weight component which can infiltrate cell walls and modify their properties (Frihart 2009). In contrast, highly pre-polymerized adhesives, typically with higher molecular weights, such as PUR and PVAc (polyurethane and polyvinyl acetate, respectively) have little effect on cell wall properties. For the case of MF resin, infiltration can be verified by UV absorption and was found to increase both hardness and elastic modulus of cell walls (Gindl *et al* 2002). A similar effect has been found with MUF (Stockle *et al* 2010), as well as reduced creep (Konnerth *et al* 2006). PF and PRF also showed increased cell wall hardness, but increases in elastic modulus were not consistently observed (Konnerth *et al* 2006, 2007, Gindl *et al* 2004). Infiltration of PRF into cell walls was also observed by UV absorbance of thin sections (Gindl *et al* 2004) and by scanning thermal microscopy (Konnerth *et al* 2008). Bromine labeled PF (Smith 1971) and UF (Bolton *et al* 1988) have both been shown to infiltrate cell walls using energy dispersive X-ray analysis. X-ray microscopy (Buckley *et al* 2002), electron energy loss microscopy (Rapp 1999) and confocal laser scanning microscopy (Xing *et al* 2005, Pakdel *et al* 2008, Cyr *et al* 2008) have also been used to probe adhesive infiltration in cell walls.

In general pre-polymerized adhesives have not been observed infiltrating wood cell walls. While PF and similar infiltrating adhesives swell cell walls (Ohmae *et al* 2002), PUR does not swell cell walls nor change thermal properties of cell walls adjacent to the adhesive in a bondline (Konnerth 2008). In addition PUR does not change the UV absorption of the cell wall or have a clear influence on hardness or elastic modulus (Gindl *et al* 2004). In contrast with these observations that indicate little of any infiltration, an earlier study showed lower modulus and higher creep in wood cell walls adjacent to both PUR and PVAc bondlines, though infiltration was not measured in this study (Gindl *et al* 2002). Instead, the inferior mechanical properties of cells near these bondlines were attributed to mechanical damage of cell walls during surface preparation. However, as with other adhesive systems, it is possible infiltration of low molecular weight components of the PUR and PVA formulations may have contributed to plasticization of cell wall components.

Despite many studies of the impact of adhesive infiltration into wood cell walls, there is still much to be learned about the effect of infiltration on the properties of cell walls. For instance, it is not known if there is a distinction in how and where different adhesives may reside in cell walls. i.e. does a particular adhesive prefer the lignin or the carbohydrate region? Does the presence of the adhesive plasticize or reinforce wood components, and if so, under what conditions. Preferred solvation of adhesive components can be predicted using solubility parameters, but details of cell wall architecture at the nanoscale, which impacts the solubility parameters of the cell wall, are still being worked out. Some studies have used techniques such as DMTA cooperativity analysis and NMR relaxation time to show close association of PF adhesive with carbohydrate components of cell walls (Laborie *et al* 2006). However, there is still much to learn about fundamental wood-adhesive interactions.

In the current study we have evaluated the combination of two inherently different analysis techniques to characterize the extent of adhesive infiltration of wood cell walls and resulting effect on cell wall properties. Fluorescent labeling of the adhesive, coupled with confocal microscopy, permits micron scale localization of adhesive components in the wood cell wall. Mechanical property measurements by nanoindentation are then correlated with microscopy visualization to determine any influence of the adhesive on properties of the wood cell wall. To establish the viability of this approach, both plywood and medium density fibreboard (MDF) have been prepared with labeled PF and soy/PF resins.

MATERIALS AND METHODS

Soy flour (toasted flour Nutrisoy 7B, donated by Archer Daniels Midland, Decatur, IL, USA) was used as received. Acriflavine was obtained from Sigma Aldrich as the hydrochloric acid salt. Phenol, paraformaldehyde and sodium hydroxide were reagent grade and used as received. The fibre for medium density fibreboard was obtained by processing radiata pine (*Pinus radiata*) chips and flash drying the fibre (8% MC) prior to use. Radiata plywood veneers were obtained from Carter Holt Harvey (Tokoroa, New Zealand) with the veneer conditioned to 12% MC prior to adhesive application.

Phenol formaldehyde (PF) resin synthesis

Phenol (337.5 g) was charged into a 2 L reactor containing water (84 g). In a separate flask acriflavine (0.8 g) and paraformaldehyde (224 g) in water (361 g) were pre-reacted before rapidly adding to the aqueous phenol solution. Sodium hydroxide (40 g, 50% solution) was then added and the reactor heated to 70°C. Cooling was available to prevent overheating. The reaction mixture was held at 70°C for 75 minutes. After this time additional sodium hydroxide (18 g, 50% solution) was added and the temperature ramped to 85°C over 15 minutes and held for a further 60 minutes before cooling and storage.

Soy-phenol formaldehyde (soy-PF) resin synthesis

The resin combining soy flour and phenolic resin was a variation on that reported by Wescott (Wescott *et al* 2005). Soy flour (233.3 g) was combined with sodium hydroxide (18.7 g), ethylene glycol (3.5 g) and defoamer (2 drops) in water (472.7 g). The soy flour was progressively added to avoid coagulation. After completion of soy flour addition the reaction mixture was rapidly stirred and heated at 75°C for 1 hour. Paraformaldehyde (33.0 g), acriflavine (0.8 g) and methanol (2.8 g) were preheated (75°C) together in water (53.4 g) before adding to the soy flour dispersion. The combined reaction mixture was heated at 75°C for a further hour. At this time phenol (68.6 g), sodium hydroxide (5.8 g) and additional water (70.4 g) were stirred in. Paraformaldehyde (41.3 g) was then added followed by additional sodium hydroxide (5.8 g). Heating at 75°C was continued for a further 90 minutes before cooling to room temperature.

Medium density fibreboard (MDF)

Mechanically blended MDF panels were formed with PF resin and soy-PF resin using a target resin loading of 10% and panel density of 710 kg/m³. PF resin (140 g) was applied to dry fibre (604 g) circulating in a mechanical blender loop. Resin was applied by spray atomization over 120 sec and fibre circulation continued for a further 120 sec. The fibre was then directed to a forming box (260 x 290 mm). A fibre mat was formed and pre-pressed to ca. 45 mm. The fibre mat (17-18% mc) was then hot-pressed to stops (9 mm) at 180°C for 135 sec.

Plywood panels

As above, plywood panels were prepared from the PF, soy-PF and 50/50 blend resins. For each resin a simple 5-ply panel was prepared by applying each resin to the veneer at a rate of ca. 140 g/m². Core veneers were coated on both sides and the coated plies laid up perpendicular. No prepress was used. A panel was formed by hot-pressing at 160°C for 300 s.

Confocal microscopy

All confocal images were acquired on a Zeiss 510 Meta confocal microscope using 488 nm excitation at the Plant Imaging Center, Department of Botany, UW-Madison (Madison, WI, USA). Green is primarily adhesive fluorescence (500-550 nm) while the red is wood autofluorescence (650-710 nm). Transverse surfaces were prepared from plywood or wax-embedded MDF. With a microtome and cells were identified for nanoindentation. Small, high quality surfaces were then prepared with a diamond knife fit in an ultramicrotome (Jakes *et al* 2008). After nanoindentation, this surface was imaged in 50:50 glycerine:water solution with a 63x lens using 3 µm optical slices. Gains were set so that cell wall autofluorescence produced a very low background in the green channel, and a strong signal in the red channel.

Nanoindentation

The nanoindenter method generally followed the same procedure as Jakes and coworkers (Jakes *et al* 2008). A Hysitron (Minneapolis, MN, USA) Triboindenter® equipped with a diamond Berkovich tip was used. Inside the nanoindentation enclosure, the relative humidity was maintained between 39 and 45% using a glycerin-water bath. The temperature was not locally controlled inside the enclosure and ranged between 21 and 28°C during these experiments. Specimens were placed inside the enclosure a minimum of 24 hours prior to experiments to allow equilibration with the conditions inside the enclosure. Indents were performed to maximum loads between 0.3 and 0.6 mN. All residual indents were imaged with a calibrated Quesant (Agoura Hills, CA, USA) atomic force microscope (AFM) incorporated in the Triboindenter. ImageJ software (<http://rsb.info.nih.gov/ij/>) was used to manually measure the contact areas from these AFM images. For this preliminary work, only the Meyer hardness (defined as maximum load divided by measured contact area) is reported.

RESULTS

Penetration and infiltration in plywood

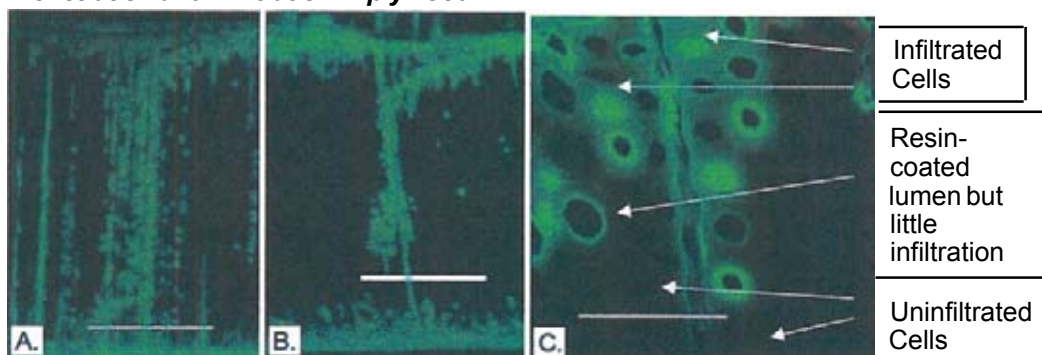


Figure 1. Confocal microscope images of cross-sections in bodne4 plywood veneers. A. PF-bonded veneers showing deep PF resin penetration (scale bar = 1 mm). B. Soy-PF-bonded veneers showing lower penetration (scale bar = 1 mm). C. Cell walls suitable for nanoindentation: cells in a single latewood file are both infiltrated and uninfiltrated with soy-PF adhesive (scale bar = 0.1 mm).

Shown in figure 1A is a veneer with PF adhesive penetration through the entire section, though soy-PF (1B) was much more localized at the bondline. 1C is higher magnification of 1B, showing a series of cells suitable for analysis taken from a row of latewood cells. The higher magnification image shows cells in individual files that are both infiltrated and uninfiltrated with adhesive.

Infiltration into veneer cell walls

While figure 1A clearly shows penetration of adhesive into lumens, infiltration into the cell wall is necessary to change properties of the wall itself. The first question we considered was whether we could accurately determine whether infiltration was occurring. Infiltration could falsely appear to be occurring if there was "bleeding"- when green fluorescence intensity in a particular pixel would be artificially high because of scattering from high intensity pixels nearby. Figure 2 suggests that bleeding is not a problem in this system. Figures 2B and 2C had intense green fluorescence in the lumina, yet the cells walls surrounding these lumina were dark, indicating that green fluorescence of a cell wall is a reliable indicator of the presence of labeled adhesive.

Our goal is to not only identify that the adhesive is present, but determine the extent of any adhesive infiltration by evaluating the fluorescence intensity within the wood cell wall. It is in this capacity a qualitative assessment can be made about relative adhesive infiltration. A higher fluorescence measurement is indicative of greater adhesive presence. This fluorescence can direct location of a nanoindentation measurement. but also be used to correlate with mechanical properties.

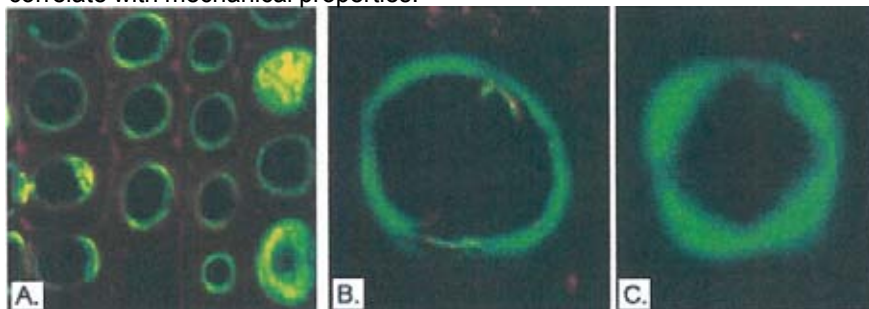
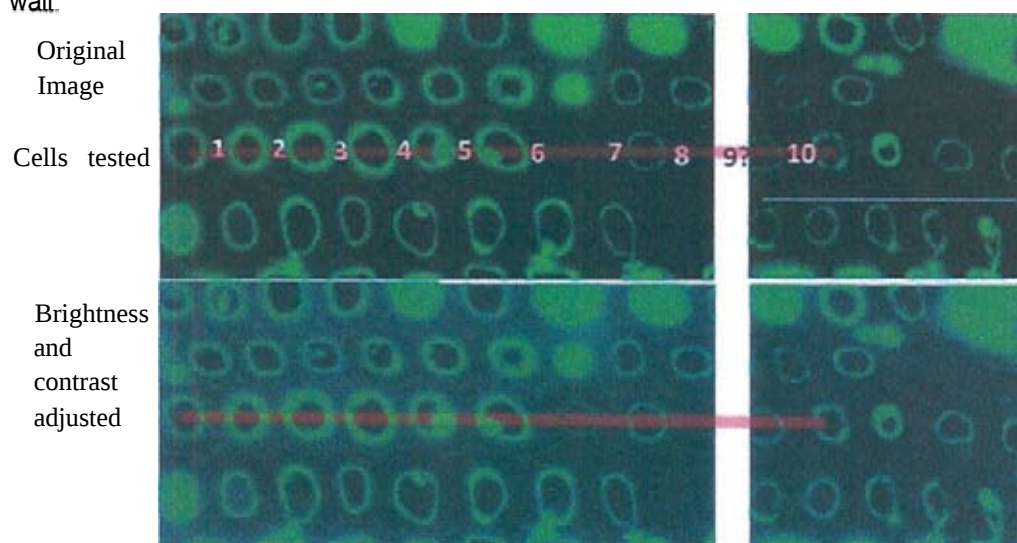


Figure 2. Confocal microscope images verifying that there is little bleed of fluorescent intensity from bright lumina to adjacent cell wall pixels (PF plywood). Pixel size = $0.45 \times 0.45 \mu\text{m}$

In general, all the cells adjacent to the bondline (top of figure 1C for instance) were completely infiltrated with adhesive. Further from the bondline, adhesive appeared to travel through lumens and therefore entered cell walls through either the S3 or lumen side. However, in adjacent rays, the adhesive sometimes appeared to be enter the cell from the middle lamella.

Nanoindentation-PF in veneers

Figures 3 and 4 show the PF-veneer surface used for nanoindentation. Indents were placed in the tangential S2 cell wall laminae in a single file of cells (highlighted with red line) that was identified to contain both infiltrated and unmodified cell walls (indent locations labeled 1-10). When originally surfaced with a microtome, these cells showed deep infiltration of resin. Final surfacing with the ultramicrotome removed material, however, and in this case the exposed surface afterward contained notably lower levels of infiltration. It is interesting to note that in this specimen, there appears to be very little adhesive infiltration into the cell wall.



Figures 3. Confocal microscope images of PF in veneer visualized after nanoindentation. Nanoindent zones are labeled 1-10. Top: confocal fluorescence. Bottom: Even with increased brightness and contrast, little infiltration is evident. Bar=100µm

AFM was used to image cell wall sections after nanoindentation. AFM revealed cracks in virtually all imaged cells (Figure 4). We believe these cracks are caused by the processes of rotary peeling, veneer drying, and pressing cycle endured by these cells, because such cracks are not typically seen in similar surfaces on solid wood specimens. Light microscopy showed many lathe checks and other cracks in the veneer, but cannot detect these cracks in the cell wall because they are so small, unless they were filled with some minimal amount of fluorescent adhesive. The lack of fluorescence in these cracks indicates no adhesive is present in the cracks. This may be because the cracks formed after adhesive cure. It is also observed that the cracks in S2 cell wall laminae (e.g. in figure 4) stop at the interface with the S3 lamina, suggesting S3 laminae remained intact and possibly served as a barrier preventing the free movement of the adhesive to the cracks. Nevertheless, work now in progress with undamaged specimens should eliminate this issue. How these cracks affected the measured hardness is unclear.

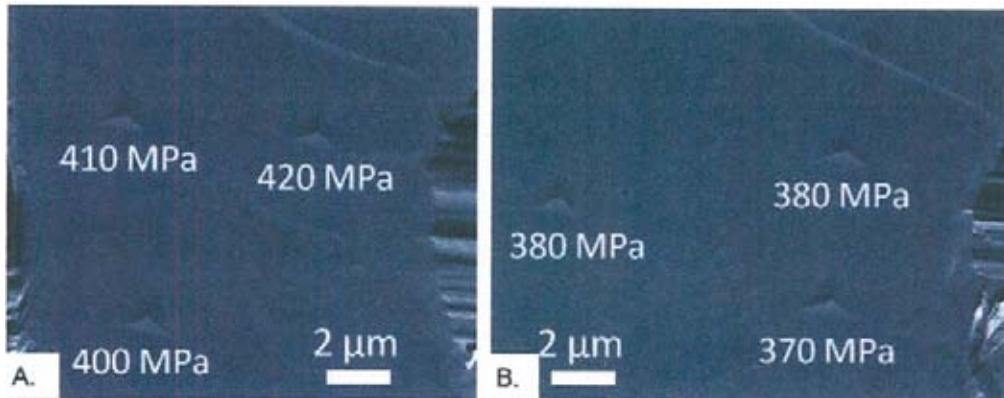


Figure 4. AFM images of indents in regions 3(A) and 10 (B) identified in Figure 3. Numbers represent Meyer hardness at each indent.

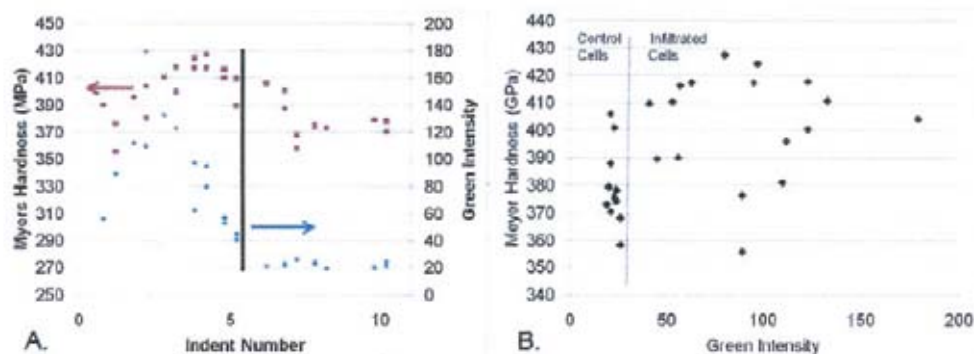


Figure 5. A: Hardness and green intensity as a function of nanoindent zone. B: Hardness vs. Green Intensity.

Shown in Figure 5 is the relative hardness of cell wall areas with the corresponding confocal fluorescence intensity measured at each nanoindent. For this sample, the correspondence between adhesive (green) intensity and hardness (Figure 5) seems weak, though a t-test comparing points to the left vs. right side of the vertical lines in Figure 5 finds $P=0.002$, meaning that the populations with high vs. low green intensity are different-

Nanoindentation-soy-PF in veneers

Shown in Figure 6 is a section of plywood bonded with soy-PF resin. Cell walls in the nanoindent zones 2-4 and the left of 5 were not infiltrated, while cells in zones 6-12 and the right of 5 appear infiltrated. Furthermore, in contrast to the PF plywood specimen, this soy-PF specimen was from a section immediately adjacent the bondline and the resin appears to have infiltrated many of the cells all the way through to the middle lamella. Increasing the brightness and contrast (Figure 6 bottom) shows that even the apparently dark cell between zones 8 and 9 contains some resin fluorescence. Interestingly, it could be speculated that the resin in this cell migrated in from neighboring cells through the middle lamella, rather than from the lumen.

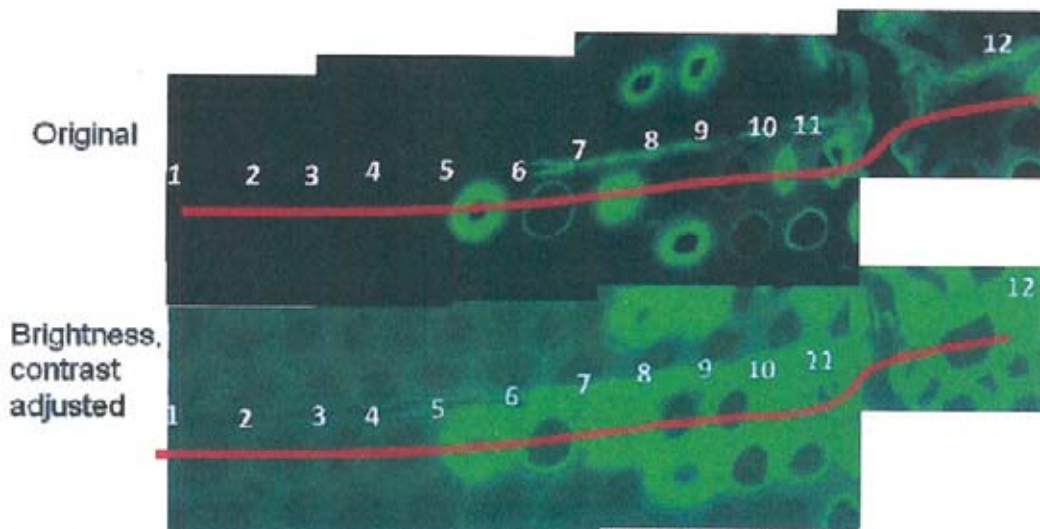


Figure 6. Confocal microscope images of soy-PF in veneer visualized after nanoindentation. Nanoindent zones follow the red line and are labeled 1-12.

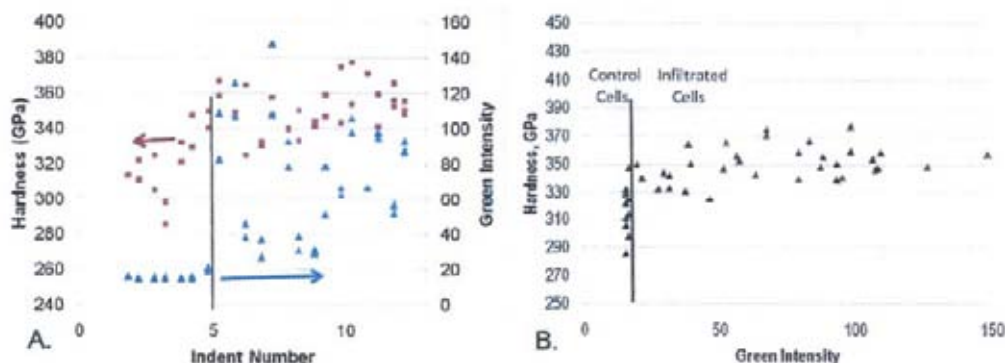


Figure 7. Nanoindentation results for soy-PF in veneer. A: Hardness and green intensity as a function of nanoindent zone (shown in figure 6) B: Hardness vs. Green Intensity.

In the soy-PF sample, we found that hardness increased 9% between control (indents 1 through 5left, green <20) and infiltrated cells (indents 5right through 12). Though small, it was statistically significant using a t test ($p=2 \times 10^{-8}$) and qualitatively similar to the 20% increase in hardness observed previously for infiltrated cells in a PRF bondline (Konnerth *et al* 2006). The smaller increase in hardness for the soy-PF may be attributed to lower resin content in the cell walls in the current study.

MDF results

Infiltration imaging: While the labeled resins were very easy to visualize in MDF, the randomness of fibre in the matrix made this type of assessment challenging. Suitable fibres for nanoindentation first had to be identified and located by confocal microscopy. Furthermore, a qualitative assessment of images tends to show (figures 8 and 9) that the soy-PF was more likely to occupy spaces between fibres. while PF alone was more prone to infiltrate the cell walls. The apparent lower infiltration of soy-PF could be a result of lower PF addition rate (replacement with soy), or a preferential absorption of PF into cell walls. In either case it suggests interesting applications for control of resin movement on fibre.

Moreover, in a contrast to veneer, for MDF fibres it was observed the PF adhesive generally enters the cell wall from the outer surface and not through the lumen.

In most of the confocal images shown so far in this paper, the red channel, showing autofluorescence of the wood, was kept very low because it was easy to tell the wood structure without it. In MDF, however, we wanted a strong signal from the wood to more clearly visualize the wood structure. While increasing the autofluorescence signal from the wood, we also seem to pick up autofluorescence of the adhesive, resulting in a green or yellow (red+green) color for pure adhesive and infiltrated cell walls, while uninfiltrated cell walls appear almost pure red.

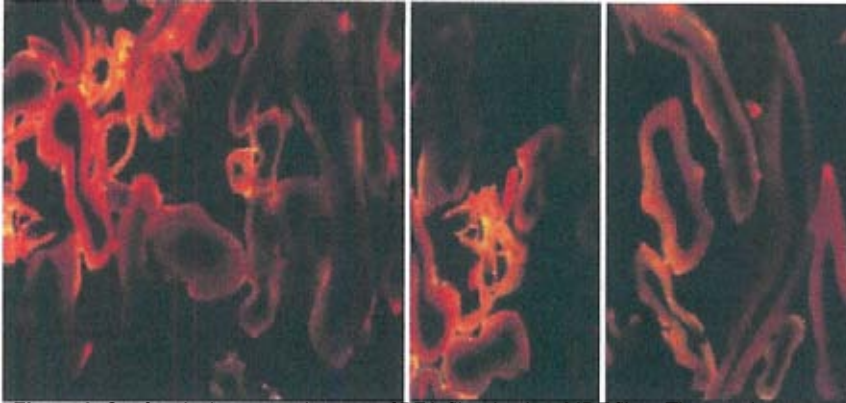


Figure 8. Confocal microscope images of PF infiltration into MDF fibre. The specimen was embedded in wax to aid in sectioning.



Figure 9. Confocal microscope images of soy-PF infiltration with more adhesive bidding evident between MDF fibres. The specimen was embedded in wax to aid in sectioning.

The combination AFM images suggest a role of cell wall micro-cracks on resin infiltration for the MDF - PF resin sample. In places where PF resin enters a cell wall, we are unsure as to whether this is caused by infiltration or by movement through micro-cracks which were not visible by optical microscopy.

We found it was difficult to obtain meaningful nanoindentation data on MDF fibres, because of cell wall damage, orientation, and lack of good controls. MDF fibres undergo physical extremes during processing so cell wall damage cannot be ruled out even in fibre cells that look intact. Cracks were observed in virtually all the AFM images of MDF cell walls we had selected for nanoindent analysis. Also, MDF fibres are found at all angles, so it is difficult to know how well the cell wall and indent direction are aligned. Finally, in MDF there are no good control cells with which to compare the infiltrated cells. One could theoretically use an uninfiltrated portion of the same cell wall as a control (as shown in Figure 10), but differences between sides in a cell have been observed and attributed to the interaction of microfibril angle and cell wall alignment relative to the indents (Konnerth *et al* 2009). Despite

all these difficulties, we still demonstrate our capability to place indents in MDF-PF cell walls (Figure 10B). A higher value of Meyer hardness is observed in the lower right-hand cell wall corner, which corresponds to the area with higher infiltration in the confocal image. However, for the reasons listed previously, we are not ready to fully interpret these results.

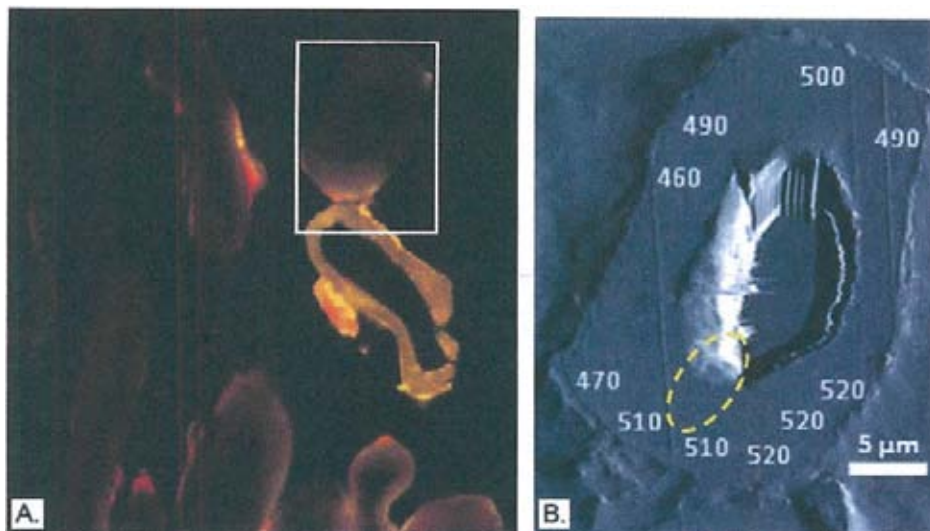


Figure 10. PF infiltration and nanoindents in MDF-PF. A. Confocal microscope image showing infiltration; B. AFM image showing an example of a crack in the cell wall. Hardness measurements are in MPa. Yellow oval highlights the crack in the cell wall. The specimen was embedded in wax to aid in sectioning.

SUMMARY

A fluorescently labeled PF resin, coupled with confocal microscopy provides a useful method of visualizing penetration and infiltration in both plywood and MDF. Minimal bleed of fluorescence was observed when a confocal microscope was used for imaging. We found increases in hardness associated with resin infiltration in the soy-PF veneer, which was observed very close to the bondline, presumably with fairly high resin content in the cell wall. In extending nanoindentation to plywood and MDF samples we have found the nanoindentation data difficult to interpret for rotary cut veneers due to damage of wood cell walls. Infiltration in MDF was also observed, and though nanoindents were attempted, damage to the cells and lack of good controls prevented us from fully quantifying the effect of resin infiltration in MDF.

FUTURE

We expect to continue this work with well characterized, undamaged cells. With intact cells, nanoindentation data will be more reliable, and we hope to generate semi-quantitative measures of resin concentration in the cell wall using confocal fluorescence microscopy. We believe this information will be useful in helping to understand the structure - property relationships of native and adhesive-modified cell walls.

ACKNOWLEDGMENT

Thanks to the New Zealand Royal Society for ISAT linkage funding received by Warren Grigsby which allowed him to visit the Forest Products Laboratory.

REFERENCES

- Bolton, A. J.; Dinwoodie, J. M.; Davies, D. A. 1988, The validity of the use of SEM/EDAX as a tool for the detection of urea resin penetration into wood cell walls in particleboards. *Wood Science and Technology* 22: 345-356.
- Buckley, C. J.; Phanopoulos, C.; Khaleque, N.; Engelen, A.; Holwill, M. E. J.; Michette, A. G. 2002, Examination of the penetration of polymeric methylene di-phenyl-di-isocyanate (pMDI) into wood structure using chemical-state x-ray microscopy. *Holzforschung* 56, (2): 215-222.
- Cyr PL, Riedl B, Wang X-M (2008) Investigation of urea-melamine formaldehyde (UMF) resin penetration in medium-density board (MDF) by high resolution confocal laser scanning microscopy. *Holz Roh Werkst* 66:129-134.
- Frihart, C. 2009, Adhesive groups and how they relate to the durability of bonded wood. *Journal of Adhesion Science and Technology* 23: 601-617
- Gindl, W.; Gupta, H. S. 2002, Cell-wall hardness and young's modulus of melamine-modified spruce wood by nano-indentation. *Composites Part A-Applied Science and Manufacturing* 33, (8): 1141-1145.
- Gindl, W.; Schoberl, T.; Jeronimidis, G. 2004, The interphase in phenol-formaldehyde and polymeric methylene diphenyl-di-isocyanate glue lines in wood. *international Journal of Adhesion and Adhesives* 24, (4): 279-286. And Corrigendum.
- Jakes, J. E.; Frihart, C. R.; Beecher, J. F.; Moon, R. J.; Stone, D. S. 2008, Experimental method to account for structural compliance in nanoindentation measurements. *Journal of Materials Research* 23, (4): 1113-1127.
- Konnerth, J.; Jaeger, A.; Eberhardsteiner, J.; Mueller, U.; Gindl, W. 2006, Elastic properties of adhesive polymers. I. Polymer films and bond lines by means of nanoindentation. *Journal of Applied Polymer Science* 102, (2): 1234-1239.
- Konnerth, J.; Valla, A.; Gindl, W. 2007, Nanoindentation mapping of a wood-adhesive bond. *Applied Physics A: Materials Science and Processing* 88, (2): 371-375.
- Konnerth, J.; Harper, D.; Lee, S. H.; Rials, T. G.; Gindl, W. 2008, Adhesive penetration of wood cell walls investigated by scanning thermal microscopy (STHM). *Holzforschung* 62, (1): 91-98.
- Konnerth, J.; Gierlinger, N.; Keckes, J.; Gindl, W. 2009, Actual versus apparent within cell wall variability of nanoindentation results from wood cell walls related to cellulose microfibril angle. *Journal of Materials Science* 44, (16): 4399-4406.
- Laborie, M. P. G.; Salmen, L.; Frazier, C. E. 2006, A morphological study of the wood/phenol-formaldehyde adhesive interphase. *Journal of Adhesion Science and Technology* 20, (8): 729-741.
- Ohmae, K.; Minato, K.; Norimoto, M. 2002, The analysis of dimensional changes due to chemical treatments and water soaking for hinoki (*Chamaecyparis obtusa*) wood. *Holzforschung* 56, (1): 98-102.

- Pakdel, H.; Cyr, P. L.; Riedl, B.; Deng, J. 2008, Quantification of urea formaldehyde resin in wood fibers using X-ray photoelectron spectroscopy and confocal laser scanning microscopy. *Wood Science and Technology* 42, (2): 133-148.
- Smith, L. A. Resin penetration in wood cell walls- implications for adhesion of polymers to wood. SUNY, Syracuse, NY, 1971.
- Stockel, F.; Konnerth, J.; Kantner, W.; Moser, J.; Gindl, W. 2010, Tensile shear strength of UF- and MUF-bonded veneer related to data of adhesives and cell walls measured by nanoindentation. *Holzforschung* 64, (3): 337-342.
- Wescott, J. M.; Traska, A. E.; Frihart, C. R.; Lorenz, L., Durable soy-based adhesive dispersions. In *International Conference on Wood Adhesives*, Frihart, C., Ed. Forest Products Society: San Diego, CA, 2005.
- Xing, C.; Riedl, B.; Cloutier, A; Shaler, S. M. 2005, Characterization of urea-formaldehyde resin penetration into medium density fiberboard fibers. *Wood Science and Technology* 39, (5): 374-384.