

# ADHESIVE PENETRATION IN WOOD—A REVIEW

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## ABSTRACT

Adhesive bond performance between wood elements is presumed to be significantly influenced by the degree of penetration of the adhesive into the porous network of interconnected cells. Research on the bondline performance has been conducted through microscopic examination and associated techniques in an effort to establish relationships with the bond performance. The purpose of this communication is to provide a technical review of research on adhesive penetration, and to promote the efficient use of adhesives in regard to cost and performance, particularly in reference to the manufacture of wood-based composites. Assessment techniques, influence on bond performance, and distinctive characteristics of common adhesives used for the wood-based composites industry were the main focus of this review. Variability between wood species, the wide variety of adhesive application and curing processes, and the many types of adhesive chemistries and formulations make sweeping generalities difficult. However, troubleshooting bonding problems and designing new adhesive systems and processes may be facilitated by understanding the fundamentals of adhesive penetration.

*Keywords:* Bonding, resin penetration, microscopy.

## INTRODUCTION

Wood is an anisotropic and porous material with many inherited anatomical features. Major elements are longitudinal tracheids in softwood species, and vessel elements and longitudinal fibers in hardwood species. The lumens of these cells are large enough to provide a good pathway for liquid-phase resin flow. Interconnecting pits are often adequate to permit resin flow. However, high molecular weight resins, or occlusions in the pits or lumens, may inhibit flow. This conglomeration of resin and wood substance is called the “interphase region.” Two substrates,

each with its own interphase, and the interface between the substrates, comprise the “bondline.” The geometry of the interphase region varies as a result of many factors, such as wood anatomy, permeability, porosity, resin viscosity, surface energy, consolidation pressure, and others. The interphase region is an uneven layer, as illustrated in Fig. 1. The geometry of the interphase is assumed to affect bond performance. Adhesive joints under load must transfer stress from component to component through the interphase region. The structural make-up of the interphase, its volume and shape, will dictate the magnitude of stress concentrations and ultimately have a significant impact on the performance of the bond.

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Marra (1992) proposed a chain-link analogy for an adhesive bond (Fig. 2), and inferred that the bond is only as good as the weakest link in the chain. Adhesive penetration plays a vital role in this analogy. Link 1 is the pure adhesive phase, unaffected by the substrates. Links 2 and 3 represent the adhesive boundary layer that may have cured under the influence of the substrates and is no longer homogeneous. Links 4 and 5 represent the interface between the boundary layer and the substrate and constitute the "adhesion" mechanism. That mechanism may be mechanical interlocking, covalent bonding, or secondary chemical bonds due to electrostatic forces. Links 6 and 7 represent wood cells that have been modified by the process of preparing the wood surface or the bonding process itself. For example, rotary-peeling of veneer causes fractures to initiate in the radial-longitudinal plane. The cells in the region may have been weakened, and thus increase the potential for failure of the bond. Planing, flaking, sanding, and other mechanical surface preparation techniques will also cause minute failures in the wood cells. Finally, links 8 and 9 represent the unadulterated wood. A properly designed adhesive bond would have the lower limit of structural integrity located at links 8 and 9. In other words, the wood should be the weakest link.

Adhesive penetration influences links 4 through 7 as proposed by Marra (1992). All of the potential adhesion mechanisms are influenced by penetration. The concept of mechanical interlocking is obviously dependent on penetration of the adhesive phase beyond the external wood surface. In addition, the combined adhesion force due to covalent bonding and formation of secondary chemical bonds is directly related to the amount of surface area contact between the adhesive and the cell wall. Greater flow along the lumen surfaces means more potential for chemical bonds to form. Pizzi (1994) concluded that secondary forces appear to be the dominant mechanism for bonding wood. It follows then that adhesive penetration into wood plays a vital role in bond performance.

Marra's chain link analogy may be expanded to consider the influence of adhesive penetration

into the cell wall. An interpenetrating network of adhesive molecules and the cell-wall polymers constitute another mechanism of adhesion (links 4 and 5). Furthermore, the act of penetration likely modifies the properties of the cell wall. The cell wall may swell or components of the cell wall may be chemically modified (links 6 and 7).

The use of polymeric resins to bond wood components has played a vital role in the development and growth of the forest products industry. Adhesives are now indispensable for the process of manufacturing wood products. However, on an equivalent weight basis, adhesives are very expensive compared to wood, and therefore their use must be judiciously controlled. In some products, such as oriented strandboard (OSB), as little as 2 percent of dry furnish weight is added as resin solids. This inevitably makes the bondline discontinuous and uneven in thickness (Conrad et al. 2004). The surface area of OSB strands, as well as the elements of other particulate wood-based composites, is not completely covered with resin. Veneered composites, such as plywood and laminated veneer lumber, have a continuous bondline, but may occasionally be starved of adhesive due to excessive penetration. Thus, flow of the adhesive over the surfaces and into the structure of the wood elements is of great importance.

This paper will discuss previous studies related to the effect of resin penetration on bond performance and microscopic detection of adhesive penetration in wood. Emphasis is given to the adhesives commonly used in the manufacture of wood-based composites (e.g. phenol-formaldehyde (PF), urea-formaldehyde (UF), melamine-formaldehyde (MF), and diphenylmethane diisocyanate (MDI)).

## DISCUSSION

### *The nature of adhesive penetration*

Adhesive penetration into wood may be categorized into gross penetration and cell-wall penetration. The former results from the flow of

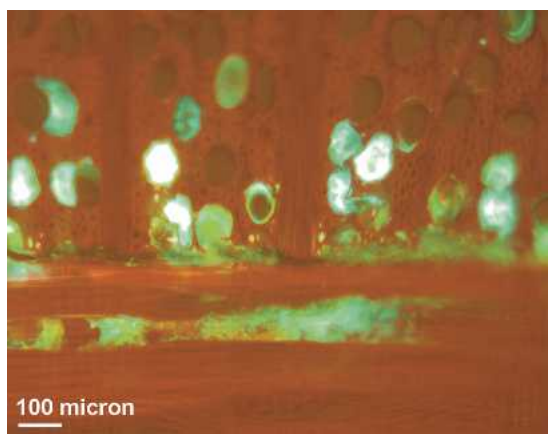


FIG. 1. Photomicrograph of a UF bondline in beech as viewed using epi-fluorescence and stained with 0.5% safranin O. Upper lamina is transverse surface, lower lamina is radial surface. Bright areas are resin. Filter set 360-nm/400-nm/420-nm (Sernek et al. 1999).

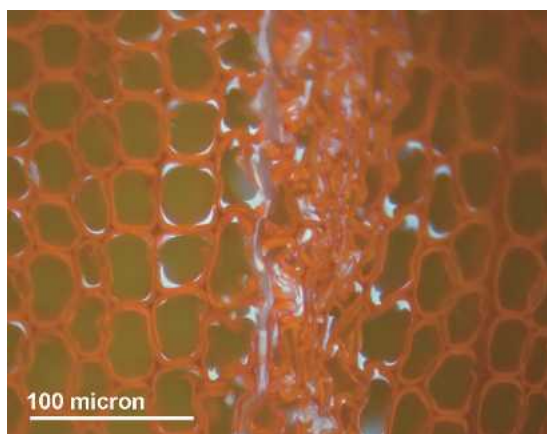


FIG. 3. Photomicrograph of a MDI bondline in southern pine using epi-fluorescence and stained with 0.5% safranin O. Transverse view of vertical bondline. Bright areas are resin. Filter set 360-nm / 400-nm / 420-nm (Kamke 2004).

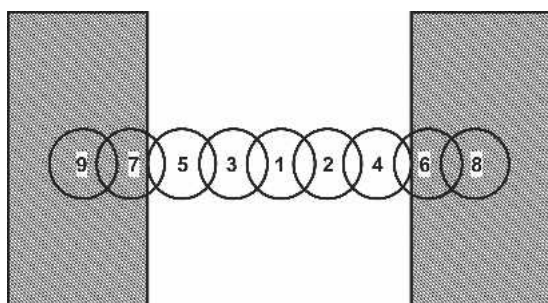


FIG. 2. Chain link analogy for an adhesive bond in wood (Marra 1992).

liquid resin into the porous structure of wood, mostly filling cell lumens. The latter occurs when resin diffuses into the cell wall or flows into micro fissures. Gross penetration has been defined as a motion of adhesive from the external surface into the capillary structure of wood and encapsulating fractures and surface debris caused by processing (Marra 1992). Gross penetration is due mainly to hydrodynamic flow and capillary action. Hydrodynamic flow is initiated by an external compression force, usually as a result of a clamp or a press employed to mate the wood surfaces to be bonded. Flow then proceeds into the interconnected network of lumens and pits, with flow moving primarily in the path of least resistance. In wood, the least resistance to

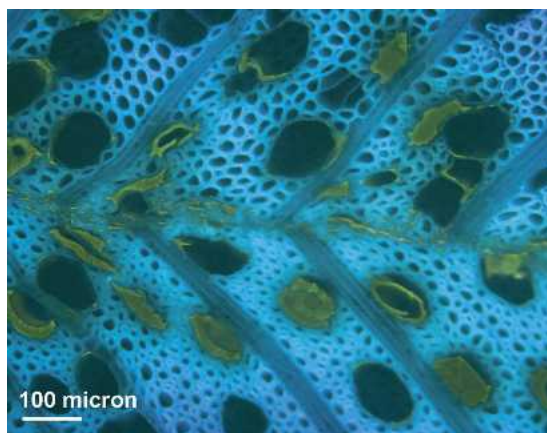


FIG. 4. Photomicrograph of a PF bondline in yellow-poplar using epi-fluorescence and stained with 0.5% toluidine blue O. Transverse view of horizontal bondline. Brown areas are resin. Filter set 360-nm/400-nm/420-nm (Zhang 2002).

hydrodynamic flow is in the longitudinal direction, following the lumens in the long and slender tracheids of softwoods, or through the vessels of hardwoods. Since vessels are connected end-to-end with perforation plates and no pit membrane, this cell type dominates the penetration of adhesives in hardwoods. Using optical microscopy, the author has observed resin in pit chambers of both hardwood and softwood species and in cell lumens in which the only entry pathway for the resin was through a pit.

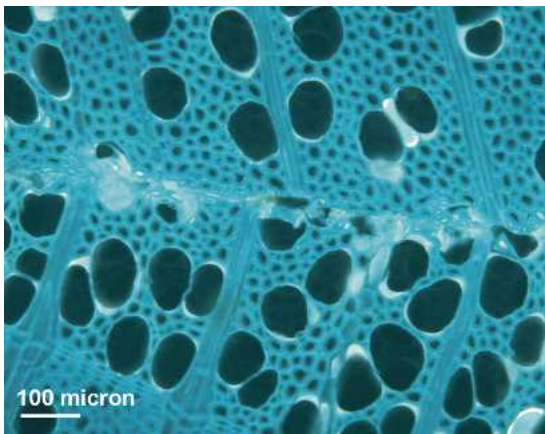


FIG. 5. Photomicrograph of a MDI bondline in yellow-poplar using epi-fluorescence and stained with 0.5% toluidine blue O. Transverse view of horizontal bondline. Bright areas are resin. Filter set 360-nm/400-nm/420-nm (Zhang 2002).

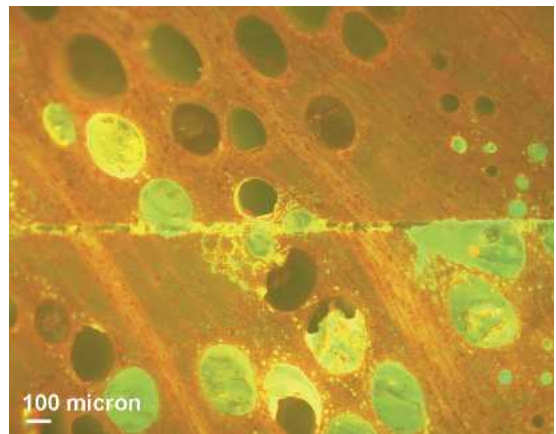


FIG. 7. Photomicrograph of a 2-part epoxy bondline in southern red oak using epi-fluorescence and stained with 0.5% safranin O. Transverse view of horizontal bondline. Bright areas are resin. Filter set 360-nm/400-nm/420-nm (Kamke 2004).

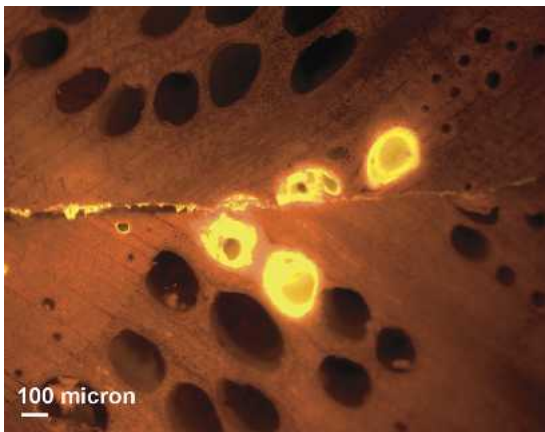


FIG. 6. Photomicrograph of a polyvinyl acetate bondline in southern red oak using epi-fluorescence and stained with 0.5% safranin O. Transverse view of horizontal bondline. Bright areas are resin. Filter set 470-nm/500-nm/515-nm (Kamke 2004).

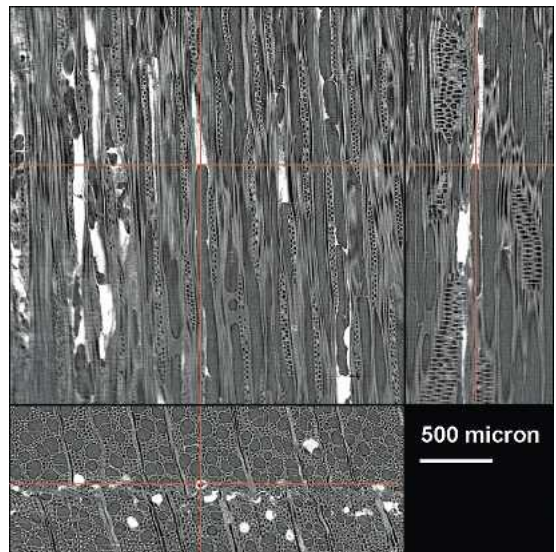


FIG. 8. Micro X-ray tomography image of PF bondline in yellow-poplar. Three mutually perpendicular planes of reference with respect to a point within the specimen are shown: Top left—tangential, Top-right—radial, Bottom—transverse (Kamke et al. 2004).

Wetting is often used as a means of assessing adhesive compatibility with a substrate. Wetting is a manifestation of flow induced by oppositely charged molecular components seeking a neutral state. Wood and the adhesives used to bond it are highly charged. Since a wood surface can spontaneously adsorb polar fluids, the character of the internal surface (i.e. lumen wall) is just as important as the external surface. Capillary action is the net result of wetting of internal sur-

face and the surface tension of the liquid (Siau 1995). As the liquid seeks new surface to neutralize charge, the liquid column is pulled through the porous network.

Polymeric adhesives are generally non-Newtonian fluids (Levenspiel 1984). Further-

more, the flow of fluids through cell lumens and pits is torturous, with significant entrance and exit effects on the capillary pathway. Waterborne adhesives, such as the phenolics and amino resins, are heterogeneous and prone to separation when the water is adsorbed by the cell wall or the high molecular weight (MW) polymer molecules are trapped by the pit membrane. Chemical interactions between the adhesive components and cell wall will restrict flow. These considerations make the discussion of the fluid dynamics of adhesive penetration one that must be restricted to generalities.

Hydrodynamic (sometimes called bulk) flow was the dominate factor for the penetration of UF resin into beech (Sernek et al. 1999). The application of a clamping force of 1.6 MPa to the bondline produced penetration that was approximately 10 times greater than the penetration that was achieved when no force was applied. Conversely, diphenylmethane diisocyanate (MDI) resin has been observed to penetrate completely through 0.75-mm-thick OSB strands within a few seconds and without the application of force (Kamke 1995), thus illustrating the importance of capillary flow for low MW resins.

Gross penetration can happen with most types of resin at low viscosity, while cell-wall penetration only occurs with a resin having a small MW component. Tarkow et al. (1966) studied the critical MW of polyethylene glycol (PEG) needed to permit penetration by the cell-wall of Sitka spruce. Their study identified a critical MW of 3000 for PEG at room temperature. The authors speculated that higher temperature would result in a larger critical MW due to increased mobility of the cell-wall polymers and greater inter-molecular volume. Broad MW distributions are typical in commercial formulations of wood adhesives. Molecular weight fractions less than 3000 are common, and therefore there is potential for at least some cell-wall penetration with most adhesives. Prior to polymerization, adhesives penetrating the cell wall will swell and plasticize the wood. This has been reported for MDI and low molecular weight PF adhesives (Marcinko et al. 1998; Laborie 2002; Frazier 2003).

Frihart (2004) discussed the implications of micrometer level penetration (gross penetration) and nanometer level penetration (cell-wall penetration) on potential adhesion mechanisms. The author noted that little is known about the influence of nanometer level penetration on adhesive bond performance. Frihart (2004) proposed four scenarios for adhesive penetration into the cell wall. In one case the adhesive simply occupies the free volume within the cell-wall—thus inhibiting shrinking and swelling. The second case claims a mechanical interlocking effect as “fingers” of cured adhesive extend from the lumen into the cell wall. The third case is an interpenetrating polymer network that is made up of the cross-linked adhesive within the free volume of the cell wall. The last case claims the formation of chemical crosslinks with the cell-wall polymeric components.

The above discussion reveals that adhesive penetration of wood occurs on two or more levels of scale. There is micro-penetration, which occurs through the cell lumens and pits. In addition, there is nano-penetration that occurs in the cell wall. One may also envision macro-penetration of adhesive through process-induced cracks. Penetration on any scale will impact bond performance.

#### *Observation and measurement*

Transmitted and reflected light microscopy, fluorescence microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are techniques that have been successfully employed to study adhesive penetration in wood. The optical microscopy techniques offer advantages of color contrast, color filtering, and specimen preparation options to improve contrast. Color (wavelength and intensity) adds another quantitative measure for discerning adhesive penetration. Transmitted light microscopy requires a thin specimen (typically 10 to 40 micron), the preparation of which may be problematic for an adhesive bond. The specimen must be soaked with water to soften before slicing, or the specimen must be embedded in a rigid polymer to provide mechanical support

during slicing, and thus prevent damage to the section. Water soaking swells the section and may modify some of the features of interest. Water soaking may also deteriorate the adhesive (e.g. urea-formaldehyde and poly(vinyl acetate) adhesives) and delaminate the section. Specimen preparation is simplified using reflected light microscopy, in which case only a clean-cut surface is required. Reflected light microscopy may require staining to discern the adhesive in the cell lumens. Fluorescent microscopy, with incident light excitation, may offer good contrast for observing bondlines on surfaces. Stains are often used to enhance the contrast between the adhesive and the wood when using fluorescence techniques. Optical microscopy may detect penetration of certain adhesives into the cell wall (Nearn 1974), but not quantitatively.

*Optical microscopy methods.*—Numerous studies have been reported concerning observation and measurement of adhesive penetration in wood using optical microscopy techniques, such as: Hancock and Northcott 1961; Hare and Kutschka 1974; Nearn 1974; Dougal et al. 1980; Saiki 1984; Kuo 1998 and many others. Most of the early studies on the examination of bondlines were limited to qualitative analyses. Digital image processing and analysis was introduced to this application in the early 1990s and permitted rapid and quantitative evaluation of adhesive penetration (Johnson and Kamke 1992).

Bright-field (transmitted light) microscopy enables examination of the bondline interface thickness, location of adhesive in the lumens, and assessment of the integrity of the cellular wood structure (Hare and Kutschka 1974). Kutschka and Caster (1987) demonstrated the efficacy of optical microscopy to study resorcinol-formaldehyde adhesive bond performance in finger-joint lumber.

Fluorescent microscopy was found superior to other optical techniques for applications where there is poor color contrast in the interphase region (Lehmann 1968; Furuno et al. 1983b; Furuno and Saiki 1988; Brady and Kamke 1988; Kuo 1998). An epi-fluorescence microscope is equipped with a three-component optical filter set. A high intensity, broadband light source

(typically mercury) produces a wide spectrum of wavelength. The excitation filter suppresses all wavelengths except for a narrow band selected for the specimen of interest. A dichromatic mirror directs the excitation beam through the objective lens and onto the specimen. Features of interest in the specimen are excited by the excitation beam, thus emitting photons that have a wavelength longer than the excitation wavelength. Reflected light, as well as fluorescing light is collected by the objective lens and passed through the dichromatic mirror. The dichromatic mirror is coated to act as a long-pass filter—only light of longer wavelength than the excitation light is able to pass. This fluorescent light then passes through an emission filter, which may be a band-pass (permits narrow band of wavelength to be transmitted) or a long-pass filter. The advantage of a long-pass filter used for the emission filter is that anatomical features of the wood are often visible along with the adhesive. The resulting image allows the observer to distinguish resin from wood by differences of color or light intensity.

Characteristic fluorescence properties of the adhesive or the wood may be sufficient to yield good color contrast. Alternatively, stains may be used to enhance or suppress fluorescence. The selection of the excitation and emission filters depends on the adhesive type and staining procedure. A mercury light source and a UV excitation filter (approx. 410-nm) was used by Furuno et al. (1983a) to observe PF bonds in flake-board specimens produced from a variety of hardwood species (the excitation filter was unknown). The specimens were stained with an aqueous solution of 0.2% acridine yellow, which was readily absorbed by the wood, but not the PF, thus enhancing the fluorescence of the wood. The authors used incident light (dark field) fluorescence (sometimes called epi-illumination). Brady and Kamke (1988) used a similar procedure to view PF adhesive bonds in Douglas-fir and aspen. However, the specimens were stained with a 0.2% aqueous solution of acridine red and viewed using epi-illumination with a 410-nm excitation filter and a 510-nm emission filter. Johnson and Kamke (1992) sup-

pressed the fluorescence of yellow-poplar wood in thin sections of PF bondlines by using a 0.5% aqueous solution of toluidine blue O. The specimens were observed using epi-illumination from a mercury light source, with a 365-nm excitation filter and a 420-nm emission filter. Sernek et al. (1999) studied the penetration of UF into beech. The cross-sections of the bondline specimens were sliced to 60- $\mu\text{m}$  thickness, treated with a 0.5% solution of brilliant sulphaflavine solution, followed by soaking in a 0.5% aqueous solution of safranin O. The specimens were observed with a mercury light source, 365-nm excitation filter, and a 420-nm emission filter. This procedure yielded bright fluorescence of the UF, with details of the wood structure still visible (Fig. 1). MDI adhesive may also be viewed using fluorescence microscopy. Kamke (2004) reported excellent image contrast of MDI in yellow-poplar and loblolly pine bondlines using epi-illumination fluorescence. The specimens were stained with a 0.5% aqueous solution of safranin O and viewed with a 365-nm excitation filter and 420-nm emission filter (Fig. 3). Fluorescence microscopy has been demonstrated to provide excellent contrast between various adhesives and wood, as illustrated in Figs. 4–7.

Automated image processing and analysis techniques have greatly simplified the task of quantitative measurement of adhesive penetration. Manual digitization was used by Brady and Kamke (1988) to measure penetration of PF adhesive into wood. They created photomicrographs of bondlines using film photography and then projected the images onto a calibrated grid. The adhesive was then measured by manually counting the appropriate grid squares, a procedure that required more than 30 minutes per image. Digital image processing and analysis (DIPA) can accomplish the same task in seconds. In addition, other parameters may be obtained, such as shape factor and hole area, which may be helpful in determining the degree of interaction between the adhesive and the cell wall. Many commercial DIPA systems are available for direct application to adhesive penetration. The technology developed rapidly during the 1990s. In general, a DIPA system consists of a

CCD (charged couple device) camera, image capture board (or integrated circuitry in the camera), a personal computer, and DIPA software with the capability of macro programming. Camera technology is changing quickly. Spectral sensitivity and the number of pixels on the chip are the critical factors for fluorescence applications. Analog cameras provide a live image on the computer screen, which makes image focusing easier. However, digital cameras and image capture speeds are now available that give the appearance of a live image to facilitate focusing. An inexpensive monochrome camera (Sony XC-57, 1/3-inch chip, 325,546 pixels, 400 lux @ F5.6) can be adequate for adhesives with a high fluorescence intensity, as demonstrated by Johnson and Kamke (1992). Color CCD cameras will permit measurement of objects with more subtle contrast by use of independent adjustment of grain and hue of the color channels. However, this comes at a cost of time and money, since color cameras have three or more chips and produce larger image files for the same spatial resolution as a grey-scale camera.

*Electron microscopy methods.*— Electron microscopy techniques permit high levels of magnification and greater depth of field than optical microscopy. The large depth of field is required for viewing fractured bondline surfaces. However, in the grey-scale image produced by SEM or TEM, the adhesive and wood phases are often difficult to differentiate. Texture differences sometimes permit clear identification in the micrograph. Unfortunately, quantitative measurements of adhesive penetration are very difficult and often unattainable with these images. Cell-wall penetration is not detectable by SEM or TEM. However, in combination with energy dispersive X-ray analysis (EDXA) or electron energy loss spectroscopy (ELLS), electron microscopy can reveal quantitative elemental concentration of elements (nitrogen and larger atomic weight) within the cell wall (Rapp et al. 1999).

Early application of SEM and TEM techniques on adhesive penetration were qualitative investigations of bondlines in plywood samples (Harada et al. 1968; Koran and Vasishth 1972; Nearn 1974; Hare and Kutscha 1974; Stephen

and Kuscha 1987). Saiki (1984) managed to identify the effect of resin penetration on the change of failure position within the layered structure of the cell wall using SEM. Koran and Vasishth (1972) detected the penetration of PF resin into tyloses-occluded vessels and paratracheal parenchyma of white oak plywood. The SEM technique was used to investigate the penetration of PF resin and the fractural morphology of adhesive joints in tension shear (Furuno and Saiki 1988). Collett (1970) pointed out the limitations of SEM in regard to the weak contrast between resin and wood cells.

Rapp et al. (1999) provided a review of previous work describing the techniques employed to detect cell-wall penetration. Using EDXA and a PF resin tagged with bromine, Smith (1971) verified that PF resin penetrates the secondary cell wall, although the degree of penetration may be different between the earlywood and latewood tracheids. Saiki (1984) proposed that PF and epoxy resins may penetrate and reinforce the cohesion between the S2 and S3 layers of the cell wall. Unless end-grain is exposed, cell-wall penetration, when present, enters from the lumen, moves through the S3 layer, and predominately resides in the S2 layer. The concentration of PF resin in the cell wall was greatest in the S2 layer near the interface with the S3 layer. SEM/EDXA was used to evaluate UF resin penetration into the cell wall of wood contained in particleboard (Bolton et al. 1988). The authors questioned the accuracy of this technique because the excitation volume of the electron beam is large in comparison to the area of measurement. Consequently, artifacts from surrounding regions, such as a resin coating in the cell lumen, may contribute to the apparent detection of resin within the cell wall. Through an analysis of their SEM/EDXA system, they concluded that UF resin likely penetrated the cell wall, but they recommended collaboration with TEM/EDXA, where the excitation volume is much smaller. The authors commented that several factors influence the size of the SEM/EDXA excitation volume, suggesting that previous research that didn't determine the electron beam volume may

have reached an erroneous conclusion regarding cell-wall penetration.

*Other methods.*— Gindl et al. (2002) detected the penetration of the melamine component of MUF adhesive in the cell wall of spruce using UV-absorbance spectra captured with a UV photometer microscope. The authors claimed the technique provided a spatial resolution between SEM/EDXA and SEM/EELS, with the advantage of no chemical pretreatment.

White et al. (1977) used neutron activation analysis to determine depth of penetration of a resorcinol-formaldehyde adhesive that had been tagged with bromine. Thin sections were cut parallel to the plane of the bondline using a microtome, with the order of the sections maintained. Approximately 25 sections were cut per bondline, which accounted for the entire interphase region. The specimens were irradiated, and then the intensity of the  $\gamma$ -ray emission from the bromine isotopes for each section was measured. The result provided a relative measure of the concentration of bromine (hence concentration of adhesive) across the thickness of the bondline, with a spatial resolution of approximately 35  $\mu\text{m}$ . On a smaller scale, Nearn (1974) used  $\text{C}^{14}$  labeled PF resin and autoradiography to detect cell-wall penetration.

X-ray spectromicroscopy was used by Buckley et al. (2002) to follow the pathway of MDI penetration into aspen. The degree of X-ray absorption depends on the atomic bonds present, level of X-ray energy, and the thickness of the specimen. For the wood MDI specimen a very thin specimen (0.15 to 0.25  $\mu\text{m}$ ) was needed. For quantitative analysis in a complex mixture, such as MDI interspersed in a cell wall, the X-ray absorption spectra of the individual components were required. For this purpose, the authors obtained X-ray absorption spectra of organosolve lignin, cellulose, cured MDI, and cured methacrylate embedding media (the thin sections required embedding). Images were captured using a transmission microscope with a tunable X-ray probe. The source of the high-energy X-ray beam was the synchrotron device at the Brookhaven National Laboratory. Results provided spatial resolution on the order of 0.05



$\mu\text{m}$ . MDI was detected in lumens of vessels and ray cells and inter cellular pits. If any MDI was present in the cell wall, it was below the sensitivity of the technique.

With the realization that wood materials are complex three-dimensional structures, Shaler et al. (1998) used micro X-ray tomography (XT) to study paper, solid wood, and a wood-resin interphase. The authors achieved a resolution of 1.2  $\mu\text{m}$  in this preliminary study. Micro XT creates three-dimensional digital images of objects containing features of various levels of electron density. Like a conventional X-ray, objects with relative high electron density attenuate the electron beam to a greater extent, and thus interfaces between dissimilar materials may be discerned in the resulting image. By rotating the specimen within the beam, and collecting successive images at a known angle of rotation, the three-dimensional image is mathematically reconstructed, and subsequently may be viewed at any plane or angle within the object. Figure 8 illustrates a view of three mutually perpendicular planes about a point within the interphase of an adhesive bond (Kamke et al. 2004). The image was created using the 5-BM-C, 42 keV, synchrotron beamline at the Advanced Photon Source, Argonne National Laboratory. The spatial resolution was 2.4  $\mu\text{m}$  per pixel, with a specimen rotation of 0.14 degree increments. This view, albeit two-dimensional for this publication, illustrates the discontinuity and complexity of the adhesive flow through the porous network of interconnecting cell lumens and pits. In this example the electron density of the PF adhesive was very similar to the cell-wall substance. Consequently, ferric chloride was added to the resin prior to bond formation. While this enhanced the contrast, incomplete mixing was achieved, so some of the adhesive was not easily distinguished from the wood in this example.

#### *Wood factors affecting penetration*

The permeability and surface energy are the two wood-related factors controlling adhesive penetration. Permeability varies by species and by direction (e.g. tangential, radial, and longitu-

dinal). The relative magnitude of radial and tangential permeability (collectively called transverse permeability) varies by species. However, longitudinal permeability may be as much as  $10^4$  greater than transverse permeability (Siau 1995). Sernek et al. (1999) observed lower penetration by UF resin in the radial direction of beech than that in the tangential direction. This was attributed to the large vessel structure and more radial pits. Wood species with low permeability, such as Douglas-fir heartwood, severely restricts resin penetration in the radial and tangential directions. High permeability of the wood surface may be problematic to adhesive bonding if this leads to starvation at the bondline. Thus, bonding endgrain is difficult.

Adhesives may be formulated (e.g. molecular weight distribution, solids content, and addition of fillers and other additives) to be compatible with any wood species, regardless of its permeability. However, natural variability of wood, and the mixing of multiple species in the manufacture of composites, often defeat custom adhesive formulations. Unfortunately, permeability is one of the most highly variable properties of wood. There are earlywood and latewood differences, as well as heartwood and sapwood differences. Pit aspiration sometimes occurs in softwoods during drying (Siau 1995), thus severely reducing permeability. White et al. (1977) noted greater penetration of phenol-resorcinol into earlywood than latewood cells of southern pine. The slope of grain with respect to the bonded wood surface greatly influences penetration. Saiki (1984) clearly illustrated enhanced penetration of adhesive when the cell lumens intersect the external surface at an oblique angle.

Sernek et al. (1999) reported that maximum depth of penetration into beech occurred at a wood moisture content of approximately 9 percent with a particular formulation of UF resin. With water-borne adhesives, water influences penetration in two opposing ways. On the one hand, low moisture content wood will draw the solvent, and polymer, more readily into the substrate. On the other hand, as water is preferentially adsorbed by the dry cell wall, the effective solids content of the adhesive increases, leading

to accelerated coalescence of the polymer and increased viscosity. Brady and Kamke (1988) noted greater penetration of PF adhesive into aspen at 15 percent moisture content compared to 4 percent. Nearn (1974) observed greater cell-wall penetration of PF resin at a wood moisture content of 25 percent compared to wood at 5 percent.

No difference in penetration of PF resin was detected between the earlywood and latewood of aspen (a diffuse-porous hardwood), but significantly greater penetration was found in the earlywood of Douglas-fir (Brady and Kamke 1988). Hse (1968) also reported greater penetration of PF into earlywood than latewood of southern pine. The author noted that the shear strength of the earlywood to earlywood bonds far exceeded the latewood to latewood bonds.

Kutscha and Caster (1987) noted the importance of adhesive encapsulation of damaged cells and the preferential penetration into earlywood zones of western hemlock and noble fir. They also observed a variation in interface thickness between the earlywood and latewood zones. Under the force of assembly of the finger joint, adhesive was displaced from the zones of the dense latewood and into the zones of the more readily compressible earlywood.

Serneck (2002) studied PF bond performance with yellow-poplar and southern pine, both untreated and after exposure to high temperature. Greater penetration occurred in yellow-poplar than southern pine. The difference was attributed to the greater permeability of yellow-poplar, due to the presence of vessels. The heat treatment had no influence on penetration. Fracture testing revealed a reduction in strain energy release rate with increasing treatment temperature. However, since adhesive penetration was not affected by the treatment, there was no correlation between bond performance and penetration.

Liquids in contact with a solid surface will spontaneously spread if the surface energy is favorable (Shaw 1991). This phenomenon is referred to as wetting. A greater surface energy of the wood promotes greater wetting. The presence of non-polar substances on a wood surface

will reduce surface energy and retard wetting by aqueous adhesive systems. Consequently, wood species with a large concentration of non-polar extractives are more difficult to bond (Hse and Kuo 1988). Wood subjected to high temperature drying conditions often experiences surface inactivation, a loss of surface energy. The migration of extractives to the surface during drying is thought to be a common cause of surface inactivation, although other causes have also been proposed (Christiansen 1990 and 1991). Therefore, even wood species with a moderate concentration of extractives, could lose surface energy as the result of a severe drying procedure (Serneck et al 2004). Surface inactivation is likely to only influence adhesive penetration during the open assembly time. During bond consolidation, while still in the liquid phase the adhesive will be subjected to hydrodynamic forces—causing bulk flow of the adhesive into the lumens.

#### *Influence of resin type and formulation on penetration*

Molecular weight distribution, viscosity, solids content, and surface tension of the liquid phase of the adhesive will all influence penetration. In addition, additives may change these characteristics. Consequently, the resin formulator has a tremendous influence over the penetration behavior of adhesives into wood. General statements comparing the penetration characteristics of various adhesive types must be offered with the knowledge that properties of specific formulations may be modified. Most of the literature has focused on PF adhesives.

Hse (1971) reported a correlation between penetration and contact angle for PF and southern pine plywood. The author evaluated 36 formulations in regard to contact angle, cure time, heat of reaction, plywood shear strength, percent wood failure, bondline thickness, and cure shrinkage. Penetration was not measured, but assumed to be inversely proportional to bondline thickness (thickness of cured adhesive between the veneers). Penetration increased with increasing caustic content. There were no clear trends observed for penetration in relation to adhesive

solids content or formaldehyde-phenol mole ratio.

Powdered adhesives, such as powdered PF used in OSB manufacture, must undergo a melt to achieve penetration. Johnson and Kamke (1994), in regard to steam-injection pressing, noted that powdered PF resin remained on the surface of wood strands during the blending process, and was only able to flow and penetrate after heating during hot-pressing. They also noted that MDI resin penetrated deeper into wood than PF resins formulated for OSB manufacture. This was probably due to low molecular weight (approximately 50% monomer) and low surface tension of the MDI resin.

Frazier et al. (1996) noted that low molecular weight of MDI resin would promote penetration into wood cell walls with true molecular mixing occurring. They further hypothesized that the MDI forms an interpenetrating network (IPN) of polyurea and biuret linkages within the cell wall. Swelling of the cell wall by MDI was also observed by Frazier (2003).

Variation of resin penetration among different types of resin becomes larger when the difference in the molecular weight (MW) of resin is considered (Near 1974; Johnson and Kamke 1994; Stephen and Kutscha 1987; Gollob et al. 1985). The use of resin with low MW components has the potential for deeper penetration than that with high MW. Stephen and Kutscha (1987) separated a commercial PF resin into two MW fractions (approximately  $\pm 1000$  MW). They reported no penetration for the high molecular weight fraction when resin drops were placed on aspen, and penetration of 1 to 2 cells deep for the low molecular weight fraction. The addition of NaOH improved the penetration of the high molecular weight fraction, which the authors assumed was due to swelling of the cell wall by the NaOH. The improved penetration may also have been due to a lower viscosity as a result of NaOH addition (Gollob 1989). Gollob et al. (1985) reported PF bond performance was associated with penetration in Douglas-fir plywood. They noted that higher MW formulations tended to dry out and had little penetration.

Zheng (2002) reported varied penetration with

blends of MDI and PF into yellow-poplar and southern pine. The penetration of the adhesive blends was characterized by a phase separation. MDI penetrated deeper and tended to be present as a thin coating on the walls of the cell lumen. PF tended to bulk the lumens and remain at the interface of the bondline. In general, the blends resulted in less penetration than either of the neat resins. The author attributed the reduction in penetration to increased molecular weight, and subsequent increased viscosity, due to the formation of urethane bonds between the PF and the PMDI.

Molecular weight distribution of resin systems will impact their ability for cell-wall penetration. Laborie (2002) reported evidence of cell-wall penetration for two PF formulations, one had a number average MW ( $M_n$ ) of 270 and a weight average MW ( $M_w$ ) of 330. The other PF had  $M_n$  and  $M_w$  values of 2840 and 14200. The more highly condensed PF resin had a broad MW distribution, including a low MW component that was similar to the low MW PF resin. Using dynamic mechanical analysis the author concluded that both resin systems penetrated the cell wall.

#### *Processing parameters effect on penetration*

Adhesive penetration can vary according to open assembly time, pressing time, temperature, and consolidation pressure involved in wood-based composite manufacture. Process-induced damage to the wood surface may also influence penetration. Certainly there is an interaction between processing parameters, adhesive formulation, and wood characteristics. These interactions are potentially complex and may mask the influence of processing parameters. For example, processing parameters may have no effect on penetration if the wood species is extremely permeable or the adhesive has an extremely low viscosity. Nevertheless, processing parameters have been shown to influence adhesive penetration.

Hare and Kutscha (1974) examined adhesive penetration and shear strength of spruce plywood bonded with PF. Drying technique and the

influence of aging were parameters in the study. They noted deeper penetration into veneer that had more severe surface damage (cell-wall fractures). This condition was associated with low shear strength, but high percent wood failure. Consequently, the authors questioned the validity of percent wood failure as the sole indication of bond performance. The authors also reported very erratic penetration in veneer that had been pretreated with either sodium hydroxide or methyl ethyl ketone. This was attributed to a dramatic increase in wettability.

Serneck et al. (1999) reported increasing penetration of UF resin into beech as open assembly was increased. More than 50 percent of the penetration occurred during the first minute. The application of consolidation pressure, in this case 1.6 MPa, increased penetration by a factor of 10. Brady and Kamke (1988) found little evidence of consolidation pressure influencing penetration of PF resin into aspen. The authors suspected that flow parallel to the bondline, also influenced by consolidation pressure, may have masked this effect. Perhaps the lowest consolidation pressure (2.1 MPa) used in this study was sufficient to yield maximum penetration, and therefore, increasing the consolidation pressure failed to increase penetration.

Temperature influences penetration by affecting resin viscosity and cell-wall permeability. Commonly used wood adhesives initially decrease in viscosity with increase of temperature, thus promoting penetration via hydrodynamic flow. However, polymerization increases viscosity and eventually overcomes the temperature effect on liquid viscosity. Wood undergoes thermal expansion, a result of increased molecular motion with increasing temperature. The temperature-induced increase of intermolecular voids promotes cell-wall penetration by polymers, which was speculated by Tarkow et al. (1966) in their study of molecular size exclusion by the wood cell wall.

White (1977) studied the influence of consolidation pressure on penetration and subsequent fracture toughness of southern pine blocks bonded with resorcinol-formaldehyde. Increasing consolidation pressure from 3 to 1000 kPa

increased penetration into earlywood, but had an erratic effect on latewood. The author suspected that the low permeability of the latewood contributed to adhesive squeezing out of the bondline during consolidation. Increasing consolidation pressure reduced fracture toughness of the latewood specimens, but had no significant influence on the earlywood specimens.

Adhesive migration into wood may be influenced by the method of consolidation or heat delivery in a hot-press. Johnson and Kamke (1994) reported increased penetration of PF into yellow-poplar strands as a result of steam-injection pressing. The authors suggested that condensate from the steam dilutes the resin and steam pressure forces the resin deeper into the wood. The use of radio-frequency heating of a veneer composite caused a reduction in penetration of UF resin in comparison to matched samples produced using conduction heat in a platen press (Serneck et al. 1999). The authors noted that the rate of polymerization was much faster using radio-frequency heating and thus reduced the time for penetration. One could speculate that penetration of adhesive would depend on location within a composite during hot-pressing, since the temperature and gas pressure history inside a composite varies by location during manufacture.

#### *Influence of penetration on bond performance*

Adhesive bond performance must be influenced by penetration. However, variability of penetration makes the development of correlations to bond performance difficult. Furthermore, comparison of bond performance between resin formulations, based solely by the criteria of penetration, is improbable. Penetration may only have a secondary affect on bond performance, whereas the effects of cohesive strength, covalent bonding, and secondary chemical bonding, all of which will likely change with formulation, may have a larger impact. Greater penetration is associated with more surface contact between adhesive and wood substance, thus increasing the potential for secondary bonding forces and covalent bonding. Penetration into cracks and

encapsulation of damaged cells at the surface will improve bond performance. Furthermore, penetration promotes a greater distribution of stress between the adherents when placed under load. Nevertheless, penetration is but one factor contributing to bond performance.

The effect of resin impregnation, independent of adhesive bonding, on the mechanical properties of wood has been investigated (Furuno et al. 2004; Miroy et al. 1995; Gindl and Gupta 2002; Gindl et al. 2004; Nakata et al. 1997; Shams et al. 2004). Significant increases in hardness, compression strength, and bending strength and stiffness have all been reported. Since the wood surrounding the interface of the adhesive bond contributes to bond performance, reinforcement of the wood in the interphase will impact bond strength and stiffness.

Wilson and Kraemer (1978) studied the influence of MW distribution on the internal bond strength (IB) of PF-bonded particleboard. The higher MW resin yielded higher IB values. The low IB of particleboard produced from the low MW PF resin was attributed to over-penetration.

Furuno et al. (1983b) noted that the slope of grain with respect to the bond interface has a significant impact on shear strength. The authors prepared softwood specimens with a controlled grain angle, up to 5-degree, into a lap-shear specimen. The greatest penetration occurred with the 5-degree grain angle, which corresponded to the greatest shear strength, but lowest percent of wood failure.

The depth of the penetration had a positive effect on the fracture toughness of loblolly pine bonded with resorcinol-formaldehyde as reported by White (1977). The author noted an increase of fracture toughness with an increase in penetration depth and concentration of adhesive in the interphase. Ebewele et al. (1986) generally supported this result. However, greater depth of penetration, with a fixed amount of polymer, reduces the concentration of polymer in the interphase. Furthermore, excessive penetration may leave too little adhesive at the interface, a condition called a "starved" bondline. If adhesive is only applied to one side of a bondline, a starved bondline has little chance to

be successful. Improvements in wet shear strength and percent wood failure were reported by Hse (1971) with increasing adhesive penetration in southern pine plywood.

The notion of an interpenetrating network of adhesive into the wood cell wall should lead to a bond with greater resistance to water infiltration. Water would have very restricted access to bonding sites, and therefore, be less likely to displace secondary forces of adhesion. The intimate contact may also reduce stress concentrations at the lumen wall when the bond is subjected to water-induced shrinking and swelling. Nearn (1974) hypothesized that full exterior quality adhesive bonds could not be achieved without cell-wall penetration. The author further reported that cell-wall penetration could be manipulated by controlling the molecular weight distribution of the resin.

#### *Future directions*

Techniques used to date to observe and measure adhesive penetration have been largely qualitative. Digital image processing and analysis does permit quantitative results. However, this approach has only been applied to two-dimensional images, which fail to capture the three-dimensional structure of a bondline. Development of a quantitative method to investigate the volumetric penetration is feasible using micro X-ray tomography (XT). This technique has been applied to cellulosic materials, including paper and wood-based composites (Shaler et al. 1998). Micro XT would reveal the pathway for penetration. The current limitations of XT are very large data files for computer analysis, limits of spatial resolution that must be balanced against field of view, and expensive equipment. At present, synchrotron radiation provides the best spacial resolution, on the order of approximately 1  $\mu\text{m}$ . Other XT instruments, which use a point source of radiation, are commercially available (Micro Photonics Inc., Allentown, Pennsylvania; Xradia, Concord, California). In the future improvements will likely be achieved in distortion-free spatial resolution to discern even sub-micron anatomical features in wood.

Variability of adhesive penetration will require extensive sampling if one is to identify any statistical significance in relation to bond performance. Furthermore, interactions with other factors will require a careful experimental design. Actual commercial manufacturing processes may have such large inherent variability that the influence of penetration may be completely masked. A well-defined experiment must consider the practical implications.

Mathematical modeling to predict the mechanical properties of an adhesive bond (e.g. fracture toughness and single-lap shear strength) should be possible based on the microstructural features of the bondline and knowledge of the cell-wall properties and solid phase properties of the adhesive. Statistical distributions of penetration parameters and anatomical features could be incorporated into such a model. Even a model based on a highly simplified wood structure could prove useful for future design of adhesive formulations and composite processing techniques. The micro XT technique could provide the basis for a more detailed mathematical analysis, or at least help to define the statistical distributions.

The significance of cell-wall penetration on adhesive bond performance is unknown. Several investigators have speculated that cell-wall penetration will lead to improved bond strength and durability. However, this is unproven. Furthermore, the nature of the cell-wall penetration must have some influence. Does polymerization occur or does the penetrant remain as an oligomer and simply disperse within the cell wall? Is there a linkage between the penetrated polymer and the bulk polymer in the lumens? What is the nature of the chemical interaction between the penetrant and the cell-wall polymers? Future research should address these questions.

#### SUMMARY AND CONCLUSIONS

A review of the literature on adhesive penetration, with a focus on wood-based composites, was presented. Interest into the influence of adhesive penetration on adhesive bond performance has been evident for several decades.

Methods of direct microscopic observation and detection were discussed, such as light microscopy, fluorescence microscopy, and electron microscopy. Other techniques, such as DIPA, neutron activation analysis, EDXA and EELS, complement the microscopy techniques and provide quantitative results. Many factors influence resin penetration, including factors related to the fluid properties of the resin, anatomical characteristics and permeability of wood, and processing conditions. The optimum adhesive penetration is not known. It is certain that adhesive penetration influences adhesive bond performance, including ultimate strength and durability. There is consensus that penetration must be sufficient to encapsulate damaged cells near the bonded interface. Furthermore, increasing penetration promotes all of the proposed adhesion mechanisms. Excessive penetration wastes resin and is counter-productive if a starved bondline results. However, no direct relationships have been reported due to the inherent difficulty of quantitatively measuring penetration and isolating its influence from other factors. Cell-wall penetration has been verified for many types of adhesives. The extent of cell-wall penetration can be manipulated by resin formulation. As analytical technology advances, direct relationships between adhesive penetration and bond performance will be identified.

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