Wood as Polar Size Exclusion Chromatography Media: Implications to Adhesive Performance

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Abstract

Although it is well known that wood can absorb liqiuds, the full impact of this phenomenon on adhesive performance is not well understood. We have observed examples where aspects of this phenomenon were not fully anticipated and had a large impact on bond quality. Using soy adhesives, several examples illustrate the extent of adhesive infiltration into wood cell walls and the impact of the infiltration on both the adhesive and wood properties.

Introduction

Water not only flows into wood cell lumens, but also infiltrates into the cell walls causing them to swell. Other polar chemicals can also infiltrate cell walls, but as the molecular weight increases (Tarkow et al. 1965) or the hydrogen bonding capacity of the chemical decreases (Mantanis et al. 1994, Obataya and Gril 2005), the absorption decreases. Although the intentional infiltration of chemicals into cell walls has long been studied, the transfer of specific components from adhesives into cell walls has not been widely appreciated. Low molecular weight components of adhesives often cause adhesion problems through formation of a weak interphase layer (Bikerman 1967) or adhesive cohesion problems by plasticization of the adhesive. However, after a liquid adhesive is applied to wood some components can move from the bulk adhesive into the cell wall by infiltration. In this respect the wood is similar to a polar size exclusion chromatography column. This separation of the adhesive components can have a large impact on the wood that absorbs these materials, the adhesive left behind in the glueline between the wood surfaces, and the bond performance.

We use the term infiltration to mean the movement of these small molecules into the cell wall. Many use the term penetration for this, but the general term penetration involves two very distinct phenomenon, flow and infiltration, governed by very different criteria (Frihart 2006). Flow is the bulk movement of adhesive through empty spaces, influenced by viscosity, surface energies, and fluid dynamics. By contrast, infiltration is the molecular mixing of adhesive components with the cell wall polymers, governed by the molecular sizes of adhesive components, swelling state of the cell wall, and the solubility parameters of both. It should be noted that small molecules with poor hydrogen bonding capacity such as toluene will not infiltrate wood nearly as well as similarly sized molecules with good hydrogen bonding such as pyridine (Mantanis 1994).

The migration of low molecular weight adhesive components from *in situ* polymerized adhesives such as phenol-formaldehyde resins, resorcinol-formaldehyde resins, urea-formaldehyde, melamine-(urea-)formaldehyde, and polymeric methylenediphenyl diisocyanate into the cell wall, and the subsequent reinforcement of the cell wall, has been discussed by Frihart (2009). It can be suspected that the infiltration and hardening of adhesive oligomers in the cell wall repairs damage to cells near the surface and modifies the cell wall; this results in a more gradual gradient of material properties between the bondline and the bulk wood, resulting in less concentration of swelling stresses when wet and therefore better bond performance. Multiple nanoindentation studies (Gindl and Gupta 2002, Gindl et al. 2004, Hunt et a1 2010) have shown a hardening or stiffening of cell walls adjacent bondlines.

Along with adhesives stiffening wood cells, we have also observed changes in adhesive properties as a result of adhesive curing in the presence of wood. This was observed when working with some soy adhesive formulations that contained up to 3 parts glycerin to 1 part soy flour. While these formulations were useful plywood adhesives, the neat adhesive, when cured, had little stiffness or cohesive strength. In contrast, soy flour alone when mixed with water and dried makes a very stiff material. How could the glycerin containing adhesive produce bonds that gave high wood failure when tested dry? We hypothesized that the glycerin had largely migrated into the wood, leaving adhesive in the glueline between the wood surfaces with a low glycerin content, and therefore properties more similar to pure soy than the soy/glycerin mixture. This paper presents some experiments which test this hypothesis and discuss the implications to wood adhesives in general. In this work, the glycerin in soy adhesives was replaced with chlorinated analogs to aid in analysis. After nanoindentation provided us with elastic modulus and hardness of the cell walls adjacent the bondline, SEM-EDS was used to measure the concentration of the glycerin analogs using the chlorine groups in the same cells. Thus, we then could look for the relationship between the movement of glycerin analogs and mechanical properties. Other work not published yet shows that at standard storage conditions (23C/50% RH) the migration rate of similar small molecules though wood is insignificant. Thus, the glycerin migration mainly takes place during the bonding process.

Materials and Methods

Soy adhesive was 21% w/w soy flour (100 mesh, 90 PDI, Prolia 100/90, Cargill Inc., Cedar Rapids, IA), 21% w/w glycerin analog (3-chloro-1,2 propanediol or 3-chloro-1-propanol) (Sigma-Aldrich. St. Louis, MO), and 58% w/w reverse osmosis (RO) water. The water and analog were mixed for 30s in an IKA Turrax homogenizer. Soy flour was then added in 3 parts with stirring after each, then mixed 2 min, scraping the sides of the container 2 times. The adhesive was left to rest 60 min before bonding.

Neat soy adhesives on the left side in Figure 1 were the same soy as above, with the exception that just tap water was used instead of water/glycerin analog; additionally PAE (polyamidoamine epichlorohydrin, Ashland Water Technologies 1920A), a wet strength agent, was added because it is used in many commercial formulations, though PAE doesn't affect the look or stiffness of the adhesive when dry. The adhesive on the right of Figure 1 also contains glycern.

Loblolly pine specimens were cut to 2.5 mm radial direction x 5 mm tangential x 5 mm longituidinal, with bonding faces surfaced with a sled microtome. A small amount of prepared adhesive was spread over the tangential face of one wood sample; then a second wood sample was placed on top. The specimen was pressed in a TA Q800 DMA in the penetration fixture with

the top probe replaced with a flat 12.5mm dia. disc, 17N (0.68MPa) load applied, equilibrated at 35C, ramp at 20C/min to 120°C, held 5 min, and ballistic (air) cooled. The samples were conditioned 1 week at 21°C, 50% RH before testing.

Nanoindentation followed the procedures recently developed by Jakes and coworkers (Jakes et al. 2009; Jakes et al. 2008) that utilize multiload indents so the structural compliance method could be used to account for edge effects and specimen-scale flexing. High quality transverse surfaces of the bondline were prepared with a diamond knife fit in an ultramicrotome (Jakes et al. 2009, 2008). A Hysitron (Minneapolis, MN, USA) TriboIndenter® equipped with a diamond Berkovich probe was used. Both the elastic modulus and hardness were assessed on the tangential side in the S2 cell wall lamina with rows of daughter cells that extended from the bondline into the wood adherend. The cells within a daughter cell row far from the bondline can be used as a control for the cells within the row near the bondline.

SEM-EDS point scans were taken with the LEO EVO 40 at a variable pressure of 52 Pascal at 1.2nA and 15kV at the center of the cell walls in the rows of cells tested with nanoindentation. EDAX analysis was performed using an IXRF 550i system with a 50-mm SDD detector (IXRF Systems, Inc. Houston, Texas). Spectra were collected for 100 seconds at each point.

Results and Discussion

Movement of glycerin analogs from Soy:PAE adhesive

Figure 1 shows the image of two neat soy:PAE adhesives. On the left is 21% soy: 2% PAE: 77% water and the right is 21% soy: 2% PAE: 21% glycerin: 56% water, after drying in an oven. Without glycerin the adhesive dries up hard and stiff, making a clear sound when tapped with a fingernail. On the right the softness of the glycerin soy is evident by the way it sags when unsupported. The neat glycerin containing adhesive also had low cohesive strength as it tears easily.

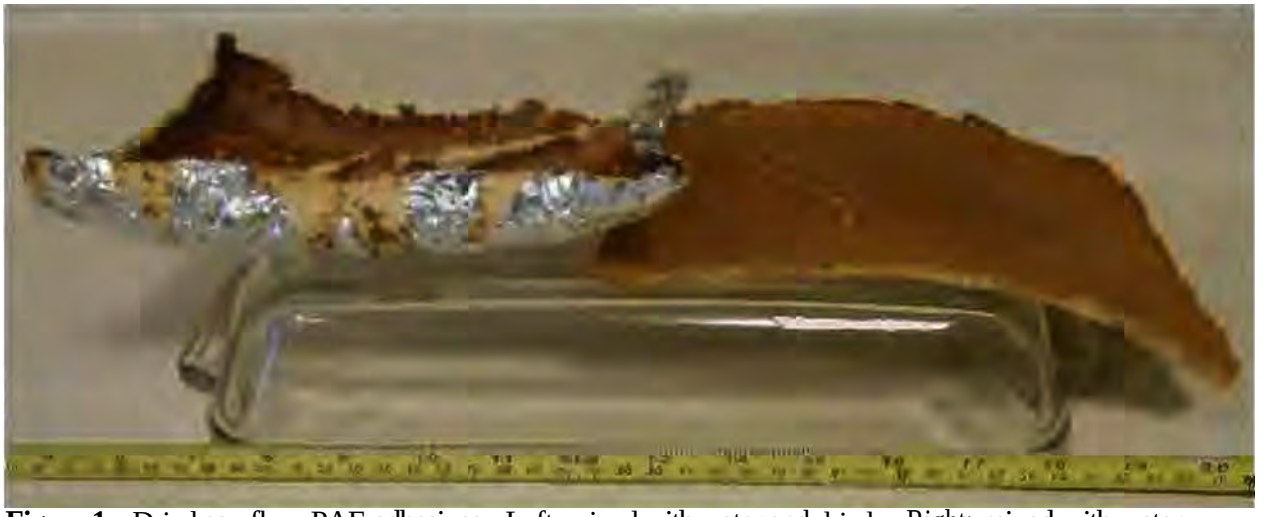


Figure 1: Dried soy flour:PAE adhesives. Left: mixed with water and dried. Right: mixed with water and glycerin- then dried.

We chose the 3 chloro-1,2 propanediol (diol) and 3 chloro-1-propanol (mono-ol) as substitutes for glycerin because they could be traced using SEM-EDS. Their solubility parameters **(Table**

1) are compared to glycerin and wood components. Lignin and cellulose are in quotation marks because of the inherent uncertainty in solubility parameters for these materials.

Table 1: Structures and solubility parameters of glycerin, glycerin analogs used in this study, lignin, and cellulose. "est"= estimated based on difference between nonchlorinated 1-propanol and 1,2-propanediol.

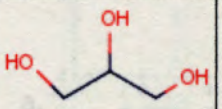
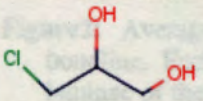
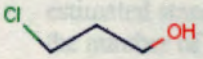
Hansen's Solubility Parameters, δ/MPa^.5					
		Total	Disper-sion	polar	H bond
	Glycerin (Hansen 2000)	36.1	17.4	12.1	29.3
	3 chloro 1,2 propanediol (est)	28.8	18.3	8.3	20.6
	3 chloro 1 propanol (Hansen 2000)	23.6	17.5	5.7	14.7
	"Lignin" (Hansen and Bjorkman 1998)	~29	~22	~14	~14
	"Cellulose" (Hansen and Bjorkman 1998)	~29	~17	~17	~16

Figure 2 shows the elastic modulus and hardness obtained by nanoindents in cells adjacent to the bondline. In regard to elastic modulus, the diol infiltrated wood (open symbols) appears to have a trend toward lower elastic modulus nearer the bondline, as would be expected if glycerin analogs had infiltrated the cells near the bondline and plasticized the cell walls. In regard to hardness, the trend for diol infiltrated cells is less conclusive. For one row of daughter cells the hardness decreases near the bondline, consistent with the trend in elastic modulus, but in the other row there is no trend with distance from the bondline. The trend for mono-ol infiltrated cells in elastic modulus and hardness is almost flat and there is not a clear relationship between properties and distance from the bondline.

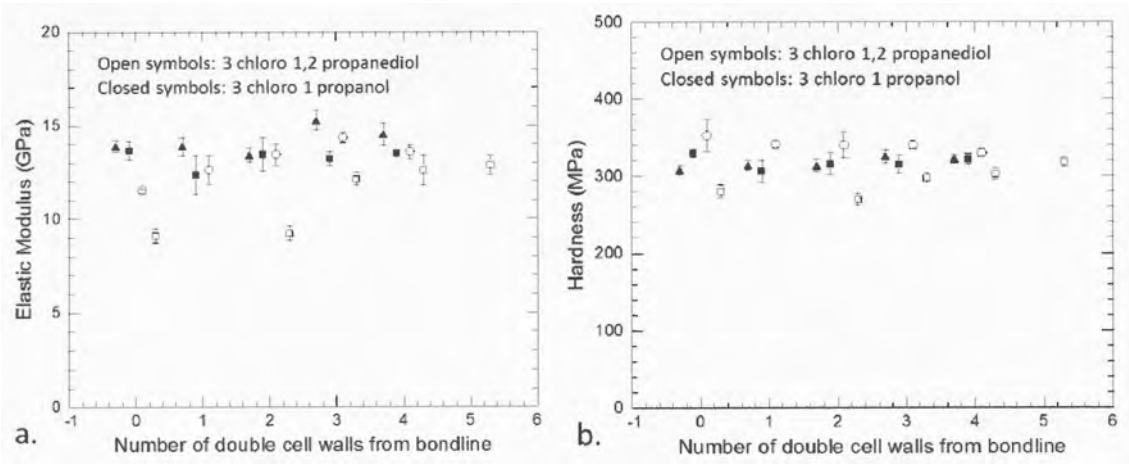


Figure 2: Average elastic modulus (a) and hardness (b) of S2 cell wall lamina near the wood adhesive bondline. Each datum represents the average of 3-8 total nanoindents placed on the S2 cell wall laminae of the double cell wall. The number 0 corresponds to the double cell wall in contact with the adhesive bondline. Each symbol represents data from a different row of cells. Error bars are the estimated standard error of the mean calculated as the standard deviation divided by the square root of the number of nanoindents. Data are slightly shifted on the x axis for clarity.

To investigate if trends in cell wall mechanical properties were related to cell wall infiltration of diol or mono-ol, SEM-EDS measurements of the same cell walls were obtained (Figure 3) to estimate the concentration of glycerin analog. Though EDS data is not quantitative and the results from the spot aimed at the center of the double cell wall might not be fully representative of the S2 cell wall lamina where the nanoindents were placed, the trends are interesting and provide motivation for future work. A striking feature is the apparently higher quantity of diol in cells adjacent the bondline compared to the mono-ol glycerin analog. The higher concentration, as well as the higher hydrogen bonding capacity of the diol, is consistent with the larger effect on cell wall elastic modulus relative to the mono-ol shown in Figure 2. The trends in diol concentration and elastic modulus with respect to number of double cell walls from the bondline are also similar. We hypothesize that the difference in analog concentration in wood might be because of differential affinity for the soy and wood, but, as yet, the data collected do not allow us to compare diol concentrations (as chlorine) in the adhesive phase to test this hypothesis.

The large potassium (K) signal may be unexpected, but dry soy flow contains approximately 2.9% K [Allen 2013]. The clear gradient for ion migration from the adhesive suggests that other ions of interest in various waterborne adhesives such as Na^+, OH^-, and H_3O^+, are likely also moving from adhesives to the wood, changing the pH and ionic content of the adhesive, most probably before cure is complete.

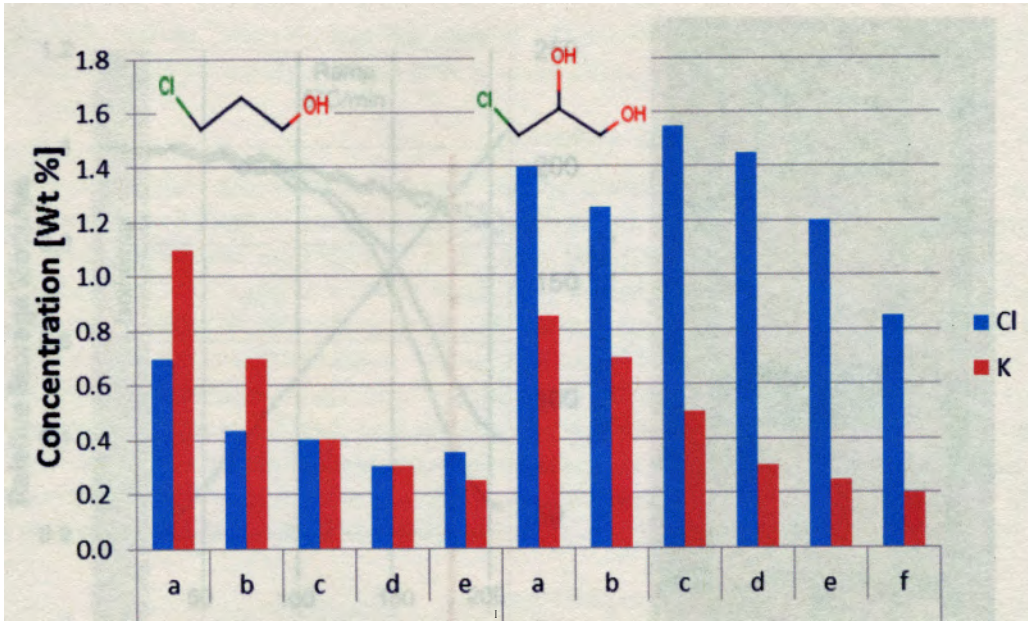


Figure 3: Concentration of Cl and K in sequiential daughter cell walls at the bondline (a) and progressing outward.

Corroborating Evidence from Heat Resistance Study

Our lab recently published work on the heat resistance of soy adhesives (O'Dell et al 2013). In that work, we measured the stiffness of soy flour:PAE adhesive (no glycerin) as a function of temperature. Because of the difficulty in obtaining suitably flat samples of adhesive bonded to wood, we measured adhesive applied to fiberglass filter payer. We found that the adhesive lost ~50–60% of its initial stiffness at a temperature 180°C, despite soy flour losing less than 0.5% of its original weight at that temperature in TGA experiments. This result would suggest that a soy:PAE bondline would fail the CSA creep test (CSA 0112.9), where the glued specimen in Figure 4 must hold a 2.1MPa load for 2 hours at 180°. Yet all four specimens held 3+ hours. We hypothesize that the small (up to a degree of polymerization 3) polysaccharides in soy flour have mostly migrated into the wood. At ~10+% of the mass of soy flour, these polysaccharides might have significant impact on thermal softening behavior. Subsequent DMA tests on soy concentrate (soy flour extracted with ethanol to remove small carbohydrates and peptides, as well as denature the protein) show much better thermal softening performance, consistent with our hypothesis. In effect, the soy flour based adhesive when applied to wood (with then a substantial part of the glycerin infiltrated to the wood material) performed more like soy concentrate (after removing the low molar mass polysaccharides) applied to glass fiber.

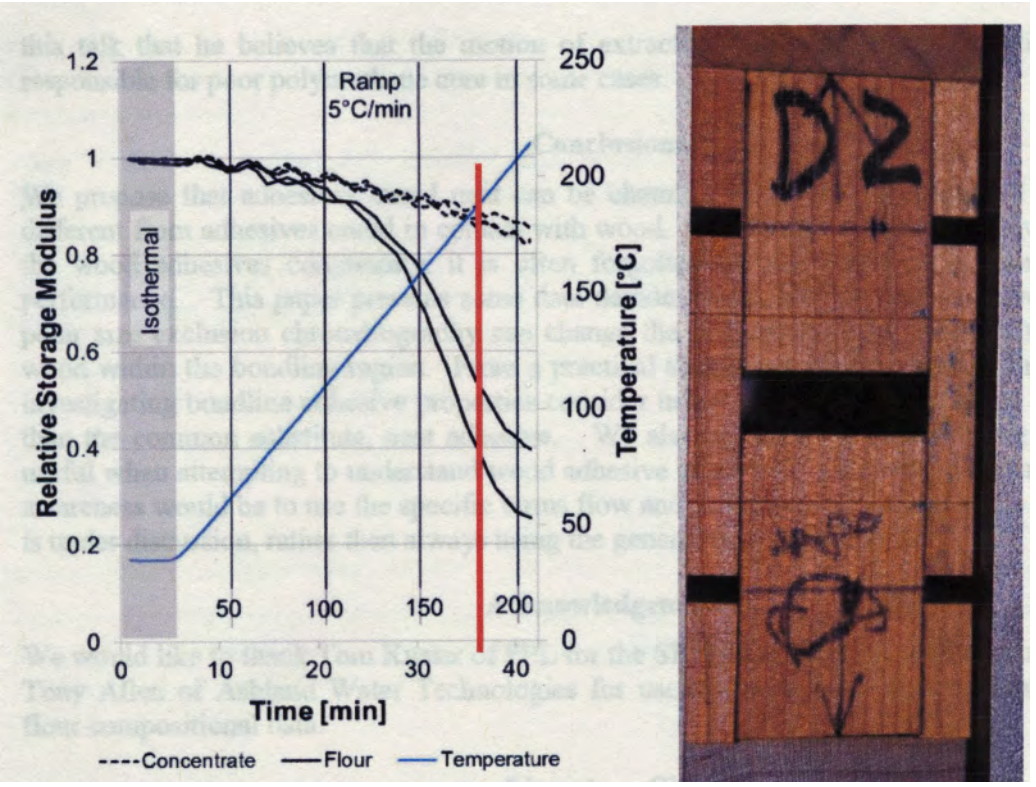


Figure 4: Stiffness vs. temperature plot for soy flour:PAE adhesive on glass cloth in DMA (left) showing a dramatic loss in stiffness at 180°C (vertical red fine) relative to room temperature (2 replicates shown solid lines). Soy concentrate (dashed lines) has low molecular weight sugars and peptides removed by ethanol extraction, and has much better performance at elevated temperanu-e. Soy flour:PAE adhesive on lodgepole pine (right) held 3+ hours at 180°C under 2.lMPa load. (O'Dell et al 2013).

Wood Adhesives 2013: Infiltration Aspects

It was notable that many of the talks at The International Conference of Wood Adhesives 2013 discussed the impact of infiltration. Frihart in his plenary presentation pointed out the need for adhesives to mend the damage to wood surfaces, which in many system we believe is partially accomplished through adhesive oligomers infiltrating cells adjacent the bondline. Grigsby's talk, "To what extent is urea formaldehyde resin really cured in medium density fibreboard?" highlighted a dramatic difference in the extractability of UF when cured neat versus on wood. Neat adhesive yields almost no cold water extractables while approximately 50% of the nitrogen was extractable from fiberboard, suggesting that at least a portion of the UF does not become part of a large, cross-linked network. Lower resin loads resulted in high extractability, consistent with the idea that UF oligomers infiltrate the cell wall but are so dilute there that many do not fully polymerize. Clearly the interaction with wood has changed the properties of the final adhesive in this case.

Another interesting talk was presented by Frazier "Structure/property analysis of polyurethane adhesives", where he tested both neat adhesive and excised bondlines, finding differences in some properties and not in others. Again the interaction with wood resulted in a final adhesive with some properties different from a neat film. One attendee pointed out in the discussion after

this talk that he believes that the motion of extractives from the wood into the adhesive is responsible for poor polyurethane cure in some cases.

Conclusions

We propose that adhesives cured neat can be chemically, morphologically, and mechanically different from adhesives cured in contact with wood. While this in one sense is well known in the wood adhesives community, it is often forgotten or overlooked in relation to adhesive performance. This paper presents some data demonstrating how properties of wood similar to polar size exclusion chromatography can change the properties of the cured adhesive and the wood within the bondline region. From a practical standpoint, we recommend that researchers investigating bondline adhesive properties consider using adhesive cured in wood contact rather than the common substitute, neat adhesive. We also point out that considering infiltration is useful when attempting to understand wood adhesive behaviors. One way to elevate the level of awareness would be to use the specific terms flow and infiltration when one or the other of these is under discussion, rather than always using the general term penetration.

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