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Mechanical Characterization of Wood-Adhesive Interphase with an Improved Nanoindentation Technique

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Abstract

An improved nanoindentation method was used to assess the hardness and elastic modulus of the bulk adhesive and wood cell walls within wood-adhesive bondlines. Improvements include a specimen preparation technique that does not require any embedment. Also, a structural compliance method was used to remove from the nanoindentation measurements artifacts arising from edges near to the nanoindents and specimen-scale flexing. Interphases between southern pine and the four adhesives phenol formaldehyde (PF), urea formaldehyde (UF), epoxy, and emulsion polymer isocyanate (EPI) were characterized. The hardness of PF was measured to be 0.87 GPa, nearly 2-3 times larger than UF, epoxy and EPI. The elastic modulus of PF was 8.8 GPa, comparable to that of UF but nearly 2-3 times larger than that of epoxy and EPI. Furthermore, we observed that the hardness of wood cell walls increased near the adhesive line for PF and UF bondlines, which strongly supports the idea that some low-molecular components of PF and UF infiltrate into the wood cell wall and improve its mechanical performances after curing. Similar increases were not found for epoxy and EPI bondines. Our results support that the widely known durable and strong bonding of wood with PF is related to the excellent mechanical performances of PF resin itself and its ability of infiltrate into and reinforce wood cell walls.

Keywords: wood bonding, interphase, nanoindentation, adhesive

Introduction

All of the potential applications of wood based composites require the formation of mechanically stable and durable bonds between wood elements and adhesives. A full understanding of the mechanisms of bond formation in the adhesive bonding of wood is necessary for the development of wood composites with improved performance. Adhesive penetration into wood structure is believed to be vital to the durability of wood-adhesive bondlines (Frihart, 2009). Adhesive penetration includes both adhesives flowing into the micron-scale cavities of wood, such as empty lumina, and adhesives infiltrating into the cell walls and modifying them. Understanding how infiltrated adhesives affect wood cell wall properties is critical to understanding how to make durable wood-adhesive bondlines.

Recently, several investigators used nanoindenatation to characterize wood-adhesive bondlines, which is based on the reasonable assumption that the infiltration of adhesives into wood cell walls might change their mechanical properties (Konnerth and Gindl, 2006; Konnerth et al, 2007). However, in this previous work the researchers first embedded wood specimens in an epoxy medium to facilitate sample preparation for nanoindentation. The possibility of undesired chemical modifications caused by the epoxy cannot be totally avoided. Furthermore, the nanoindentation tests adopted the standard Oliver-Pharr method (Oliver and Pharr, 1992) for data analysis. This method assumes the tested samples are homogeneous half spaces and are rigidly supported in the testing machine. However, these assumptions will be violated during testing of cell walls because of the free edge between the cell wall lamina and lumen, which are usually in close proximity to the indents, elastic discontinuities across the cell wall, and the possibility of flexing of the cellular structure during indenting. Jakes et al (2008, 2009) recently proposed a structural compliance method to correct for the above factors. This method has been demonstrated to be effective in the micromechanical measurement of wood cell walls (Jakes et al, 2008). In this paper, a specimen preparation technique that eliminates the need for epoxy embedment (Jakes et al. 2008, 2009) and this structural compliance method were adopted to characterize the mechanical properties of cell walls and adhesive in four wood adhesive bondlines, namely PF, UF, epoxy and EPI.

Materials and Methods

Materials. Southern pine veneers with a thickness about 5 mm were bonded together with PF, UF, epoxy and EPI adhesives with the bonding parameters shown in Table 1.

Sample preparation. The common method of embedding wood or wood composites specimens in an epoxy medium was rejected in this study because it might result in unpredictable chemical modifications in the cell walls. A new sample preparation procedure developed by Jake et al. (2008) was used to eliminate these possible artifacts.

First, small blocks (5×5 mm in cross section) containing the bondline were cut from the two-ply wood laminates. A gently sloping apex was created using a sliding microtome on the transverse surface of the blocks with the apex positioned in the bondline (Fig. 1). Next, an ultramicrotome (Leica UC6) fit with a diamond knife was used to cut the tip of the apex. This preparation technique produces an exceptionally smooth and flat surface area of approximately 0.2 mm^2.

	Temperature(℃)	Time (Min)	Pressure (MPa)	Application Rate (g/m^2)
PF	158	6	1.2	80
UF	125	5	1.4	150
Epoxy	Room temperature	180	0.86	174
EPI	Room temperature	Overnight	1.4	180

Nanoindentaion. The polished blocks were glued to steel discs and transferred onto the magnetic holder of a Hysiron TriboIndenter equipped with a diamond Berkovich probe with radius less than 100 nm. During the test period, the relative humidity (RH) in the chamber of the instrument was maintained between 42 and 45% using a glycerin-water bath. Specimens were placed inside the enclosure overnight to allow equilibration with the conditions inside the enclosure. Nanoindentation testing was performed both on the pure adhesives and the cell walls with different distance to bondline. To account for potential artifacts arising from edges nearby the nanoindents and specimen-scale flexing, the structural compliance method was employed. More detailed information on this method could be found in Jakes et al (2008, 2009). Residual indents were imaged with a Quesant (Agoura Hills, CA, USA) atomic force microscope (AFM) incorporated in the TriboIndenter.

Results and Discussion

Table 1 Bonding parameters for the four kinds of adhesives

Figure 1 Schematic diagram showing the procedure of unembeddment sample preparation

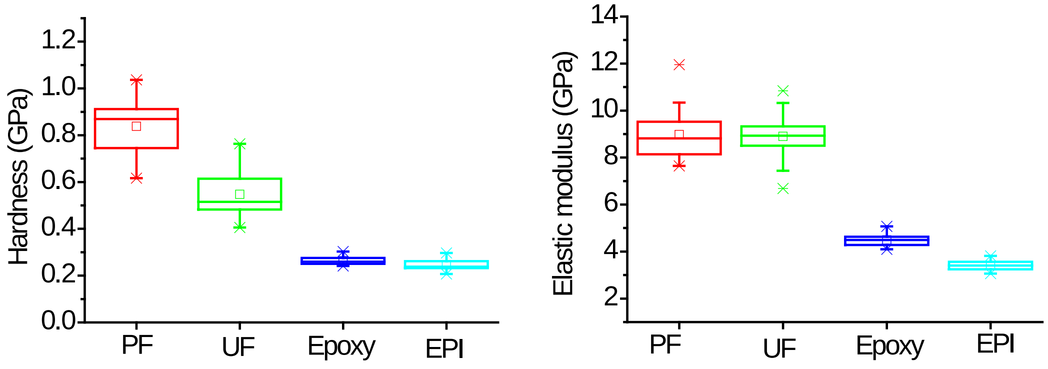
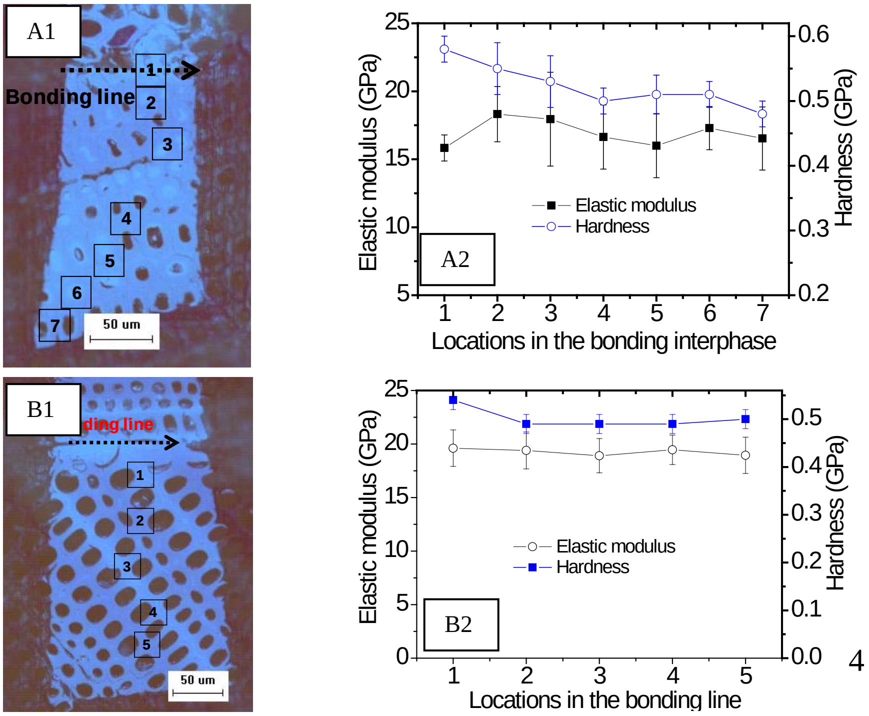


Figure 2 The elastic modulus and hardness of the four wood adhesives

Figure 2 shows the elastic modulus and hardness of the four wood adhesives tested. The elastic modulus of PF was about 8.8 GPa, comparable to that of UF but nearly 2-3 times of epoxy and EPI. EPI has the lowest elastic modulus (3.3 GPa) among the four wood adhesives. The hardness of PF resin was measured to be 0.87 GPa, nearly 2 times the hardness of UF and 3 times the hardness of epoxy and EPI. EPI has the lowest hardness (0.25 GPa) among the four adhesives. Our results indicate PF resin is the most rigid wood adhesive, which is mainly because of its aromatic phenol groups linked by methylene groups along the chain and between chains. EPI is the softest adhesive because of its flexible linear polyester backbone. According to the view point of Frihart (2009), wood adhesives could be classified into two groups. One is *in situ* polymerized adhesives, which is made up of small molecules that cross-link to form relatively rigid polymers after curing. PF, UF and epoxy belong to this group. The other group is called pre polymerized adhesives, consisting of higher MW molecules and is rather flexible after curing. EPI belongs to this group. However, significant difference can also exist among the same group of adhesives, which originates from their different chemical structure.



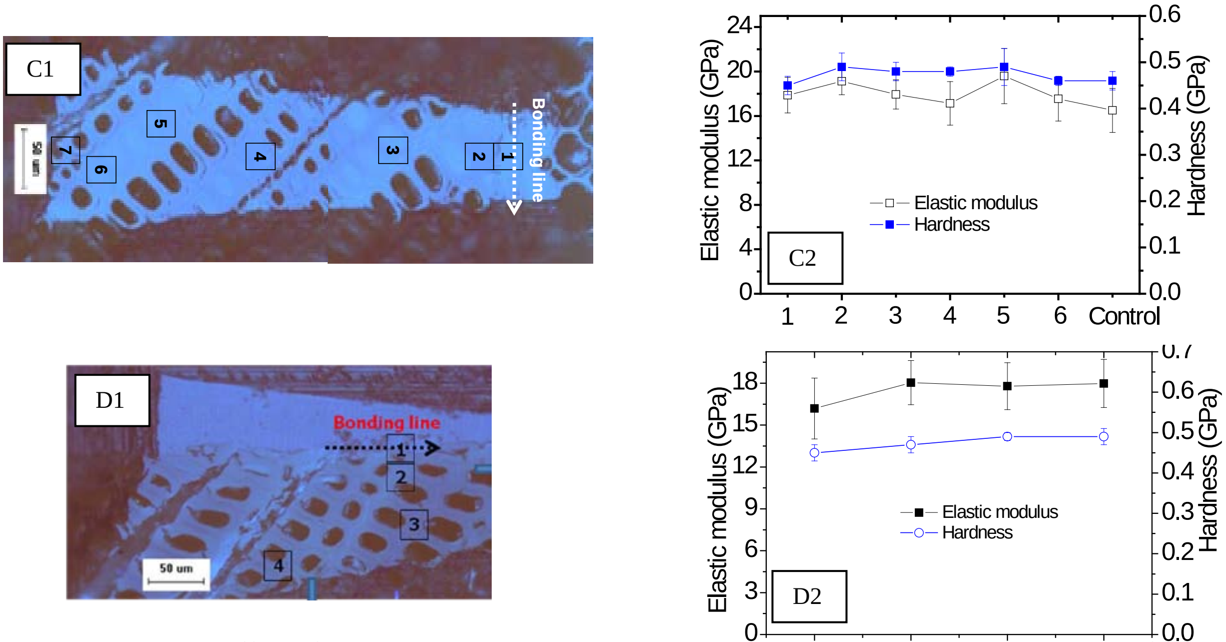


Figure 3 The effect of distance to adhesive line on the elastic modulus and hardness variation of wood cell wall. A: PF; B: UF; C: Epoxy; D: EPI. The higher is the x-axis number, the greater is the distance to adhesive line.

Figure 3 shows the change of elastic modulus and hardness of wood cell walls with the distance to the adhesive line. For PF resin bondlines, cell wall hardness increased significantly for cell walls near the bondlines, while this trend is not so obvious for elastic modulus. The result strongly supports the idea that some low-molecular segments of PF resin penetrate into the wood cell wall and improve it mechanically after curing. However, similar patterns of variation were not observed for the other three adhesive bondlines. For UF resin bondlines, only the cell wall very close to the adhesive line was significantly hardened because the penetration of UF was not as deep into the wood structure as that of PF resin. Although epoxy was found to have a very good capability of flowing into lumina far from the bondlines, changes in wood cell wall mechanical properties were not observed. As for EPI adhesive, no changes in mechanical properties were observed; likely because adhesive infiltration into cell wall will be limited because EPI has too large molecular weight.

Conclusions

1. Of the wood adhesives tested, PF has the highest elastic modulus and hardness, followed by UF, epoxy and EPI in turn.
2. Wood cell walls near UF and PF bondlines had increased hardness, but the elastic modulus was not modified.
3. Mechanical properties of wood cell walls near epoxy and EPI bondlines were not modified. .

4. The durability and strength of wood-PF bondlines is likely because of the high mechanical properties of the PF itself and its ability to infiltrate and strengthen wood cell walls near the bondline.

Acknowledgement

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