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Mechanical characterisation of wood-adhesive interphase cell walls by nanoindentation

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Abstract

The elastic modulus, hardness, and creep factor of wood cell walls in the interphase region of four different adhesive bonds were determined by nanoindentation. In comparison with reference cell walls unaffected by adhesive, interphase cell walls from melamine-urea-formaldehyde (MUF) and phenol-resorcinol-formaldehyde (PRF) adhesive bonds showed improved hardness and reduced creep, as well as improved elastic modulus in the case of MUF. In contrast, cell walls from the interphase region in polyvinylacetate (PVAc) and one-component polyurethane (PUR) bonds showed more creep, but lower elastic modulus and hardness than the reference. Considering the different cell-wall penetration behaviour of the adhesive polymers studied here, it is concluded that damage and loss of elastic modulus to surface cells occurring during the machining of wood is recovered in MUF and PRF bond lines, whereas damage of cell walls persists in PVAc and PUR bond lines.

Keywords: adhesive diffusion; bond line; cell wall properties; interphase; mechanical characterisation; nanoindentation.

Introduction

With the increasing importance of reinforced polymer composites of wood and other natural fibres, the mechanical interactions in the adhesive bonds of such materials are the focus of much attention. A wood adhesive bond consists of an adherent, an adhesive layer, and a zone termed the interphase, where the adhesive and adherent are mixed with each other. The mechanical properties of wood and natural fibres as adherents are well known and data are available on these materials (Kollmann and Côté 1968; Bledzki and Gassan 1999). The determination of mechanical properties for adhesives is less easy, but in recent studies the micro- and macro-mechanical properties of adhesive films and *in situ* properties of adhesive polymers in wood bond lines could be determined (Broughton and Hutchinson 2001; Gindl et al. 2004a,b; Konnerth et al. 2006a,b). The stress-strain behaviour in adhesive bonds is significantly influenced by the interphase (Gindl et al. 2005), which may act as an important factor when failure occurs. In the case of wood adhesive bonds, the interphase consists of wood cell walls, which are often significantly damaged as a result of surface preparation (Singh et al. 2002), a phenomenon termed the mechanical weak boundary layer (Dunky and Niemz 2002). The second constituent of the interphase is the adhesive, which penetrates the adherent surface and can fill microscopic cell cavities (Suchsland 1958; Fengel and Kumar 1970; Furuno and Goto 1975; Saiki et al. 1975; Sernek et al. 1999; Buckley et al. 2002). Its properties depend on factors including the polymer type and viscosity, and the surface energy. Parallel to its presence in microscopic cell cavities, polymer was also observed in cell walls (Bolton et al. 1988; Rapp et al. 1999; Gindl 2001; Gindl et al. 2002, 2003). Polymer in cell walls can have a significant effect on the mechanical properties (Gindl and Gupta 2002; Gindl et al. 2004a,b). Accurate knowledge of the mechanical properties of all bond-line components is necessary to understand the mechanical behaviour of the composite wood-adhesive interphase and ultimately the stress transfer across the total adhesive bond.

Nanoindentation is a method for testing hardness at very small scale that has been applied to the study of mechanical properties of a variety of materials (Fan et al. 2002; Li and Bhushan 2002; Lichtenegger et al. 2002). It was introduced for the study of cell wall mechanics by Wimmer et al. (1997) and Wimmer and Lucas (1997).

In the present study, the influence of adhesive penetration into the wood cell wall on the mechanical properties was studied using nanoindentation. For this goal, four adhesive polymer systems, typically used for wood adhesives, were applied.

Material and methods

Specimen preparation

Adhesive bonds were manufactured using four representative wood adhesives: polyvinyl acetate (PVAc, PV/H Holzleim Standard; Henkel Austria GmbH, Vienna), melamine-urea-formaldehyde (MUF, Dynomel L-435 with hardener H469; Dynea Austria GmbH, Krems, Austria), phenol-resorcinol-formaldehyde (PRF, Aerodux 185 with hardener HR150; Friebe, Mannheim, Germany), and one-component polyurethane (1K PUR, Purbond HB110; Collano AG, Sempach, Switzerland).

Pieces of spruce wood (*Picea abies*) with a length of 100 mm, a width of 100 mm, and a thickness of 15 mm, were bonded by their radial anatomical planes (inclination of the annual rings was

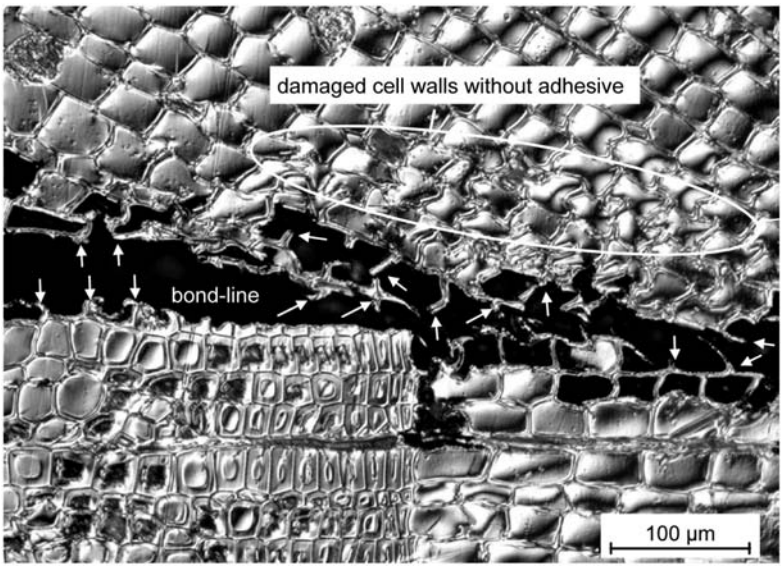

Figure 1 Light microscopy image of a wood joint with a PVAc bond line. Arrowheads indicate selected locations of interphase wood cell walls that were tested.

approx. 60–90°). For adhesive formulations the procedure recommended by each manufacturer was followed and curing was carried out at ambient temperature. Post-curing and conditioning were conducted by storing the specimens in a standard climate (20°C, 65% relative humidity) for 3 weeks. Pieces with a length of 2 mm, a width of 2 mm, and a thickness of 0.5 mm were taken directly from the adhesive bond region (Figure 1), dried overnight in an oven at 60°C, and embedded in an epoxy resin (Spurr 1969) by alternating vacuum-pressure treatment. To reduce the possibility of cell wall penetration, no further dehydration with any solvent was performed; rapid embedding and curing was used instead. A smooth surface was cut using a Leica Ultracut-R microtome equipped with a Diatome Histo diamond knife. The embedded and sectioned bond-line specimens were glued to metal discs with epoxy resin for magnetic clamping to the nanoindenter sample stage.

Nanoindentation (NI)

Nanoindentation was chosen for characterisation of wood cell walls in the interphase of adhesive bonds. NI has already been used in a number of interphase studies for metal and glassfibre composites (Gao and Mader 2002; Li et al. 2002; Kim and Hodzic 2003; Gregory and Spearing 2005; Urena et al. 2005), for polymers (VanLandingham et al. 2001; Konnerth et al. 2006b) and for wood cell walls (Wimmer et al. 1997; Gindl and Schoberl 2004; Gindl et al. 2004a,b).

All NI experiments were performed on a Hysitron TriboIndenter system (Hysitron Inc., Minneapolis, USA; www.hysitron.com) equipped with a three-sided pyramid diamond indenter tip (Berkovich type). The samples specified were clamped magnetically to the indenter stage. Two different specimens for each wood-adhesive bond line were examined by performing 32–43 indents in the S2 layer of earlywood reference cell walls (i.e., cell walls unaffected by adhesive) and up to 98 indents in the S2 layer (distant from microcracks) of bond-line cell walls for each adhesive type. Experiments were performed in load-controlled mode using a pre-force of 1.5 µN and a three-segment load ramp (Figure 2): load application within 3 s, hold time 20 s, and unload time 3 s. The peak load was 150 µN for all indents in the experiment, resulting in an indent diameter of less than one-third (Gindl and Schoberl 2004) of the cell wall thickness to avoid any influence of the embedding material. Pre-positioning of the indenter tip was achieved using an incident light microscope. Imaging of the cell walls was performed on the indenter stage using scanning probe microscopy (SPM) with the indenter tip and a scanning size of 20 × 20 µm. The indent positions on the cell walls were marked on the SPM image and executed from this mode. All indent positions were verified by SPM after the indentation procedure. Indents with insufficient distance to cell wall borders were removed from the data set.

An incident light microscopy image of a PVAc-bonded specimen as used for nanoindentation is shown in Figure 1. Cell walls and cell-wall fragments from the first row of cells adjoining the central adhesive layer, where adhesive penetration is possible, were the object of nanoindentation measurements. These cell walls were in direct contact with the adhesive and showed varying degrees of damage due to machining of the bonded wood surfaces. For comparison, cell walls (not visible in Figure 1) at a distance of more than 500 µm from the bond line, where no influence of adhesive penetration was expected, were tested as a reference.

The load-indentation depth curves recorded during NI experiments were evaluated according to the Oliver and Pharr (1992) method. From the load-depth graph recorded during NI experiments, the peak load (P_{max}) and the contact area (A) at the end of the holding segment were determined and the hardness was obtained by dividing P_{max} by A. From the initial slope of the unloading curve, the unloading stiffness (S) was determined and the reduced elastic modulus E_r was calculated according to the following equation:

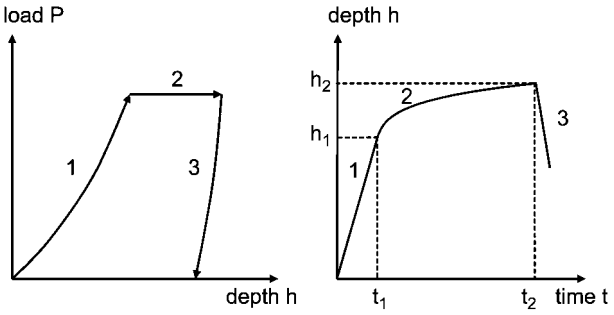

Figure 2 Schematic load-indentation depth graph with loading (1), holding (2), and unloading (3) segments (left), and corresponding indentation depth-time graph (right).

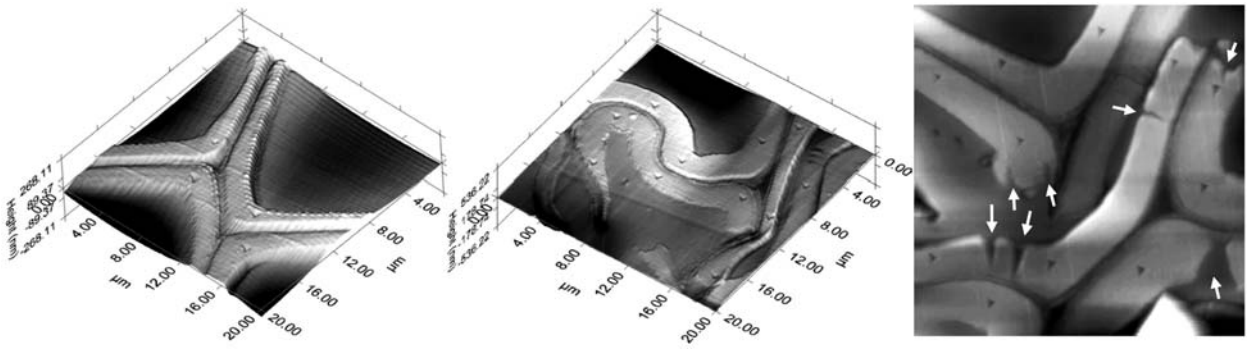

Figure 3 Scanning probe microscopy images 20 μm×20 μm of wood cell walls showing the position of indents from nanoindentation. Left: reference cell walls at a distance of >500 μm from the bond line. Middle and right: deformed and broken cell walls in the interphase region of an adhesive bond. Arrowheads indicate microcracks in the cell wall.

$$E_r = \frac{1}{2}\sqrt{\pi}\frac{S}{\sqrt{A}}. \quad (1)$$

E_r is termed the reduced elastic modulus because it takes into account the compliance of the indenter tip according to Eq. (2):

$$\frac{1}{E_r} = \left(\frac{1-\nu_m^2}{E_m}\right)_{material} + \left(\frac{1-\nu_i^2}{E_i}\right)_{indenter}. \quad (2)$$

Since the elastic modulus of the diamond indenter tip is very high (E_i=1140 GPa, Poisson's ratio ν_i=0.07), the effect of indenter compliance on E_r is negligibly small in soft materials such as wood and adhesive polymers, and no correction was performed.

Indentation creep C_{IT} (CSM Instruments 2002) was defined as the relative change in indentation depth while the applied load remained constant during the holding time (Figure 2):

$$C_{IT} = \frac{h_2 - h_1}{h_1} \times 100. \quad (3)$$

Results and discussion

SPM images from unaffected reference cell walls distant from the bond line and cell walls within the bond line region are shown in Figure 3. The small size of the indents is perceptible. Their small dimensions with respect to the overall cell-wall thickness ensures that the measured cell-wall properties remain unaffected by the surrounding embedding medium or adhesive.

The results from nanoindentation measurements are presented in Figure 4. The elastic modulus, hardness, and indentation creep factor show clear effects of adhesive on the mechanical properties of cell walls. Statistically homogenous groups were identified by a one-way ANOVA evaluation (α=0.05). The elastic modulus of interphase cell walls is clearly dependent on the type of adhesive applied (Figure 4a). The elastic modulus of cell walls contacting PUR or PVAc adhesive is significantly reduced with regard to reference cell walls situated far away from the bond line. In contrast, the elastic modulus of interphase cell walls in contact with PRF is equal to the elastic modulus of reference cell walls, and cell walls from the MUF bond line reveal a significantly improved elastic modulus compared to the reference. The results of hardness measurements by means of nanoindentation (Figure 4b) are similar, with the exception of interphase cell walls in the PRF-bonded specimens, which show a very significant increase in hardness compared to reference cell walls.

Differences in the elastic modulus and hardness of interphase cell walls compared to reference cell walls (Figures 4a and 4b) are well in line with data published on the penetration of adhesives into wood cell walls. For PVAc and PUR, no detectable penetration of adhesive into the wood cell wall was found (Buckley et al. 2002; Singh et al. 2002; Backman and Lindberg 2004; Gindl et al. 2004a,b). It is therefore assumed that interphase cell walls in these bond lines are unaffected by adhesive penetration. The observed reduction in the mechanical properties of interphase cell walls in PVAc and PUR bond lines compared to cell walls far from the bond line, as observed by nanoindentation, is most probably a result of damage that occurs during machining of the wood surface. In contrast, abundant diffusion of phenol-formaldehyde and melamine-formaldehyde based adhesives into the cell wall has been repeatedly proven (Gindl 2001; Gindl et al. 2002). Apparently, the presence of MUF and PRF adhesives in the cell walls recovers the loss of elastic behaviour due to machining and even improves the mechanical properties compared to cell walls unaffected by adhesive.

The viscoelastic behaviour of interphase cell walls is described by the indentation creep factor (Figure 4c). With regard to this parameter, interphase cell walls differ significantly from reference cell walls, as their creep was significantly enhanced in PVAc- and PUR-bonded cell walls, whereas a reduction in creep was observed in PRF and MUF bond lines. Therefore, it is assumed that a damaged cell wall exhibits higher creep, which only can by reduced by adhesive penetration into the cell walls.

Conclusions

Based on the results reported, the following conclusions may be drawn.

Interphase cell walls in MUF bond lines experience a significant improvement in elastic modulus and hardness in parallel with a reduction in creep compared to reference cell walls unaffected by adhesive. PRF performance

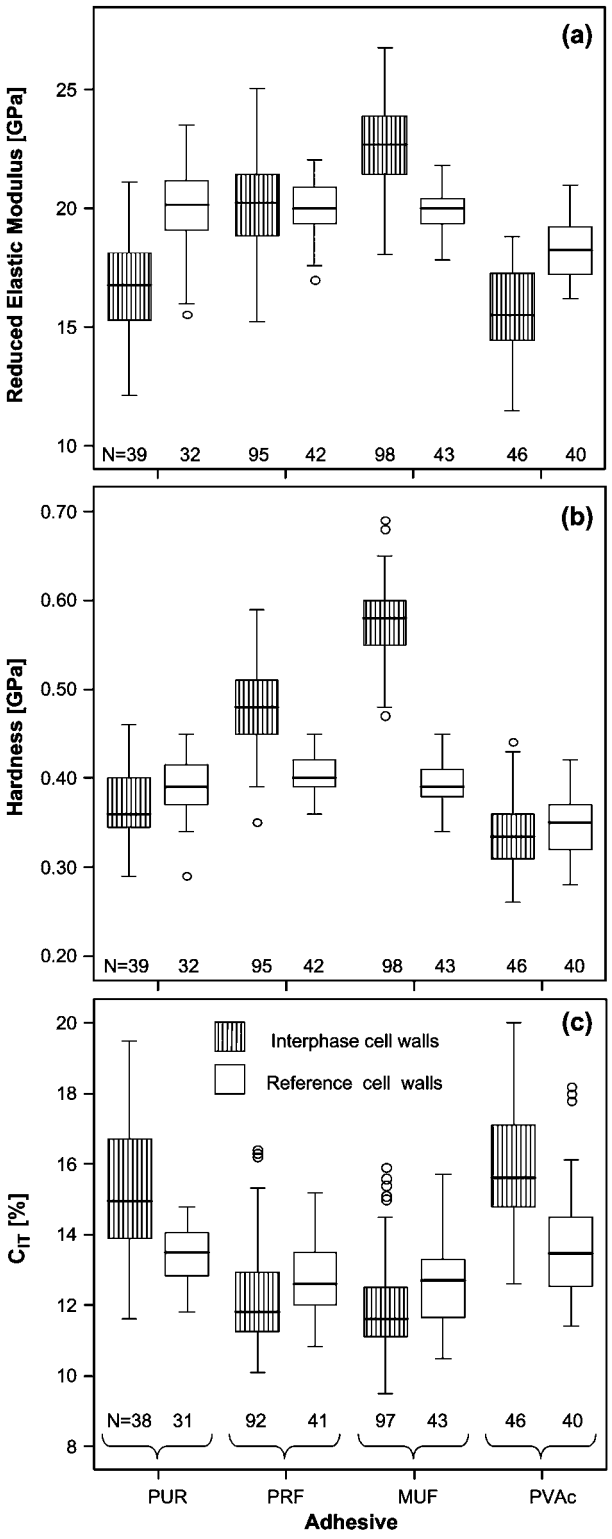

Figure 4 (a) Reduced elastic modulus, (b) hardness and (c) indentation creep C_{IT} from nanoindentation of interphase cell walls with adhesive contact compared to reference cell walls distant from the bond line (PUR, one-component polyurethane; PRF, phenol-resorcinol-formaldehyde; MUF, melamine-urea-formaldehyde; PVAc, polyvinylacetate; N, number of indents). C_{IT} measurements were made at a peak load of 150 μN, with application of load within 3 s and a holding time of 20 s.

is similar to MUF, with the exception of the elastic modulus, which is of the same magnitude as for reference cell walls.

Interphase cell walls in PVAc and PUR bond lines have diminished elastic modulus and hardness and increased creep compared to the reference.

Acknowledgements

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