Short Note

Adya P. Singh, Arif Nuryawan, Byung-Dae Park* and Kwang Ho Lee

Urea-formaldehyde resin penetration into Pinus radiata tracheid walls assessed by TEM-EDXS

Abstract: This paper reports a new method of detecting urea-formaldehyde (UF) resin penetration into the cell walls of radiata pine (Pinus radiata D. Don) by means of transmission electron microscopy (TEM) in combination with energy-dispersive X-ray spectroscopy (EDXS). The quantifications of penetrated UF resin in the ultrathin cuts of cell walls were realized by detecting nitrogen (N) element by TEM-EDXS. Both line scan and area mapping revealed N in cell walls in contact with resin-filled lumens but not in those in contact with empty lumens. Thus, UF resin had penetrated the cell walls from the lumen side.

Keywords: cell wall, Pinus radiata, TEM-EDXS, UF resin penetration

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Introduction

Polymeric resins as wood adhesive offer possibilities for developments in wood-based composite industries, which can give rise to a huge range of products. As pointed out by Kamke and Lee (2007), the physical and chemical characteristics of both the wood and adhesive influence wood-adhesive bonding. It is important to understand the adhesive penetration process into the cell walls. Light microscopy (LM), confocal laser scanning microscopy (CLSM), ultraviolet (UV) microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and synchrotron radiation X-ray tomographic microscopy (SRXTM) are important instruments in this context (Singh et al. 2002, 2008; Gindl et al. 2003; Xing et al. 2005; Kamke and Lee 2007; Hunt et al. 2010; Adamopoulos et al. 2012; Gavrilović-Grmuša et al. 2012; Hass et al. 2012). While the visualization of adhesives in cell lumens is relatively easy by LM, the assessment of adhesive penetration into the cell walls needs CLSM (Xing et al. 2005; Singh et al. 2008; Hunt et al. 2010), UV microscopy (Gindl et al. 2002, 2003), combination of UV and confocal Raman microscopy (Gierlinger et al. 2005), combination of SEM and energy-dispersive X-ray spectroscopy (EDXS) (Bolton et al. 1988), nanoindentation in combination with atomic force microscopy (AFM) (Hunt et al. 2010), and electron energy loss spectroscopy (EELS) in combination with TEM (Rapp et al. 1999).

The aim of the present study is the quantitative determination of urea-formaldehyde (UF) resin penetrated into the cell walls by means of TEM-EDXS.

Materials and methods

UF resin of 1.0 formaldehyde/urea (F/U) mole ratio (nonvolatile solids content 60.9 wt%, viscosity 195 mPa s, gel time 194 s) was prepared according to Park and Jeong (2011), and P. radiata veneers were glued according to Singh et al. (2013), which were specifically developed to facilitate the ultrathin sectioning of resin-penetrated wood tissues.

Small rectangular pieces from the paired veneers were sectioned dry on a sliding microtome (without softening because UF resin is sensitive to moisture) parallel with the wood grain to obtain 90 μm thick sections. Small pieces cut from the sections were placed directly in 100% acetone-Spurr resin mix for resin infiltration. After gradually increasing the concentration of resin, samples were embedded in pure resin. The resin was polymerized at 65°C over 24 h.

Ultrathin sections (80–90 nm in thickness) were cut transversely across resin-filled tracheids on an ultramicrotome equipped with a diamond knife. The sections were stained for 7 min either with 2% aqueous uranyl acetate or 2% uranyl acetate prepared in 50% ethanol. Staining was necessary to clearly visualize the resin adhesive (appearing as globular particles 400 nm or less in size) in infiltrated cell lumens.

*Corresponding author: Byung-Dae Park, Department of Wood Science and Technology, Kyungpook National University, 80 Daehak-Ro, Buk-gu, Daegu 702-701, Republic of Korea, e-mail: byungdae@knu.ac.kr

Adya P. Singh and Arif Nuryawan: Department of Wood Science and Technology, Kyungpook National University, 80 Daehak-Ro, Buk-gu, Daegu 702-701, Republic of Korea

Kwang Ho Lee: Center for Research Facilities, Chonnam National University, Gwangju 500-757, Republic of Korea
An H-7100 Hitachi TEM instrument was available (75 kV), and TEM-EDXS was carried out with a detector X Max. The nitrogen (N) content as an indicator for the UF resin was detected in double cell walls with empty and resin-filled lumens. An average N-value is presented for each measurement. Each measurement was performed on at least three ultrathin sections prepared from three different sample blocks.

Results and discussion

The N-content of the cell walls was performed by TEM-EDXS either in line scan or area mapping mode across the double cell walls, and the results are presented in Figures 1 and 2. Figure 1 shows the typical results of the line scan mode at two different locations of a double cell wall, with lumen filled with the resin only on one side. As expected, N-counts on the resin-containing lumen were high. The counts rapidly decreased toward the lumen-S3 interface and then stabilized across the double cell walls (S3 to S3). The two line scans at different locations show a similar pattern of N-distribution across the double cell walls.

The EDXS mapping (Figure 2b and d) corresponds to the TEM images and illustrates well the N-distribution in cell walls in contact with resin-filled lumen on either side (Figure 2a) and in contact with the lumen filled with the resin only on one side (Figure 2c). Also here, the N-content of the UF resins in the lumens is high and the N-concentration is much lower in the cell walls. Nevertheless, N is homogeneously distributed throughout the double cell walls. These results clearly indicate that UF resin not only fill the cell lumens but also penetrates the cell walls and that the N-concentration in the double wall is fairly uniform.

Quantitative measurements (Table 1) reveal that N was detected only in the cell walls in contact with UF resin-filled lumens. Cell walls surrounded by empty lumens do not contain N. The concentration of N is greater in the cell walls in contact with UF resin-filled lumens on both sides. This indicates that N present in the cell walls originated from UF resin in the lumen and that resin had penetrated into cell walls starting from the lumen. It appears that the resin penetrated all cell wall regions, including the middle lamella, located most remote from the lumen adhesive-S3 layer interface. This means that the resin readily diffused through the cell walls. Like TEM-EELS, which has been successfully applied for quantification of melamine N in resin-penetrated cell walls (Rapp et al. 1999), TEM-EDXS proved to be a powerful high-resolution technique with a high sensitivity for N detection, which enables measurements directly on the submicrometer size UF resin particles in the lumens and across the cell walls.

As discussed by Frihart (2004), an assessment of adhesive penetration is important at both microlevel (lumen penetration) and nanolevel (cell wall penetration), because the interaction of adhesive with the cell walls can involve both physical and chemical linkages. Mechanical interlocking occurs in the former case via penetration of the resin into cell wall cracks and intermolecular spaces within the cell walls, and covalent and hydrogen bonds are formed in the latter case. Lang et al. (2013) interpreted their Fourier transform infrared (FTIR) data that reaction occurs between the -NH-CH₂OH groups of an UF prepolymer with wood carbonyl (C=O) and hydroxyl (-OH) groups. Cell wall penetration can therefore further strengthen adhesive bonding with wood via chemical interaction with cell wall polymers in contact with the adhesive at adhesive-cell wall interface as well as with the penetrated adhesive.
Conclusions

TEM-EDXS provided evidence that 1.0 F/U mole ratio UF resin not only penetrates cell lumens but also cell walls. This is the first time that cell wall penetration was demonstrated by TEM-EDXS.

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References


