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Using UV-Microscopy to Study Diffusion of Melamine-Urea-Formaldehyde Resin in Cell Walls of Spruce Wood

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Summary

Using UV-microscopy, absorbance spectra of a cured melamine-urea-formaldehyde resin and secondary cell walls of spruce wood glued with this resin were determined. Analysis of the spectra showed that peaks characteristic for both coniferous lignin and melamine resin were present in cell walls of tracheids embedded in the resin. A quantitative estimate indicated a melamine content of the resin embedded cell walls of 6.2 %. It could be demonstrated that UV-microscopy is well suited for the investigation of resin diffusion into the wood cell wall.

Introduction

Adhesion is the state in which two surfaces are held together by interfacial forces, which may be valence forces, interlocking action, or both (Vick 1999). The performance of bonded wooden joints depends on how well these mechanisms are understood. Valence forces are produced by the interaction of prevailing atoms, ions, and molecules. Mechanical interlocking takes place through an adhesive that has penetrated the porous surface while it is liquid, then anchored itself through solidification. Both bonding mechanisms are generally acknowledged but the extent to which valence forces or mechanical interlocking action develop in a wooden glueline is still uncertain. A number of theories have been suggested, such as the mechanical entanglement/interlocking theory, the diffusion theory, the covalent chemical bond theory or the theory of specific adhesion by secondary forces (Marian and Stumbo 1962; Collett 1972; Wake 1976; Steiner 1989; Pizzi 1992). Mechanical interlocking is a mechanism of importance in wood (Boeglin *et al.* 1996), because penetration into the fine microstructure increases the surface area of contact between the glue and the wood. It is therefore reasonable to assume that the most durable structural bonds to wood not only develop when a glue has penetrated deeply into cell lumina, but also when the glue has diffused into the cell wall.

The process of penetration into cell lumina has been extensively investigated at the microscopic level (Suchsland 1958; Fengel and Kumar 1970; Hare and Kutscha 1974; Furuno and Goto 1975; Saiki *et al.* 1975; Brady and Kamke 1988; Sernek *et al.* 1999), however, only a few studies provide evidence of a possible diffusion of glue into wood cell walls. By means of electron microscopy combined with energy-dispersive x-ray analysis (EDAX), Smith and Côté (1971) detected bromine-masked phenol formaldehyde resin in cell walls adjacent to glue lines. Bolton *et al.* (1988) using the same analytical technique, investigated urea-formaldehyde resin penetration in particle board, and Rapp *et al.* (1999) analyzed melamine resin in cell-walls through electron energy loss spectroscopy.

In this study, UV-microscopy was utilized to investigate the diffusion of melamine-urea-formaldehyde resin in cell walls. UV-microscopy has been repeatedly applied to determine lignin in cell walls (Fergus *et al.* 1969; Scott *et al.* 1969; Fukazawa and Imagawa 1981), but rarely for other UV-absorbing substances. As melamine resin has high absorbance in the ultraviolet spectrum due to its triazine-ring structure (Nowak-Ossorio and Braun 1982), UV-microscopy should be suitable to address the question of possible diffusion of adhesives into wood cell walls.

Material and Methods

A melamine-urea-formaldehyde (MUF) resin containing 65 % solids in water was manufactured at A.R.I. Ltd., Greece, at laboratory scale. The MUF resin consisted of 1.8 moles melamine, 4.9 moles urea and 7.9 moles formaldehyde. The viscosity of the resin was 300 cp. Molecular weight distribution of the resin was measured by GPC (gel permeation chromatography). GPC measurements were effected using a Shimadzu LC-9A liquid chromatograph with a Rheodyne injection loop. Two Plgel columns (Polymer Labs) with pore diameters 100 Å and 500 Å, respectively, were used. DMF containing 0.5 % LiCl was used as eluent. Detection was effected by a Shimatzu RID-6A differential refractometer. Calibration was done using polyethylene glycol standards (Polymer Labs). Correction of the molecular weights of the resins for the incorporation of solvent molecules was considered necessary. Resin samples were dissolved in DMSO and the solutions (ca. 0.5 %) were introduced into the injection loop of the liquid chromatograph after filtration through a 0.45 µm filter. The temperature of the columns was kept at 70 °C and the flow rate was 1 ml/min.

Two small cubes (10 × by 10 × by 10 mm^3) of spruce (*Picea abies* L. Karst.) were glued together at their tangential faces. The resin was cured for 10 min at 120 °C; no catalyst was added. Slight mechanical pressure was applied perpendicular to the glued plane using a rubber band. Five small prisms, 5 mm long and 1 mm by 1 mm transversally were prepared from the cubes. Each prism showed the glue line centered on the cross-section and laterally. The prisms were dehydrated in a graded alcohol-acetone series and subsequently embedded in Spurr's resin (Spurr 1969). Cross sections 1 µm in thickness were cut using an ultramicrotome equipped with a diamond knife. Thin sections were placed on quartz-glass slides and immersed in deionized water.

Determination of UV-absorbance

UV-absorbance spectra were acquired at three locations using the MPM800™ photometer microscope (Carl Zeiss). Firstly, the absorbance of S2 layers of tracheids positioned about 0.5 mm away from the glue line was measured. These tracheids had empty cell cavities and were assumed to be unaffected by the resin. Secondly, the absorbance of pure MUF resin cured in tracheid lumina, located close to the glue line, was measured. Finally, the absorbance of adjacent S2 layers of resin-filled tracheids were measured as a third location (Fig. 1). With the monochromator set to 5 nm bandwidth and a scanning stepwidth of 1 nm, absorbance spectra were measured at wavelengths between 235 nm and 350 nm. A circular measuring spot of 0.5 µm in diameter allowed an accurate beam placement in the center of 3 µm thick cell walls. The relatively large bandwidth of 5 nm provided sufficient light energy for the UV-detector to ensure a high signal-to-noise ratio (Thoburn-Burns 1993). For each of the three locations 50 spectra were acquired, averaged and plotted. For comparison, absorbance spectra of drops of liquid urea-formaldehyde (UF) and of MUF resin, placed onto quartz slides and covered with quartz-glass slips, were also determined.

Quantitative estimate of melamine diffusion

According to Fergus *et al.* (1969) and Scott *et al.* (1969), the lignin concentration of wood cell walls can be calculated from the UV absorbance using Beer-Lambert's law A = C e d, with A being the absorbance, C (gg^{-1}) the concentration, e ($gg^{-1}\mu m^{-1}$) the coefficient of extinction and d (µm) the thickness of the microsection. Since the absorbance of a mixture of two substances is the sum of the individual absorbencies, the absorbance due to the presence of melamine in the cell wall is obtained by subtracting the spectrum of melamine unaffected cell walls. With the assumed concentration of 0.3 gg^{-1} melamine (calculated from the molar ratio of M : U : F = 1.8 : 4.9 : 7.9) the melamine extinction coefficient and the melamine concentration in cell walls can be determined.

Fig. 1. Transverse section through a glue line as seen during determination of UV-absorbance. The circular measuring spot (arrowhead) is positioned in the center of the secondary cell wall of a tracheid filled with glue. During sectioning the cured MUF resin left a distinct wavy-rippled pattern (black arrow).

Results

The absorbance spectra acquired at the three different locations revealed significant differences (Fig. 2). At the first location, the MUF-unaffected cell wall layers, an absorption maximum at 280 nm was measured. At the second location, the cured MUF resin in the cell lumen gave an absorbance maximum at 242 nm. The absorption sharply declined at wavelengths higher than 270 nm. At the third location, the secondary walls of fully MUF-embedded tracheids showed two absorbance maxima, a first one at 241 nm and a second one at 280 nm.

With the assumption of 0.3 gg^{-1} melamine of lumen-cured MUF resin and a measured absorption maximum of 1.3, a

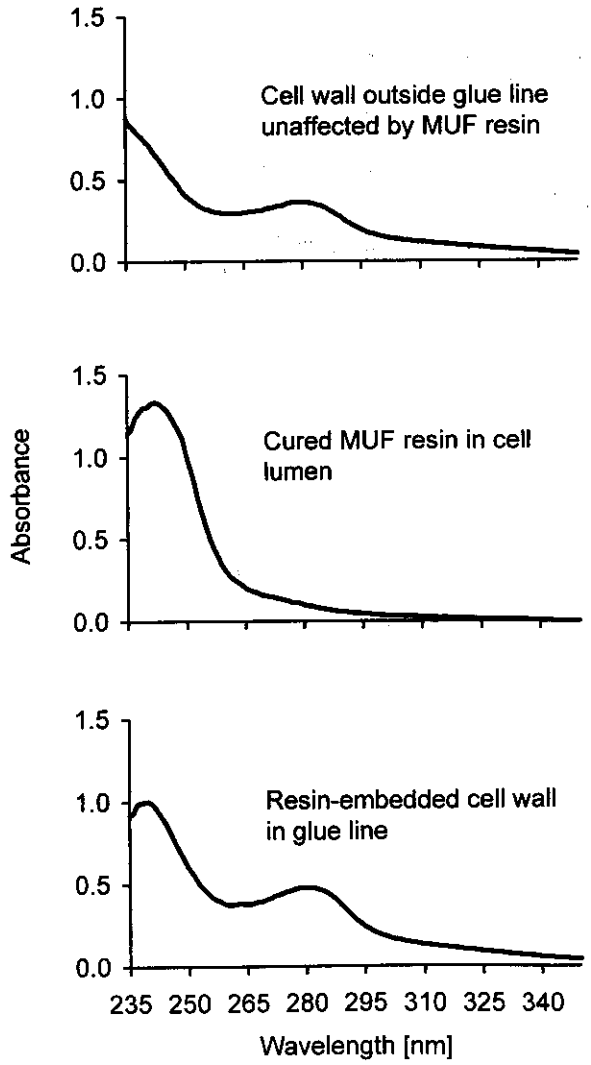

Fig. 2. UV-absorbance spectra of cell walls outside the glue line, cured melamine-urea-formaldehyde (MUF) resin in cell lumina and resin embedded cell walls. Each spectrum was compiled from 50 measurements.

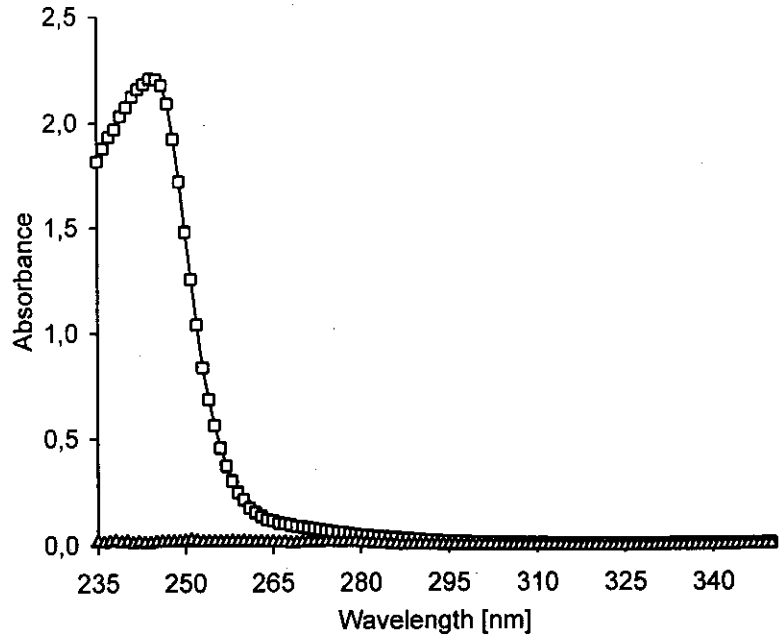

Fig. 3. UV-absorbance spectra of liquid melamine-urea-formaldehyde (MUF, squares) resin and urea-formaldehyde (UF, triangles) resin averaged from ten measurements each.

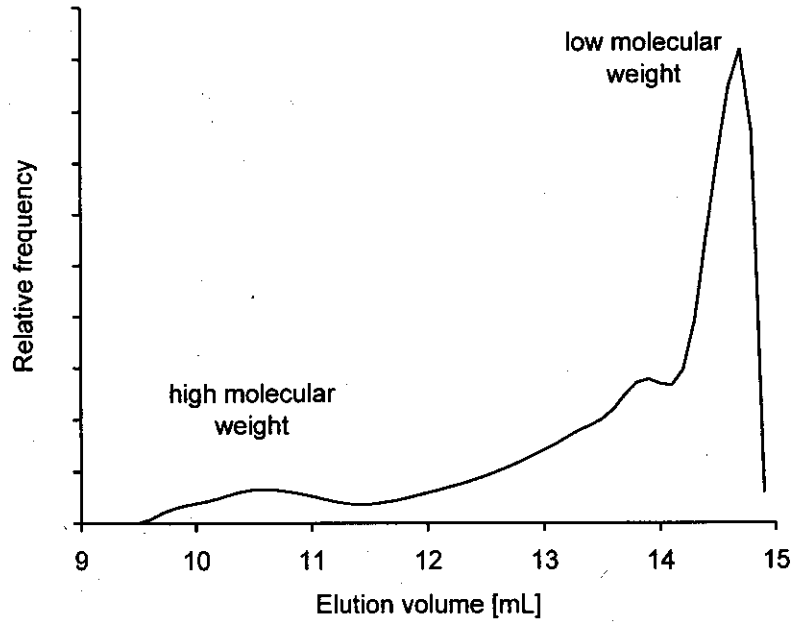

Fig. 4. Chromatogram (GPC) showing molecular weight distribution of the MUF resin as used in this study (elution solvent was dimethyl formamide with 0.5 % LiCl).

coefficient of extinction e_{241nm} of 4.33 $gg^{-1}\mu m^{-1}$ was calculated. The subtraction of A_{241nm} of cell walls unaffected by resin from A_{241nm} of fully MUF-embedded cell walls, resulted in $A_{241nm} = 0.27 \pm 0.049$. Using again the Beer-Lambert's law a concentration of melamine in the cell wall of 6.2 ± 0.12 % could be calculated.

Figure 3 shows the average absorbance spectrum of the liquid MUF resin drops compared with liquid UF resin. Strong absorbance was seen at 244 nm for MUF while liquid UF resin did not absorb within the investigated range of wavelengths.

Figure 4 shows a chromatogram as the detector signal output (relative frequency) versus elution volume. The elution volume refers to the volume of the mobile phase required to elute the solute from the column at maximum concentration. In general, elution volume is inversely related to apparent molecular weight, higher volumes correspond to smaller molecules, i.e. molecules with lower molecular

weight. It can be seen that the molecular weight distribution of a MUF resin is a broad one. The final resin is a mixture containing a high percentage of very low molecular weight oligomers that correspond to methylolated urea and melamine (at elution volume around 14.5 ml) as well as larger molecules with molecular weight of the order of 20 000 (at elution volume around 10.0 ml).

Discussion

The diffusion of organic and inorganic liquids into the wood cell wall has been the subject of a number of studies. By measuring the swelling of the wood, the diffusion of liquids can be investigated. In his extensive work, Stamm (1964) has demonstrated that the rate of swelling due to diffusion and also the swelling equilibrium decreased with increasing size of the molecule in the liquid. However, Mantanis *et al.* (1994) showed that even relatively large molecules such as pyridine and benzyl alcohol (molecular weight 79 and 108, respectively) are able to swell the cell wall significantly, because of their high capacity to establish hydrogen bonds. Given the fact that the melamine monomer has a molecular weight of 126 and high capacity to develop hydrogen bonds due to its three amino groups, a swelling of the wood cell wall seems plausible from a chemical point of view, as a large amount of low molecular weight compounds are present in the investigated MUF resin (Fig. 4). Also, the high temperatures (120 °C) during curing of the MUF resin favored the diffusion of melamine, because elevated temperatures dramatically increase the rate of swelling, and some liquids that swell wood only slowly or not at all under room temperature conditions will do so by raising the temperature (Mantanis *et al.* 1995).

Rapp *et al.* (1999) were the first and presumably the only ones so far, to report a direct proof of melamine diffusion into cell walls. Using electron energy loss spectroscopy in combination with TEM, they achieved a spatial resolution of 50 nm. The spatial resolution achieved by the UV-microscope (0.5 μm) is clearly lower but sufficient to assure uncontaminated spectra from the center of the secondary cell wall. Considering the optical properties of the MPM800 UV-microscope, the measured volume has a slightly conical shape with a diameter of the measuring spot extending only to 0.502 μm at the bottom of 1 μm thick sections. In practice, the measured volume may be slightly larger due to light scattering. In any event, in cell walls with a thickness of only 3 μm, the distance from the border of the measuring spot to the cell wall-glue interface would be still above 1 μm, which should widely exclude the possibility of contamination of the cell wall spectra from cured resin in the cell lumina.

Since UF resin did not absorb within the investigated wavelengths (Fig. 3), the peak at 242–241 nm observed with MUF resin (Fig. 2) can be clearly attributed to melamine. Small differences between absorption maxima of melamine in the lumen (242 nm) versus melamine in the cell walls (241 nm) might have been caused by the selective diffusion of low-molecular weight compounds into the cell wall. Differences in molecular weight distribution usually imply minor shifts in UV-absorbance (Gottwald and Heinrich 1998).

The quantitative estimate of melamine content in the secondary cell wall of 6.2 % lies well under the 20 % reported by Rapp *et al.* (1999). These authors soaked their samples for 7 days in an aqueous solution of melamine, which might explain in part the differences.

Discrepancies might also occur because of varying lignin contents in the measured cell walls. In our results, the lignin content of the resin-embedded cell walls is practically equal to that of the cell walls unaffected by the resin. Since only earlywood cells were measured the effect of changing lignin content on resin determination may not exceed 2 % (Fergus *et al.* 1969; Fukazawa and Imagawa 1981).

It is assumed that the coefficient of extinction of melamine in the resin-embedded cell walls (4.33) is equal to that of melamine in the cell lumina. As Figure 2 shows, a small difference of 1 nm exists between the melamine peaks of these two locations which affects slightly the extinction coefficient. Taking this into account, the actual melamine content of the investigated cell walls may be in the range between 5.2 to 7.2 %.

Conclusions

It is demonstrated that UV-microscopy is a suitable method to study resin diffusion in wood cell walls. The detection of melamine resin using UV microscopy is simple and does not require chemical pretreatment, as required with bromination of samples for electron microscopy in combination with EDAX (Smith and Côté 1971; Bolton *et al.* 1988). The spatial resolution is lower than the one achieved by electron energy loss spectroscopy, but clearly superior to the one achieved through EDAX when used with a scanning electron microscope. In SEM-EDAX the excitation volume is 6 μm wide and 4 μm deep (Bolton *et al.* 1988).

The results shown confirm that resin diffusion into the wood microstructure is present and can be seen as a potential mechanism of the mechanical interlocking in wood-gluing. The effect of resin diffusion on the stability of glue joints will be the subject of future research.

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