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Measurement of cell wall penetration in wood of water-based chemicals using SEM/EDS and STEM/EDS technique

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Summary The penetration of bulking chemicals (glycerol, PEG 200, PEG 1500 and pentaerythritol) into the cell wall of wood, *Pinus sylvestris*, has been studied. A number of different methods for determining the distribution of chemicals in the cell wall were used. Measurements of the increase in cell wall thickness showed that glycerol and PEG 200 resulted in greater cell wall bulking compared to PEG 1500 and pentaerythritol.

Examination with SEM/EDS-linescan confirmed these results. However, the better resolution possible with the STEM/EDS-linescan revealed an inhomogenous distribution of the chemical in the cell wall. This is believed to be due to microcracks in the cell wall which are the result of the initial drying of the wood. This general damage to the cell wall could be the reason for the failure to find a stabilizing chemical and method.

Introduction

A number of chemical treatments to improve the dimensional stability of wood have been tried. The only way to obtain a good stabilizing effect is to bulk or fill the wood cell walls with a chemical and thus prevent shrinkage or swelling, Furuno and Goto (1978), Wallström and Lindberg (1995a). Bulking occurs by deposition of a chemical in the cell wall structure when the solvent carrier (methanol, water etc.) is removed during drying. There are three possible bulking treatments for the cell wall, namely; bulking of nonbonded-leachable (NBL), nonbonded-nonleachable (NBNL) and bonded-nonleachable (BNL) chemicals.

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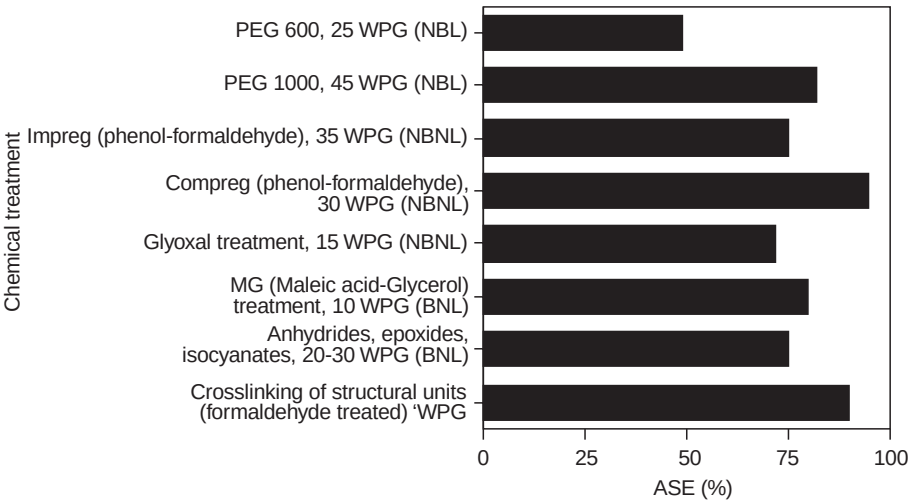

Fig. 1. Anti-shrink efficiency (ASE) resulting from different chemical treatments and weight percent gain (WPG). Håfors (1990), Stamm (1959), Meyer (1984), Minato and Yasuda (1992), Fujimoto (1992), Razzaque (1982) and Rowell and Youngs (1980)

A summary of ASE- (anti-shrink efficiency) and WPG- (weight percent gain) values for some chemical treatments are shown in Fig. 1.

The results in Fig. 1 show that none of the treatments reached 100% percent in the ASE-test. The ASE test commonly used is mild compared to the conditions encountered in general outdoor use of wood products. Improved results in ASE would be of great commercial and financial interest and more research in this area is thus needed.

Water vapour entering dry wood is absorbed into the cell wall which swell and the overall dimensions of wood increase. After ca. 20–28% water is absorbed (based on the oven-dry weight of wood) and the cell wall has swollen to its maximum, additional water will condense in the lumen or in other void spaces until they become filled, Meyer (1984).

For cell wall bulking treatments, it has been shown that the wood volume increase following treatment is directly proportional to the theoretical volume of chemical added. At chemical loadings in the cell wall of about 20–25 weight percent gain (WPG), the volume of dry treated wood is nearly equal to its green volume, Rowell and Ellis. (1978).

To obtain a good bulking result, with high ASE-value, about 25 WPG of the impregnation chemical must be absorbed into the cell walls. The results presented in Fig. 1 clearly do not fulfil this requirements.

Bulking treatment of solid wood with large dimensions can be costly because the diffusion of the impregnant is time dependant. If the treatment is only aimed at affecting the surface of solid wood or wood particles for particle boards, fiberboards, flakeboards, chipboards, MDF, Parallam etc. acceptable bulking can be obtained under relative short diffusion times.

The work presented in this paper has been carried out to obtain a better understanding of cell wall bulking mechanisms and the distribution of the impregnation chemicals in the cell wall. To do this SEM/EDS and STEM/EDS techniques have been used to investigate the mechanisms of wood stabilization.

Experimental

Wood samples

Sliced veneers of pine sapwood (*Pinus sylvestris*) with dimensions 150 × 90 × 3 mm (longitudinal × tangential × radial) were used. The prehistory of the specimens are not known but the wood was moistened with steam before cutting the samples (from the bulk wood) and dried afterwards at 150 °C. Thereafter the specimens were impregnated and dried. The impregnation solutions consisted of 20 per cent by weight of PEG 1500, PEG 200, glycerol or 7 per cent by weight of pentaerythritol respectively, in water. The impregnation scheme was 0.5 hour in vacuum followed by 1 hour at 1.2 Mpa and 20 °C.

Preparation of impregnating chemicals

Before impregnation, the chemicals were potassium stained in order to help identify their location in the cell wall during SEM- and TEM- EDS-analysis. The chemical solutions were prepared by dissolving PEG 1500, PEG 200, glycerol and pentaerythritol in water and adding an equimolar amount of $KMnO_4$ to oxidize one primary alcohol (-CH_2OH) group, per molecule to a carboxyle (-COOK). As an example 100 g of PEG 1500 was dissolved in 400 ml of water and 10.5 g $KMnO_4$ added. Precipitated MnO_2 was filtered off and the filtrate adjusted to the desired concentration for treatment of the wood samples.

The carboxylates of glycerol, pentaerythritol and PEG 200 were prepared in a similar way.

TEM-specimen preparation

An eutectic composition of 60 wt.% camphor and 40 wt.% naphtalene (C/N) was used for specimen preparation, Thaulow et al. (1971/72).

The C/N eutectic fills the lumen and supports the cell walls when glycerol impregnated TEM-specimens, 3 × 3 mm in cross section, were cut from sample blocks using an ultramicrotome, LKB 2088 Ultratome V equipped with a diamond knife. Thin specimens, 100–200 nm, were cut from a mesa of about 1 × 1 mm. The microtomed specimens were placed on 200 mesh copper grids and then heat treated in a vacuum oven for 15 minutes at 40 °C to remove the C/N eutectic which sublimes in the vacuum leaving no residue.

SEM specimen preparation

The samples of wood used in the SEM/EDS-investigations were the bulk specimens left over after preparation of the TEM specimens (3 × 3 mm in cross-section). The SEM specimens were sputter coated with a thin layer of carbon using a Balzers SCD 050 sputter coater.

SEM/EDS and STEM/EDS

The SEM/EDS-analysis were performed using a CamScan S4–80DV Scanning Electron Microscope (SEM) coupled with LINK exL analytical equipment and software (exL-MAP .01-0891). The LINK-system has a silicon detector with an 8 μm thick beryllium window and an energy resolution of 140 eV.

$K_{K\alpha}$ X-rays, with a peak energy of 3.32 keV, are counted in a 140 eV wide digital window and redistributed to a line scan curve across the tangential cell walls in late wood.

Five specimens from each group of the four impregnated specimens were investigated.

The settings used were; accelerating voltage (15 kV), working distance (37 mm), beam current (0.4×10^{-10} amperes), tilt angle of the specimen (0 degree) and analysis time at each point (0.6 s). These were the same throughout the entire study. The total acquisition time was 300–500 s depending on the thickness of the cell wall.

The line-analysis (line scan) method was also used for the measurement of K-concentration and location in a Transmission Electron Microscope (TEM), JEM-2000 EX with LINK AN 10/85S analytical equipment and software (ADM). The detector is of the same type as used in the SEM/EDS analysis. The analysis time in the STEM/EDS-line scan was about 10 s at each point.

Drift in specimen is a problem when calculating the total acquisition time, which is about 500 s.

Results and discussion

From earlier experiments, Fig. 2 after Wallström and Lindberg (1995a), it is known that cell wall thickness increase is about 25% over oven dried thickness after impregnating with glycerol and PEG 200. For PEG 1500 and pentaerythritol the increase in cell wall thickness is less.

These results show that the bulking chemical diffuse into the cell walls during the impregnation process and add their volume to the volume of the cell wall polymers. This is especially true for PEG 200 and glycerol.

In Fig. 3, an example of the cell wall thicknesses of an unimpregnated specimen compared to the PEG 200 impregnated specimen is shown.

The results from the SEM/EDS-linescans, signal minus background, are shown in Fig. 4. The measured S/N (Signal/Noise)-ratio was between 4 to 7 for the analyzed specimens, which offers a resonable safety factor. The count level, which is proportional to the number of K-atoms under the beam, is lowest for PEG 1500 and increases for the pentaerytritol, PEG 200 and glycerol impregnated samples respectively.

If it is assumed that one primary alcohol per molecule is oxidized to -COOK during preparation of the impregnated specimens, it follows that there will be one K-atom per impregnating molecule. The number of counts indicated in Fig. 4

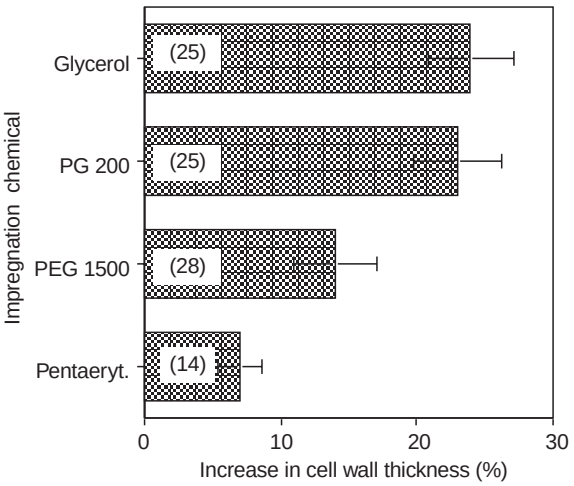

Fig. 2. Mean values of cell wall thickness increase in percent after impregnation and drying compared to dried control specimens without stabilizing chemicals after Wallström and Lindberg (1995a) amount of added chemical as a percentage of the dry weight of wood is shown in parenthesis

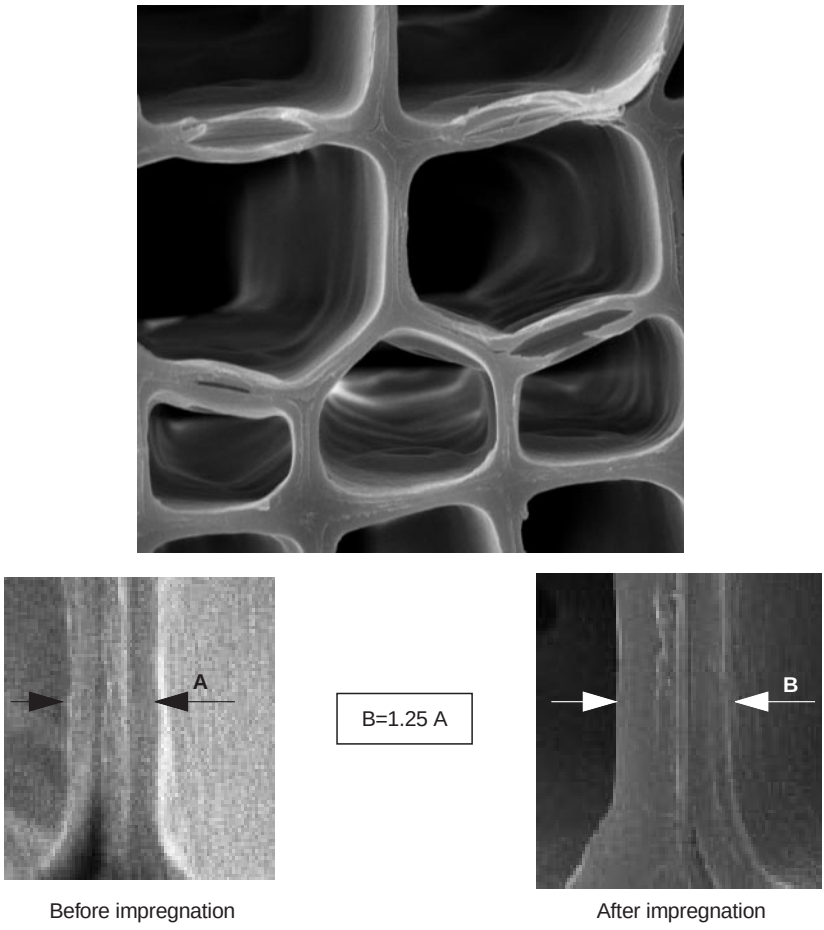

Fig. 3. An example of cell wall swelling. Swedish Pine (*Pinus sylvestris*) impregnated with 20 w/o PEG 200

should therefore be approximately proportional to the number of K-atoms per unit volume. For the same number of impregnating molecules in the cell wall the same count rate should be obtained from the X-ray microanalysis.

From Fig. 4 it can be seen that the glycerol count rate is relatively even across the cell wall at a level of about 105. For the other chemicals, equivalent figures are about 54 for PEG 200, about 26 for PEG 1500 and about 47 for pentaerythritol.

The bulked volume per glycerol molecule is less than half of that for a PEG 200 molecule which means that for the same cell wall swelling using PEG 200, (see Fig. 2 and Table 1) only about half the number of molecules are required.

For the glycerol and PEG 200, the results from both cell wall thickness measurements and the EDS line scans supports the assumption that only one of the hydroxyl groups are oxidized in the glycerol and PEG 200 molecules. However, if more than one of the hydroxyls are oxidized there can be 2–3 K-atoms (glycerol) or 2 K-atoms (PEG 200) in each molecule. The discussion above holds only for the scenario where the same number of K-atoms are present in the molecules respectively.

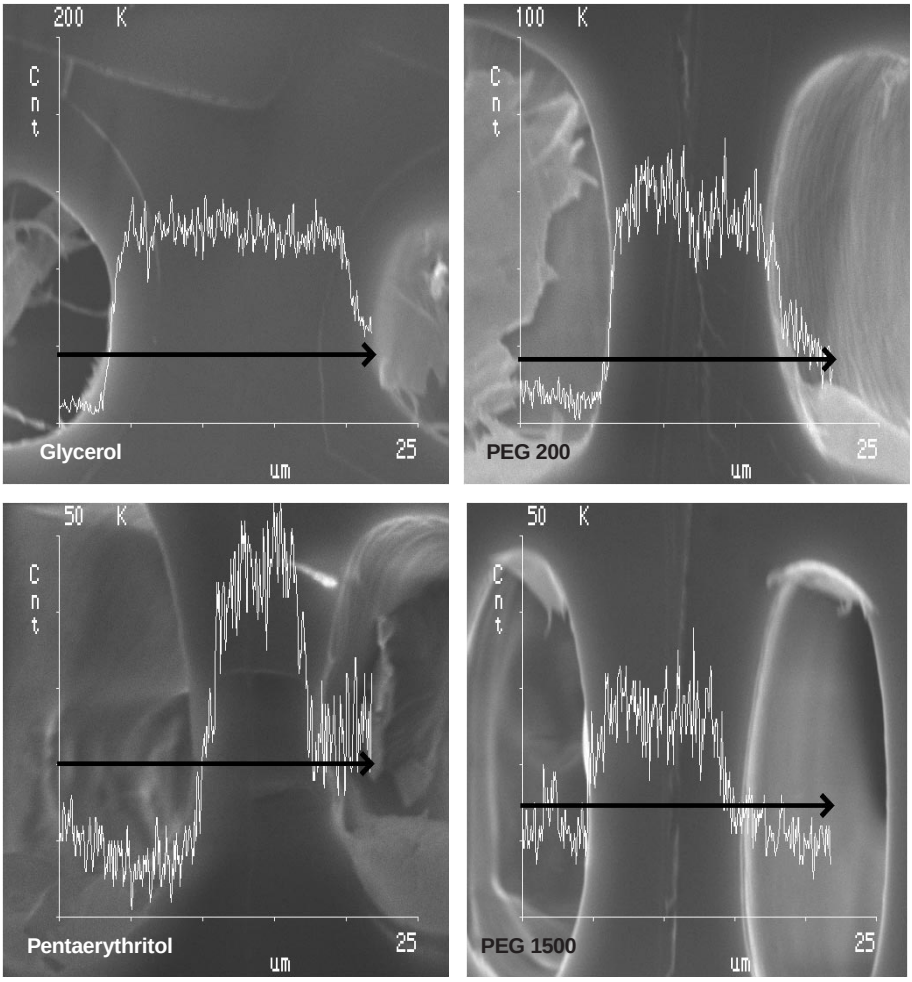

Fig. 4. EDS-linescan for Swedish Pine cell walls impregnated with K- stained-; glycerol, PEG 200, pentaerythritol and PEG 1500. The linescan signal (counts) is the peak counts minus the background counts

From the cell wall swelling measurements and considering the PEG 1500 molecule volume, the number of PEG 1500 molecules should be about 6% of the number of glycerol molecules, resulting in a count level of about 6. It can be seen that the measured count number for PEG 1500 is four times expected.

Table 1. Oxidizing sites and volume per molecule of impregnation chemicals

Impregnating chemical	Number of possible oxidizing sites per molecule	Volume per molecule (nm^3)
Glycerol	3	0.12
PEG 200	2	0.29
PEG 1500	2	2.31
Pentaerythritol	4	0.20

It was also thought that PEG 1500 would not penetrate the cell wall easily due to its high molecular weight, i.e. the molecule is too large, Horioka et al. (1974). Rowell (1984) studied the weight gain of wood after impregnating with a variety of chemicals. Calculating the molecule sizes and comparing this to the weight gains from his results showed that a molecule can have a maximum volume of about 0.17 nm^3 in order to cause a weight gain of the chemical inside the cell wall, Wallström and Lindberg (1995b). A volume of 0.17 nm^3 is that of a molecule six times the size of a water molecule.

Another problem with PEG 1500 is the solubility parameter, wood/polymer compatibility. The solubility parameter decreases for PEG as the molecular weight increase. PEG 1500 has a hydrophobic character due to the extending repeated unit. However, the cell wall swelling for PEG 1500 is 60% of the the cell wall swelling of glycerol, see Fig. 2.

An explanation for the much greater count level and cell wall swelling than expected can be that the molecules weights are polydisperse, Apostolov and Fakirov (1992), leading to smaller molecules more easily penetrating and resulting in a greater number of K-counts per unit volume.

The count level for pentaerythritol from cell wall swelling data is estimated to be around 30. The actual measurement is 47 i.e. about 50% more than expected. For pentaerythritol it is not possible to have smaller molecules, which may show that the pentaerythritol can be oxidized at more than one hydroxyl group (four possible sites).

WAXS (Wide Angle X-ray Scattering) Wallström et al. (1995) shows free crystalline chemical in lumen, rays, extractive channels etc. for all impregnation cases. The chemical part that is not inside the cell wall is adsorbed (crystallized) on the free surfaces leading to the cell wall thickness (volume) increase differing from the weight loading. This is most apparent for pentaerythritol and PEG 1500 which have WPG-values of 14 and 28 respectively. The amount of added chemical and cell wall swelling are therefore not closely coupled.

The results in Fig. 4 show a smoothed level of counts from the cell wall penetrating molecules. The smoothing is an effect of low lateral resolution. A non-critical evaluation of the results in Fig. 4 indicates a lower concentration of PEG 1500, PEG 200 and pentaerythritol molecules near or in the middle lamella but this was not seen for the glycerol. The results do not give a detailed picture of how the molecules are dispersed in the different cell wall layers. The SEM/EDS resolution is dependant on the pear shaped electron interaction volume.
The operating conditions were the same in the SEM/EDS investigations so the excitation volume would be the same. The shape of the excitation volume is dependent on many factors. For low atomic number material the excitation volume is pear-shaped, Bolton et al. (1988). This would also be likely in the present case.

The X-rays can be emitted from the interaction volume giving a resolution almost independent of the beam diameter. The origin of the low resolution in the present study is shown in Fig. 5.

The interaction volume in SEM/EDS-analysis depends on the energy of the beam (accelerating voltage) and material parameters, Bowen and Hall (1975). The spot size is of minor importance since small beam diameters do not give correspondingly better resolution.

The resolution for the SEM/EDS-analysis is about 2 μm compared to about 0.4 μm for the STEM/EDS-analysis, measured by the method described in Lindberg (1987). The better resolution for the STEM/EDS depends on the thinner

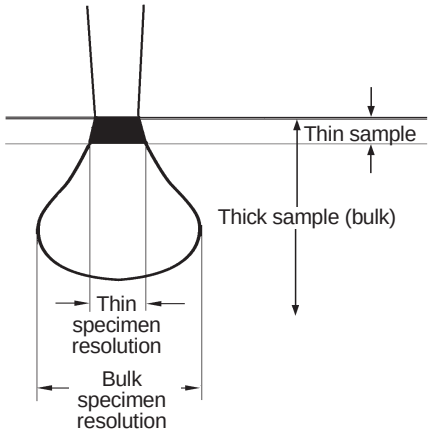

Fig. 5. A schematic diagram of the excited volume within a bulk specimen (SEM/EDS) and thin specimen (STEM/EDS)

specimen and smaller interaction volume, i.e. the resolution is more closely related to the set beam diameter, see Fig. 5.

In the STEM/EDS-analysis, the limiting factor is the count rate, which is a function of the number of incoming electrons (assuming constant specimen thickness and composition) that decreases with decreasing beam diameter.

Figure 6 shows a STEM/EDS-analysis of potassium in a glycerol (20 w/o) impregnated specimen.

The line scan curve shows that most of the chemical is concentrated in the vicinity of the outer secondary wall layer (S_1) and in relatively low concentrations inside the S_2 cell wall layer and in the ML (middle lamella). The count rate curve increases from the lumen towards the inside of S_2. This reflects the resolution of the analysis and the concentration at this analyzing geometry is thus believed to be evenly dispersed in the S_2 cell wall layer. The thickness of S_2 is about 1 μm.

Figure 7 shows the different layers in the pine cell wall.

For conifers, the distribution of the principal chemical constituents within the various layers of the cell wall are as follows, Panshin and Zeeuw (1980):

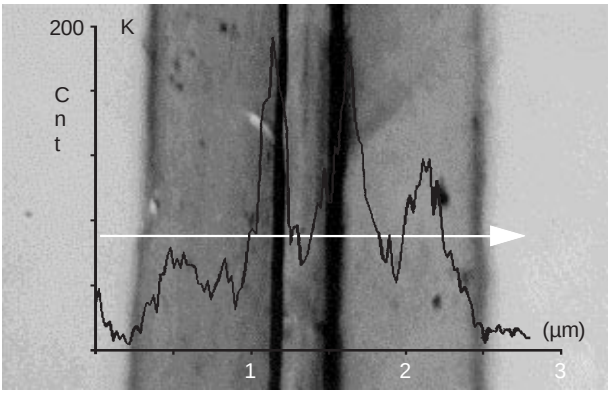

Fig. 6. STEM/EDS-linescan for potassium stained glycerol impregnated into Swedish pine cell walls

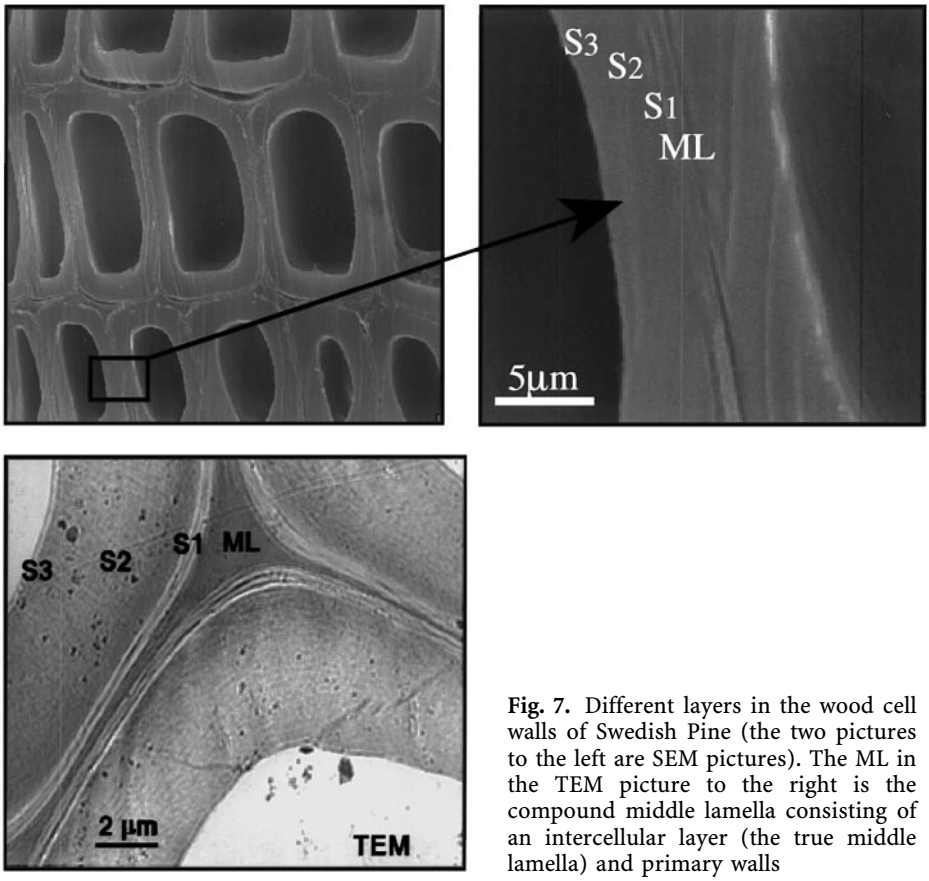

Fig. 7. Different layers in the wood cell walls of Swedish Pine (the two pictures to the left are SEM pictures). The ML in the TEM picture to the right is the compound middle lamella consisting of an intercellular layer (the true middle lamella) and primary walls

Table 2. Cell wall polymers

Layer, (volume %)	Cellulose, %	Hemicellulose %	Lignin, %
ML, (2)	10	15	75
S_1, (16)	29	34	37
S_2, (74)	54	30	16
S_3, (8)	50	36	14

If the impregnation molecules are dissolved in water it would be expected to find them interacting with wood polymers in a similar way as water. The wood polymers have different affinities to water and impregnation polymers due mostly to their additive hydrogen bonding part of the solubility parameter.

Lignin absorbs only limited amounts of water, about 2 percent, Back (1987). The cellulose polymer is hydrophilic but its fringed micelle type of crystallinity allow it to adsorb water at the crystal surfaces and in small amounts in the restrained amorphous regions. The cellulose chain is linear and stiff and strongly restrained in the amorphous regions between the crystalline parts. In fact, cellulose would be a small target for the molecules under investigation.

The hemicellulose has a solubility parameter close to that of cellulose. However, the hemicellulose is amorphous with a molecule chain that is highly branched. The hemicellulose molecular structure thus provides a large free volume for the chemicals to enter.

The discussion above and the data in Table 1 support the low concentration of glycerol molecules in the ML and the somewhat higher level in the S_2 layer of the cell wall. The glycerol concentration in the S_3 was not resolved in the present experiment.

The high glycerol concentration in the S_1 layer also remains to be explained. The P cell wall part, which lies between the intercellular layer and the S_1 layer, is too thin to give the number of counts shown from this area in Fig. 6. The P layer is so narrow that it is not even found in the TEM picture in Fig. 7. The origin of glycerol counts must therefore be at or in the vicinity of the S_1 layer. Although the S_1 layer is thinner than the resolution of the analysis, it reflects a high concentration of glycerol. In the S_1 layer the hemicellulose polymer amounts for 34 percent of weight which gives the layer a greater possibility to absorb glycerol. The hemicellulose content in S_2 is not much less and if the hemicellulose content is proportional to the amount of absorbed chemical the same count rate in the S_2 layer would be expected.

Studying the penetration of MMA (methyl metacrylate) monomer into wood cells wall, using fluorescence dye or phosphotungstic acid, Furuno and Goto (1973), observed in TEM and fluorescence microscope that the polymerized monomer preferentially arranges itself in high concentrations along the outer layer of the secondary wall (S_1) and dispersed through the S_2 layer which supports the present TEM microanalysis.

Furuno and Goto (1974) also suggest that transient pores or loose regions are formed parallell to S_2 fibrills and radially across the S_2 layers during swelling.

Electron and fluorescence microscopy observations were carried out while studying the penetration of PEG 400 and PEG 1000, added with silver nitrate or rhodamine, into the wood cell wall.

Saiki (1973) also found silver grain precipitation along the microfibrils in the S_2 layer using a replica technique and TEM. A low concentration of silver grains was observed in the ML, P and S_3 layers, with more silver in the S_1 and S_2 layers. This does not agree with Furunos results or those of the current work where the concentration is high near or in the S_1 layer.

The uneven distribution of the chemical in the secondary wall (see Fig. 6) might be the result of the presence of microcracks which can act as fast diffusion paths. Microcracks are believed to be formed in wood cell walls during the initial drying from green state, Kifetew et al. (1998) and Thuvander et al. (1998).

The presence of fast diffusion paths from the lumen would increase the concentration of impregnant in drying cracks near ML. In order to obtain a stabilization effect, the stabilization chemical must be dispersed at the molecular level which means that wood should be without microcracks.

A water soluble chemical which will fulfil the above requirements must be able to maintain the systems energy when the exchange between water and impregnant molecule take place.

The transient pores and microcracks mentioned above might be the same phenomena. This can be the answer to the fact that there is no impregnation-chemical or method which has so far resulted in an ASE-value of 100.

Conclusions

PEG 200 and glycerol is found in the cell wall in amounts which are comparable with the measured (SEM) cell wall swelling.

For PEG 1500 only, the low molecular weight fractions are believed to produce the cell wall swelling.

The molecule architecture of pentaerytritol, the solubility parameter and the fact that the chemical readily crystallize is believed to give the limited impregnation effect observed.

STEM/EDS show a very uneven distribution in the cell wall of the impregnation chemical in dried wood. This is believed to be a result of microcracks formed in the initial drying from the green state. The microcracks caused by drying the wood may be one answer to the fact that there is no impregnation-chemical or method which has so far resulted in an ASE-value of 100 or long term stability.

References

Apostolov AA, Fakirov S (1992) Effect of block length on the deformation behaviour of polyetheresters as revealed by small-angle X-ray scattering. J. Macromol. Sci.-Phys. B31: 329–355

Back EL (1987) The bonding mechanism in hardboard manufacture. Holzforschung. 41: 247–258

Bolton AJ, Dinwoodie JM, Davies DA (1988) The validity of the use of SEM/EDXA as a tool for the detection of UF resin penetration into wood cell walls of particleboard. Wood Sci. Technol. 22: 345–356

Bowen DK, Hall CR (Ed.) (1975) In: Microscopy of Materials: 37. London: The Macmillan Press Ltd

Fujimoto H (1992) Weathering behaviour of chemically modified wood with maleic acid-glycerol (MG) mixture. FRI Bulletin. 176: 87–96

Furuno T, Goto T (1973) The penetration of MMA monomer into woody cell wall. Mokuzai Gakkashi. 19: 271–274

Furuno T, Goto T (1974) Structure of interface between wood and synthetic polymer. (5). Penetration of polyethylene glycol into woody cell wall. Mokuzai Gakkashi 20: 446–452

Furuno T, Goto T (1978) Structure of the interface between wood and synthetic polymer. XI. Mokuzai Gakkaishi. 24: 287–293

Horioka K, Kiyokawa N, Tominaga H (1974) Research for improvement of wood. Dependence of molecular weight of polyethylene glycol on the dimensional stabilization of wood. Bulletin of the Experiment Forests, Tokyo University of Agricultur and Technology. 11: 57–71

Håfors B (1990) The role of the Wasa in the development of the polyethylene glycol preservation method. In: **Rowell, R.M.; Barbour, R.J.** (Ed): Archaeological wood: Properties, chemistry, and preservation. Advances in Chemistry Series. Nr 225: 195–216, Washington: American Chemical Society

Kifetew G, Thuvander F, Berglund LA, Lindberg H (1998) The effect of drying on wood fracture surfaces from specimens loaded in wet condition. Wood Sci. Technol. 32: 83–94

Lindberg H (1987) Electron microscopy and microanalysis of polymers and polymer blends. PhD thesis: 48

Meyer JA (Ed.) (1984) Wood-Polymer Materials. In: Chemistry of solid wood. Adv. in Chem. Ser. (ACS). 207: 257–289.

Minato K, Yasuda R (1992) Improvement of acoustic and hygroscopic properties of wood by some non-formaldehyde cross-linking agents. FRI Bulletin. 176: 97–106

Panshin AJ, De Zeeuw C (Ed.) (1980) Textbook of Wood Technology. pp 107, New York: Macgraw and Hill

Razzaque MA, Banks WB (1982) Dimensional stability and sorption characteristics of wood treated with alkylene oxide. Bino Biggyan Patrika. 11: 17–23

Rowell RM, Ellis WD (1978) Determination of dimensional stabilization of wood using the water-soak method. Wood and Fiber. 10: 104–111

Rowell RM, Youngs RL (1980) Dimensional stabilization of wood in use. Forest Products Laboratory Research Note FPL-0243
Rowell RM (1990) Chemical modification of cell wall polymers as potential treatments of archaeological wood. In: **Rowell, R.M.; Barbour, R.J.** (Ed): Archaeological wood: Properties, chemistry, and preservation. Advances in Chemistry Series. Nr 225: 421–431. Washington: American Chemical Society
Saiki H (1973) Electron microscopy of wood cell wall impregnated with aqueous solution of silver nitrate. Mokuzai Gakkaishi. 19: 367–372
Stamm AJ (1956) Dimensional stabilization of wood with carbowaxes. Forest Products Journal. 6: 201–204
Stamm AJ (1959) The dimensional stability of wood. Forest Prod. J. 9(10): 375–381
Thaulow N, White EW (1971/72) General method for dispersing and disaggregating particulate samples for quantitative SEM and microscopic studies. Powder Technology. 5: 377–37
Thuvander F, Kifetew G, Berglund LA (1999) Modeling of cell wall drying stresses in wood. Wood Sci. Technol. (in press)
Wallström L, Lindberg KAH, Johansson I (1995) Wood surface stabilization. Holz Roh-Werkstoff. 53: 87–92
Wallström L, Lindberg KAH (1995a) Wood surface stabilization with Polyethyleneglycol, PEG. Wood Sci. Technol. 29: 109–119
Wallström L, Lindberg KAH (1995b) Wood surface stabilization. Technical report. ISSN 0349–3571