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Distribution of added chemicals in the cell walls of high temperature dried and green wood of Swedish pine, *Pinus sylvestris*

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Abstract High temperature dried and green wood of Swedish pine was impregnated with glycerate and silver nitrate. TEM and STEM/EDS on ultramicrotomed specimens was used to reveal the location of silver in the cell wall. The silver was precipitated by a new method using silver nitrate impregnated after which the wood had been impregnated with potassium glycerate. A significant difference in the distribution of the silver was observed. In the green wood, there was a homogenous distribution of the impregnant compared to the dried specimens. The inhomogenous distribution in the dried specimens is believed to be the result of damage inside the wood cell walls which in turn will have a negative effect on dimensional stabilizing results. The darker compound middle lamella observed is believed to be an artefact.

Introduction

Wood is a natural, environmentally friendly, CO_2-neutral material used for many applications. As a building material it has been used for a very long time as timber, solid beams, glued beams, boards for frontage and more. Engineered wood has, during last decades, emerged as a building material in the form of beams, wall material for both inside and outside, floor material etc. However, this natural material adsorbs and desorbs water, swells and shrinks and eventually degrades in a relatively short time.

The macroscopic swelling/shrinkage is about 4 percent in the radial direction, 8 percent in the tangential direction and a very small movement in the longitudinal direction. The small longitudinal dimensional change is the result of the cell wall elementary fibril orientation in the S_2 secondary wall, while the movement in the radial direction is a sum of the movement in low density spring wood and high density summer wood. In the tangential direction, the high density summer wood dominates the larger swelling/shrinkage.

The adsorption and desorption of water into the cell wall is followed by large dimensional changes. It has been shown that the change in cell wall dimensions is at least as large as the volume of water adsorbed or desorbed, Meyer (1984), Boutelje (1973) and Wallström et al. (1997).

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The major disadvantage with wood is the effect of dimensional changes near the interface at the cell wall level between wood/paint, wood/glue and varnish/wood which decreases the service life considerably.

The situation is worse for engineered wood, where the manufacturing processing steps compress the structure leading to a spring back action, when the material is subjected to change in the water vapour levels leading to large deformations even in the plane of a board.

Wood cell walls have a complex structure with several laminates of elementary fibrils in a matrix. The matrix consists of hemicellulose and lignin whilst the elementary fibrils consist mostly of crystalline cellulose. The cell and cell wall structure have been described elsewhere (Dinwoodie 1989, Kollman et al. 1968 and others).

In order to minimize swelling and shrinking of the cell wall, dimensional change must be limited. A lot of research has been performed in this area including: mechanical stabilization through cross lamination, coating and water repellent treatments, depositing water soluble or water insoluble bulking agents within the cell wall structure to keep the wood in a swollen state, replacing the hygroscopic hydroxyl groups with less hygroscopic groups, heat treatment and chemical cross linking of cell wall components.

However, the results so far from the point of view of overall properties and economics, have not been as good as expected.

The objective of this work was to investigate the dispersion of added chemicals inside the cell wall. The ideal result would be that the bulking chemicals are solved in between the water absorbing molecule chains and thus create a blend where the energy gain to absorb water does not exist.

Experimental

Materials

Specimens of Swedish pine sapwood (*Pinus sylvestris*) with dimensions $30 \times 2 \times 2$ mm (longitudinal × tangential × radial) of green wood and high temperature dried quality (oven dried at 103 °C for 24 hours) were used in the experiments.

The specimens were impregnated with an aqueous solution of 20 w/o potassium stained glycerol, K-glycerate.

The impregnation scheme was 15 minutes in vacuum followed by 4 hours at 0.5 Mpa. The specimens were then kept in the impregnation bath at atmospheric pressure for a period of 8 weeks followed by air drying.

The air dried specimens were then reimpregnated with an aqueous solution consisting of 20 w/o glycerol and 5 w/o silver nitrate, $AgNO_3$.

The impregnation scheme was 15 minutes in vacuum followed by 4 hours at 0.5 Mpa. The specimens were then kept in the impregnation bath at atmospheric pressure for 6 days followed by air drying.

Before TEM-specimen preparation, 3 mm of the specimen length was cut away.

TEM-specimen preparation

An acrylic polymer (Unicryl) polymerized at 55 °C, was used as lumen filling material. The polymer was used as a cell wall supporting material when the wood specimens for TEM were cut from the specimen block using an ultramicrotom, LKB 2088 Ultratome V equipped with a diamond knife. Thin specimens, 100–200 nm, were cut from a mesa of about 1×1 mm and placed on 200 mesh copper grids.

STEM/EDS

The STEM/EDS-analysis of Ag-concentration and location was performed with a Transmission Electron Microscope (TEM), JEM-2000 EX with LINK AN 10/85 S analytical equipment, software-ADM. The LINK-system has a silicon detector with an 8 μm thick beryllium window and an energy resolution of 140 eV.

The $Ag_{L\alpha}$ X-rays, with a peak energy of 2.98 keV, were counted in a 140 eV wide digital window and redistributed to a line scan curve across the wood cell walls. Five specimens from each of the two groups of the impregnated specimens were investigated.

The analysis time in the STEM/EDS-line scan was about 10 s at each point.

Results and discussion

Figure 1 shows part of a cross-section of a cell. The horizontal cell wall is a tangential wall which, in the right part of the picture, continues into a radial cell wall. The lignin rich middle lamella and corner thickenings are dark compared to the rest of the cell wall.

In the lower right hand corner of the Figure, where the scale bar is, the polymer used for supporting the cell walls during cutting has been pulled away from the lumen surface during the microtoming or due to surface tension. In the inset picture the different cell wall layers are named. These are the middle lamella, including the intercellular layer and the primary walls (the compound ML) and the secondary walls, S_1, S_2 and S_3.

The silver is a product from the possible reaction between potassium glycerate and silver nitrate:

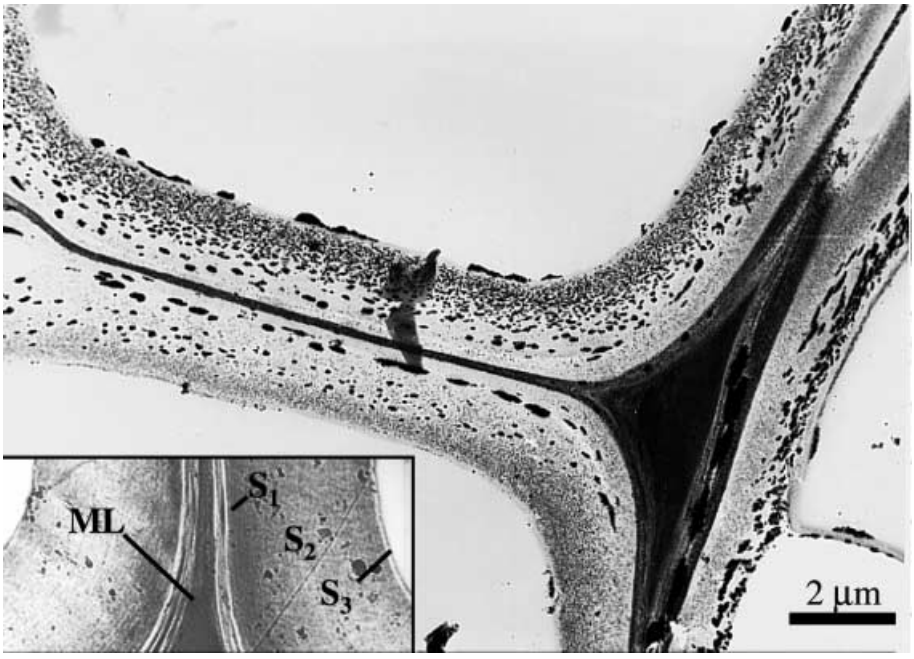

Fig. 1. TEM micrograph of cell walls from high temperature dried pine, *Pinus sylvestris*, impregnated with an aqueous solution of 20 w/o glycerate, resulting in a WPG of 25 w/o, followed by an aqueous solution of 5 w/o silver nitrate and 20 w/o glycerol, Wallström et al. (1997). The dark spots are silver grains which provides good electron contrast

The silver grains are thus expected to show where the glycerate molecules are located in the cell wall. Impregnation only with silver nitrate or silver nitrate impregnated into earlier glycerol impregnated wood did not result in silver precipitation.

In an earlier paper (Wallström et al. 1997) the potassium distribution through the cell wall was analyzed. Potassium is a part of the glycerate molecule because there are attraction forces between the negative glycerate and the positive potassium ions. The potassium was believed to be found in relatively high concentrations in the S_1 layer and in relatively low concentrations in the ML, S_2 and S_3 layers. However, studying the distribution of silver grains in wood dried prior to glycerate/glycerol + $AgNO_3$ impregnation show scattered high concentration between the S_1 and S_2 layers, see Figs. 1, 2, 3.

There is a change in microfibril orientation between the S_1 and S_2 layers which causes a structural discontinuity (greatest separation between cell wall microfibrils, Davies 1968). Fengel (1971) showed that, after drying, spruce suffered from fissures which were observed in the weakest region, i.e. between S_1 and S_2. In earlier work, Wallström et al. (1997) used wood specimens from not controlled drying and storage before the impregnation studies. These specimens could therefore contain coalesced cracks compared to the specimens used in the present study.

The EDS silver line scan in Fig. 2 shows that the concentration across the cell wall is very uneven. At the start in the left cell wall surface the beam partly crosses a silver grain at the lumen surface of the cell wall. A higher concentration of silver can be observed compared to the cell wall surface to the right. Continuing in the direction of the arrow, the concentration from the lumen side inwards is rather high, the silver grains are many and close together. They reach two thirds of one cell wall thickness before the ML. Looking at the analyzed line from the opposite lumen, the situation is about the same, with only a slightly lower count rate being seen. The area closer to the ML has little silver, only larger dots are shown in both the picture and the spectrum. The analysis line crosses two large dots of silver close to the ML, but these are not representative of the areas beside the ML. The areas beside the larger dots are lean in silver. The silver concentration in the ML is relatively high but does not reach the number of counts found in the larger silver grains crossed by the line of analysis at both sides of the ML.

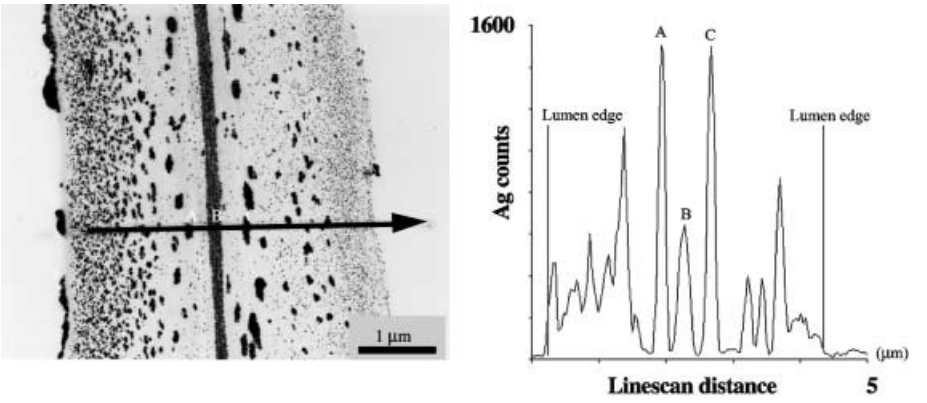

Fig. 2. The distribution of silver resulting from the impregnation scheme described in high temperature dried pine wood

The microcracks mentioned earlier can also be the reason for the higher concentration of silver in the direction from the lumen towards the ML and, as can be seen, this distribution differs between the different cell walls.

The silver concentration in the ML is high compared to other parts of the cell wall especially in the S_1 and S_3, see Fig. 3.

Cracks in a material should act as sinks for diffusion of moveable material. After diffusion the damaged regions would be expected to be enriched with K-glycerate or silver, while the zones around will be depleted due to better compatibility for the diffusant itself compared to diffusant/wood molecule compatibility. This situation is well known in stainless steel (18/8-steel) where, after heat treatment, chromium depletion of austenite adjacent to the grain boundaries, where chromium carbides forms, take place (Brick et al. 1977).

The high concentration of added chemicals in the ML has been observed earlier (Bailey et al. 1969, Fengel et al. 1971, Yata et al. 1979 and others). Fengel and Yata used copper instead of silver as indicator.

Bailey et al. (1969) impregnated a 2% solution of silver nitrate into wood dried to 30% moisture content, followed by hydrazine hydrochloride as precipitant. On drying, a permanent in situ black deposit of silver was left in the cell walls of Douglas fir (*Pseudotsuga menziesii*) which was examined using TEM. Fengel et al. (1971) impregnated air dried sapwood of pine (*Pinus sylvestris*) with an aqueous solution of copper sulfate and this was then studied in TEM. Yata et al. (1979) studied cell wall penetration of copper sulphate in Hinoki and Karamatsu sapwood. Thin sections were in contact with the precipitant, 1% Na_2S solution. In TEM the distribution of CuS particles was observed.

It is believed that the silver (or copper) distribution is governed by the relative porosities of the various layers in the cell wall. According to the above results, the highest porosity is in the middle lamella region.

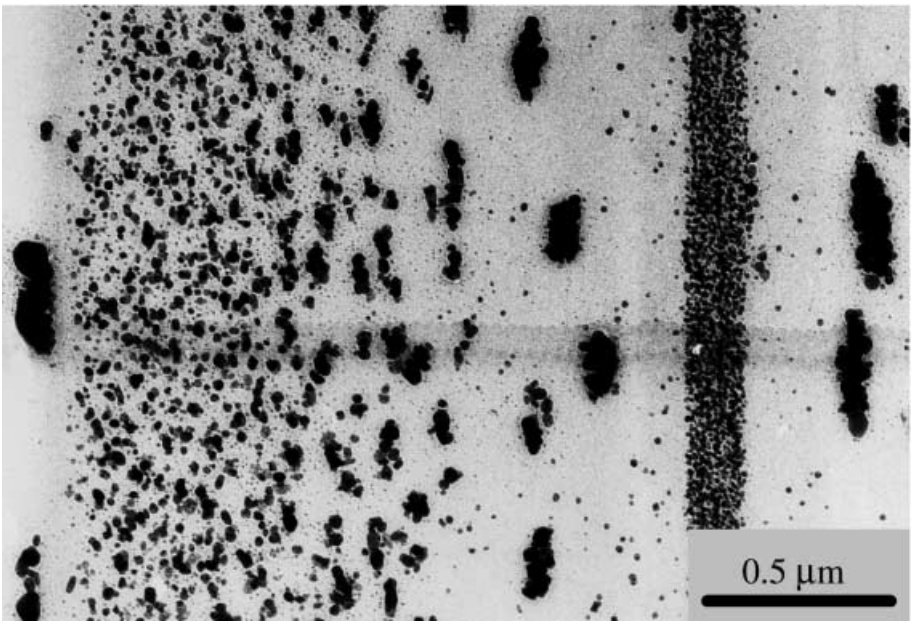

Fig. 3. Magnified area of the picture in Fig. 2

However, making thin specimens by cutting or solvent casting can give rise to thickness artefacts i. e. differing thickness across the section of the sample. Thickness artefacts in polymers have been investigated by other researchers, Lindberg (1987). The density of PC (polycarbonate) and PMMA (polymethyl metacrylate) are nearly the same (1.2 g/cm^3) but the mean atomic number differs slightly ($Z_{PMMA} = 1.15\ Z_{PC}$). The difference in mean atomic number should give a higher scattering power for electrons through PMMA. The PMMA should appear darker in a TEM/STEM picture. STEM micrographs of mechanical and cast blends of PC/PMMA are shown in Figures 4 and 5.

The micrographs show that the PC phase appears much darker due to its thickness being much larger than the PMMA phase.

One possibility is that mechanically blended PC/PMMA specimens can be affected by ultramicrotoming. PC is more difficult to cut which results in stresses followed by plastic deformation of the other phase and also in thinning. Another possibility is that internal stresses present from the mechanical blending are relaxed when the thin section is cut. However, the above explanations can be excluded because the cast thin specimens show similar results.

The most likely explanation for the variation in thickness are surface tension effects between the two phases and between the phases and their surroundings.

If the ML in wood is more porous, its density should be less 80 and result in a lighter image compared to the rest of the cell wall. However, in this work, the ML was seen to be darker compared to the other cell wall layers even without silver particles as shown in Fig. 6. An explanation for this might be that this part of the cell wall gives a thicker section compared to other parts after ultramicrotoming the specimens. If the ML is thicker, it would wrongly be seen as containing a higher amount of silver than the other cell wall layers.

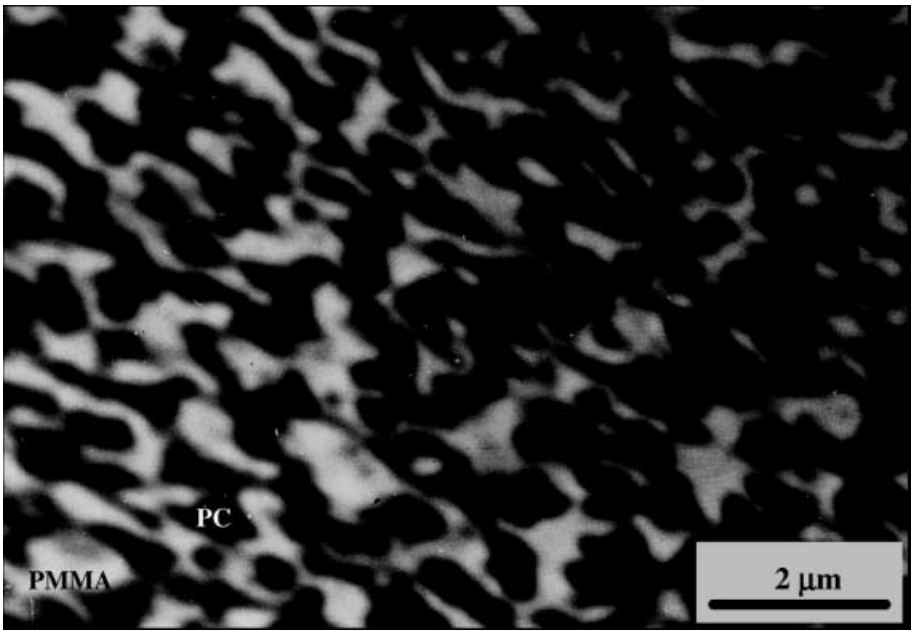

Fig. 4. STEM micrograph of a PC/PMMA (50 w/o) mechanically mixed blend

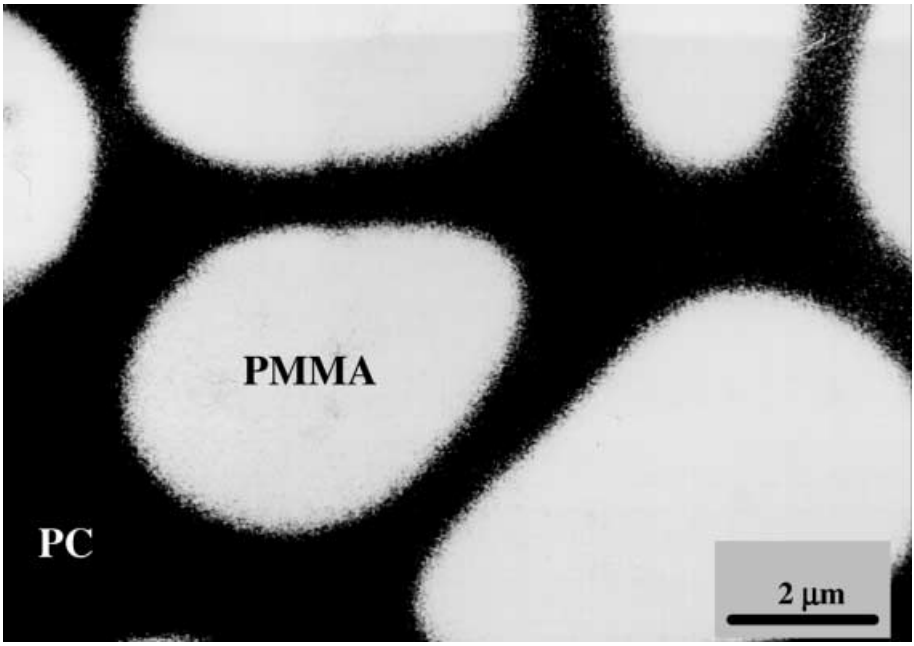

Fig. 5. STEM micrograph of a PC/PMMA (50/50 w/o) cast specimen

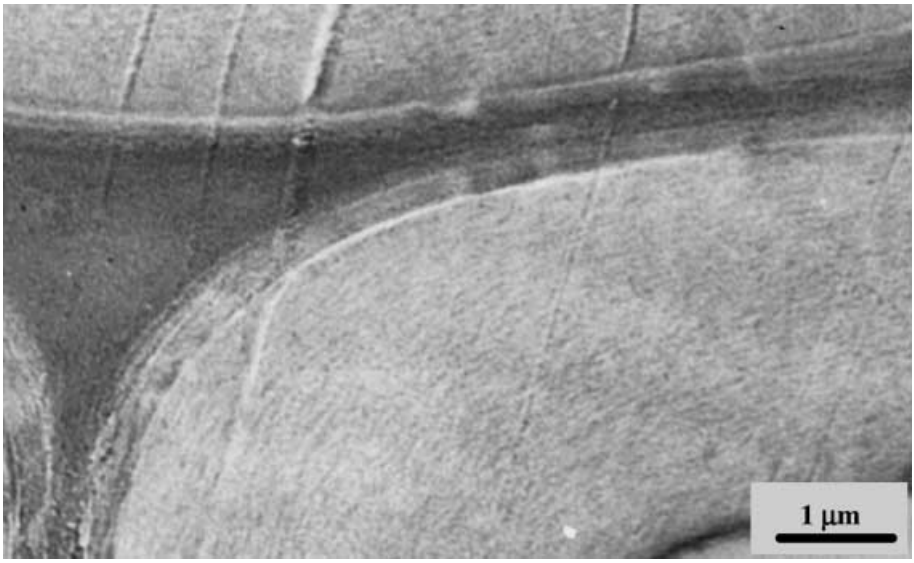

Fig. 6. TEM micrograph of an unimpregnated pine cell wall

Wood specimens which where not dried from green state before impregnation, show a silver dispersion which is much more even compared to the one in high temperature dried specimens, see Fig. 7.

The images and the EDS spectra in Fig. 8 and 9 show a more even distribution of silver particles in the S_2 cell wall layers compared to the specimens which were

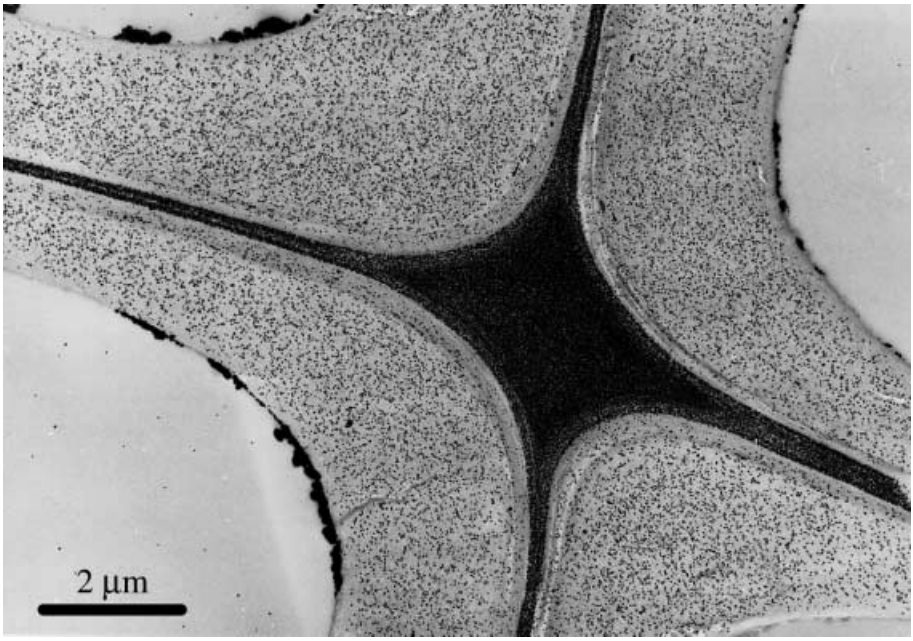

Fig. 7. TEM micrograph of cell walls in pine impregnated, in the green state, in an aqueous solution of 20 w/o glycerate, resulting in a WPG of 25 w/o, followed by an aqueous solution of 5 w/o silver nitrate and 20 w/o glycerol

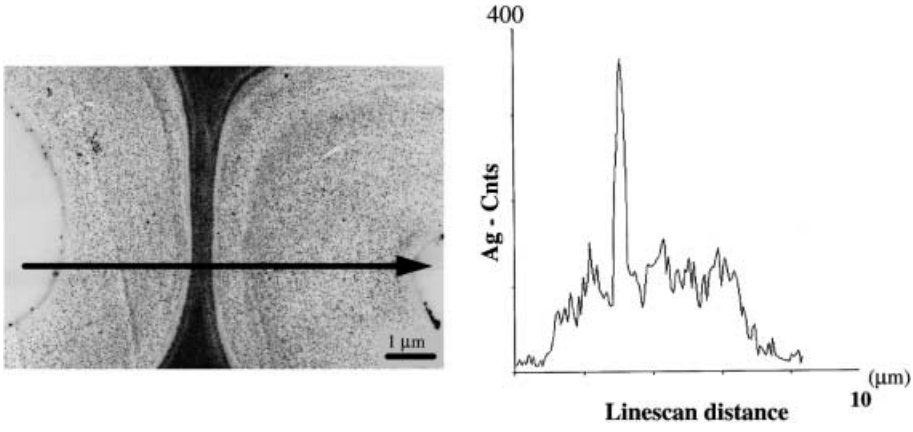

Fig. 8. The distribution of silver in the cell walls of pine kept in the green state prior to impregnation

dried prior to impregnation and also a decrease in the count rate close to the ML (S_1) and close to the lumen (S_3) and a high silver concentration in the ML.

Drying of wood affects its cell walls. The reason for this might be that the relaxation process among the wood polymers does not have the time needed to decrease the free volume when the drying of the wood occurs and therefore some damage will be induced (Kifetew et al. 1998). The result of this will be the

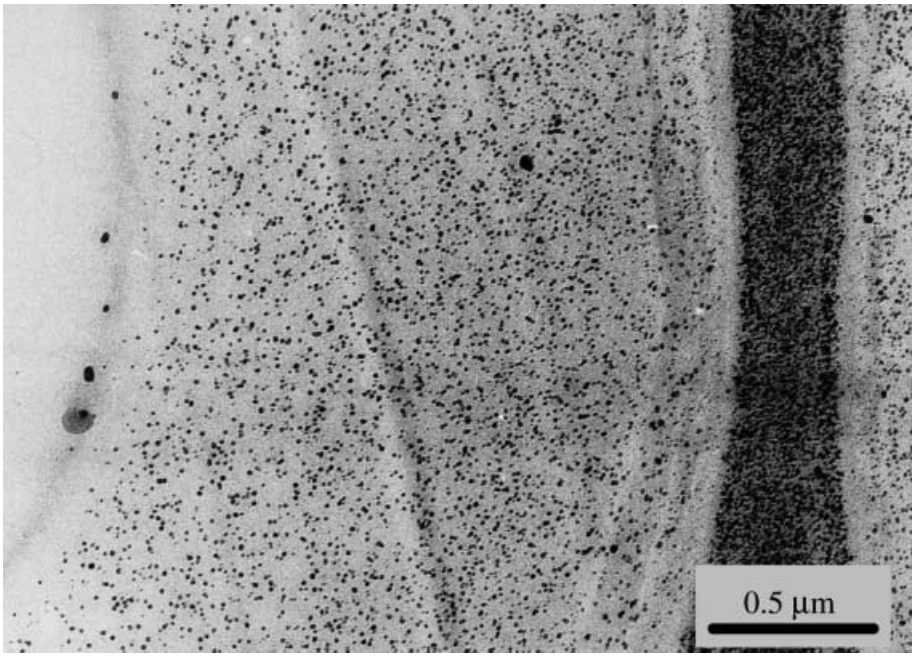

Fig. 9. A close up of the image in Fig. 8

inhomogenous distribution of the impregnation chemical which in turn will result in a decrease in the dimensional stabilization. The best stabilizing effect will be achieved, if all areas inside the cell wall which have affinity to water, are occupied. This is not the case in the high temperature dried specimens or the specimens studied in the earlier work, Wallström et al. (1997).

The glycerate (glycerol) molecules are believed to be soluble between the hemicellulose molecules. Hemicellulose is the molecule in the cell wall which the impregnation chemical will be in close contact with, occupying the free volume.

There is no significant difference in the stabilizing behaviour between glycerol and its K-carboxylate (K-glycerate) unpublished work done by the Swedish Institute for Wood Technology Research (Trätek). According to this result, the solubility of the K-glycerate molecule inbetween the cell wall polymers would not differ much from the solubility of glycerol.

Conclusions

The result of the cell wall bulking is that greater local concentrations of silver, assumed to be attached to the glycerate molecules, are found in the dried specimens. It is believed that this inhomogenous distribution is a result of damage in the cell wall during drying.

In specimens that have been impregnated in the green condition and thereafter properly dried, a relatively homogenous distribution of silver is seen. This will result in a better dimensional stabilizing effect compared to wood impregnated in the dried condition.

The darker compound middle lamella (ML) in the wood specimen observed in the current work is believed to be an artefact due to variations in thickness of the microtomed specimens.

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