Micromorphology Studies of Modified Wood Using a Surface Preparation Technique Based on UV-Laser Ablation

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ABSTRACT

The objective of this paper is to demonstrate a UV-laser ablation technique as a tool for sample preparation in microscopy studies of modified wood. Improved techniques for studying the microstructure of modified wood are crucial for a deeper understanding of many of their physical, mechanical and durability properties. The surface preparation technique is described in this paper. An illustration of micrographs of the micromorphology and polymer distribution in some examples of modified wood is also presented. It is clearly demonstrated that in contrast to conventional surface preparation techniques used for light microscopy and scanning electron microscopy (SEM), *i.e.* razor blade and microtome cutting techniques, UV laser ablation does not introduce any mechanically induced micro cracks and redistribution of polymers or other mobile substances in the prepared surface. Results also show that, in particular, this technique seems to be suitable for studying polymer distribution in resin impregnated wood, as well as detection of micro cracks in modified wood cell walls.

INTRODUCTION

Studies of the microstructure, or micromorphology, of modified wood may add valuable insight about their physical and mechanical properties. Certain wood modification processes may indeed result in critical alterations of the wood microstructure, *e.g.* micro cracks in the wood cell-walls as well as intercellular separations, which consequently also may affect many properties of the final products. The level and distribution of polymer-filled cell lumen are other micro structural features of great importance for wood modification concepts based on resin impregnation and in-situ polymerization. Many studies and reviews have been published regarding physical, mechanical and durability properties of modified wood (see *e.g.* Militz 1993, Schneider 1994, Schneider and Phillips 2000, Sugiyama *et al.* 1998, Rapp 2001, Militz 2004, Lande *et al.* 2004, Rowell 2005, and Hill 2007). Only very limited information has, however, been published about the microstructure of such materials.

The conventional preparation techniques for microscopy studies of wood and wood based materials involve microtome or razor blade cutting of the wood surfaces in wet/moist conditions. This mechanical cutting process certainly introduces uncontrolled damage and artifacts such as micro cracks, distortion and contamination of the wood surface morphology. Consequently, one possible reason for the lack of micro structural information of *e.g.* certain modified wood may be due to the fact that many of these materials are very dense which combined with difficulties of moistening the samples means that traditional microtome sample preparation is complicated or even impossible. Some attempts have been made to study wood and wood composites microstructure by means of surface polishing and/or replication techniques (Wu 1998, Balasuriaya *et al.* 2001, Ishimaru and Iida 2001).

Seltman (1995) introduced a new technique based on ultraviolet (UV) laser irradiation, or so-called excimer laser ablation, as a means for wood surface modification as well as sample preparation of wood for microscopic studies. The idea originates from the medical field where excimer (*i.e.* excited dimer) laser systems are used for delicate eye surgeries, *e.g.* eye refractive surgery (LASIK). In this type of surgery, the excimer laser ablation is in principle used as a procedure for a clean and precise removal, or ablation, of thin layers of the cornea to remodel its refractive properties. Since the cornea does not grow back, the method can permanently correct refraction errors such as short-sightedness (myopia) and astigmatism.

The excimer laser was invented by Basov *et al.* (1970). The applications in the medical field were pioneered in the 80's by Blum and co-workers (Linsker *et al.* 1984, US patent 4784135). They found that UV light from a pulsing excimer laser is well absorbed by biological as well as organic substances in general. In contrast to burning or mechanical cutting of the material, the high photon energy of the excimer laser pulse in this case adds just enough energy to break covalent molecular bonds of the surface tissue, which effectively disintegrates into the air in a controlled way through ablation rather than burning. The laser ablation is greatly affected by the ability of the material to absorb energy, therefore the wavelength of the ablation laser should have a minimum absorption depth. Accordingly, the excimer lasers can remove exceptionally fine layers of surface material, *i.e.* the UV light is typically absorbed within the first nanometer of the tissue. One of the most important characteristics with this ablation process is that it enables a removal of thin layers with almost no heating or change to the remainder of the material which is left intact. These features makes the technique also well suited to precision micromachining of organic materials such as wood and other lignocellulosics as well as certain polymers and plastics. The experience so far regarding wood and wood composites (Seltman 1995, Wu and Seltman 1998, Stehr *et al.* 1998, Kopp *et al.* 2005, Mertens *et al.* 2006, Segerholm *et al.* 2007) implies a number of obvious advantages compared with conventional sample preparation techniques: 1) the wood micro structure is efficiently revealed with no mechanically induced micro cracks and redistribution of polymers or other mobile substances in the prepared surface, 2) no wetting and drying cycle is needed, 3) well defined notches can be cut in narrow zones of samples, 4) the technique is operator independent (high reproducibility). A general observation is also that the treatment does not generate any significant heat on most wood and wood composite samples, in contrast to other "burning" laser irradiation techniques such as a typical carbon dioxide laser.

The mechanism of this UV laser surface treatment or ablation process on wood is not fully understood, but the basic principle is that the UV irradiation breaks covalent molecular bonds in the lignocellulosic material. It is also evident that there is a selective absorption of the UV light in certain wood cell-wall polymers or substances. For example tissues with a higher concentration of lignin, e.g. the middle lamellae, seems to undergo a preferential ablation (valid for the wavelength 193 nm).

The main objective of this paper is to demonstrate and present some principles regarding the UV (or excimer) laser technique as a means for sample preparation for micromorphological studies of modified wood.

MATERIALS AND METHODS

The modified wood material examples in this study were chosen from three types of commercially available or pilot plant produced products: 1a) and 1b) Furfurylated Scots pine sapwood and radiata pine with a weight percent gain (WPG) of approximately 80% and 30% respectively, produced at Kebony ASA in year 2004 (at that time named Wood Polymer Technologies) at their pilot scale production unit at Porsgrunn (Lande *et al.* 2004); 2a) and 2b) Heat treated birch (collected from advertisement material produced by Scandinavian Finewood AB in year 2008) and spruce (produced by Stora Enso in year 2004) following the ThermoWood D (Anonymous 2003) procedure; and 3) Acetylated Scots pine sapwood produced by A-Cell AB in year 2004 in an acetylation pilot plant at Chalmers (now placed at SP in Borås). The method of acetylation followed a simplified procedure without use of any catalyst or co-solvent in the reaction (Rowell *et al.*1986, Larsson Brelid 1998). The acetylation level was approximately 20% WPG.

From each modified wood product, smaller blocks with dimensions of ca 4 x 10 x 20 mm^3 were initially prepared with a band saw, approximately corresponding to the R x T x or T x R x L directions (R = radial, T = tangential and L = longitudinal main directions in wood, respectively). From these blocks, sections with the size of approximately 4 x 10 x 1.5 mm^3 were cut by the UV laser, approximately corresponding to R x T x L, or T x R x L, directions. Only cross sections of the wood samples were studied. The samples were ablated (or “cut”) by the laser beam transverse the fiber direction.

The principles for the surface preparation technique based on UV-Laser ablation applied in this work were developed at KTH during the mid 90’s (Seltman 1995). The UV laser used was a pulsing krypton fluoride (KrF) exciplex laser (Lumonix PM886), emitting radiation with a wavelength of 248 nm. The principles of this KrF laser is that it absorbs energy from a source which causes the krypton gas to react with the fluorine gas producing krypton fluoride, a temporary complex, in an excited energy state. In fact, most "excimer" lasers are of this noble gas halide type, for which the term excimer (short for excited dimer) is incorrect since a dimer refers to a molecule of two identical or similar parts. A more suitable but less frequently used name for such lasers is exciplex (short for excited complex) laser. The excited KrF compound then undergoes a stimulated emission of radiation, *i.e.* a laser light, with the wavelength 248 nm.

The laser beam passes through a series of lenses and masks to create a suitable focal point where the specimen surface is placed with the help of a positioning device. This feeding board is connected to the laser by a computer controlled position-sensitive trigger pulse generator. The pulse width was 20 ns. The pulse frequency was varied between 5–10 Hz, and the energy level of the output pulses was ca 300–400 mJ.

Scanning electron microscopy (SEM) was used to evaluate the microstructure of prepared the samples. The apparatuses were a) Hitachi Tabletop Microscope TM-1000, and b) JSM-5310LV (Jeol Ltd., Tokyo, Japan). The microscopes were adjusted to a low vacuum mode (LV-SEM) to obtain pictures without require sputtering of the surface of the specimens.

RESULTS AND DISCUSSION

Figures 1a and 1b show examples of the effect of UV-laser ablation perpendicular to the grain of a heat treated birch sample (a) and a furfurylated Scots pine sample with a WPG of ca 80% (b), respectively. The direction of the laser beam treatment was perpendicular to the fibre direction, in Figure 1a approximately in the tangential direction, and in Figure 1b in the radial direction. As can be seen the laser treatment clearly reveals the typical cellular structure of a wood cross-section. Note the non-treated zone (the upper ¼ part) in both micrographs representing a wood cross-section prepared with a band saw. It should be remarked that such machined wood surfaces have a high degree of crushed and damaged wood cells which is a distinctly different surface morphology compared with the ablated wood surfaces, which reveals the actual intact wood microstructure.

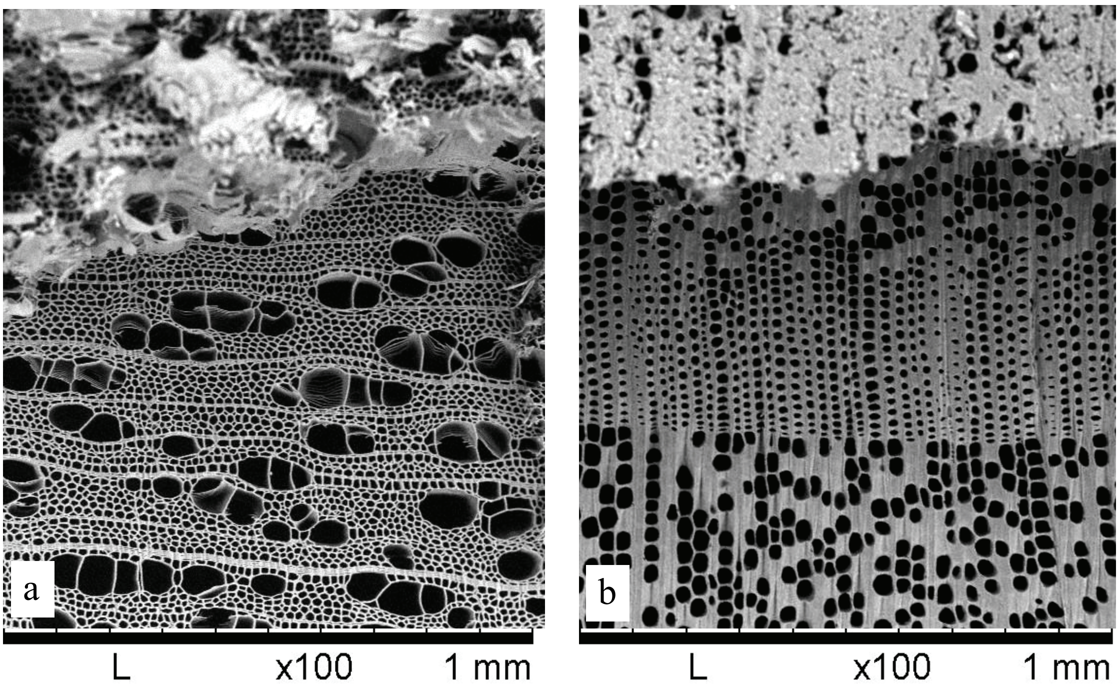

Figure 1: Micrographs showing a UV laser ablated zone (the lower ¾ part) of a) heat treated birch (TR-plane) and b) furfurylated Scots pine with ca 80% WPG (RT-plane).

Figure 2 shows examples of micromorphology images of a furfurylated Scots pine sample with a high WPG (a) and a furfurylated radiata pine sample with a lower WPG level (b). In this case, it can be observed that the high-WPG samples have a higher proportion of polymer-filled lumen in the earlywood, compared with the low-WPG samples.

Furfurylated Scots pine ~80% WPG *Furfurylated radiata pine ~30% WPG*

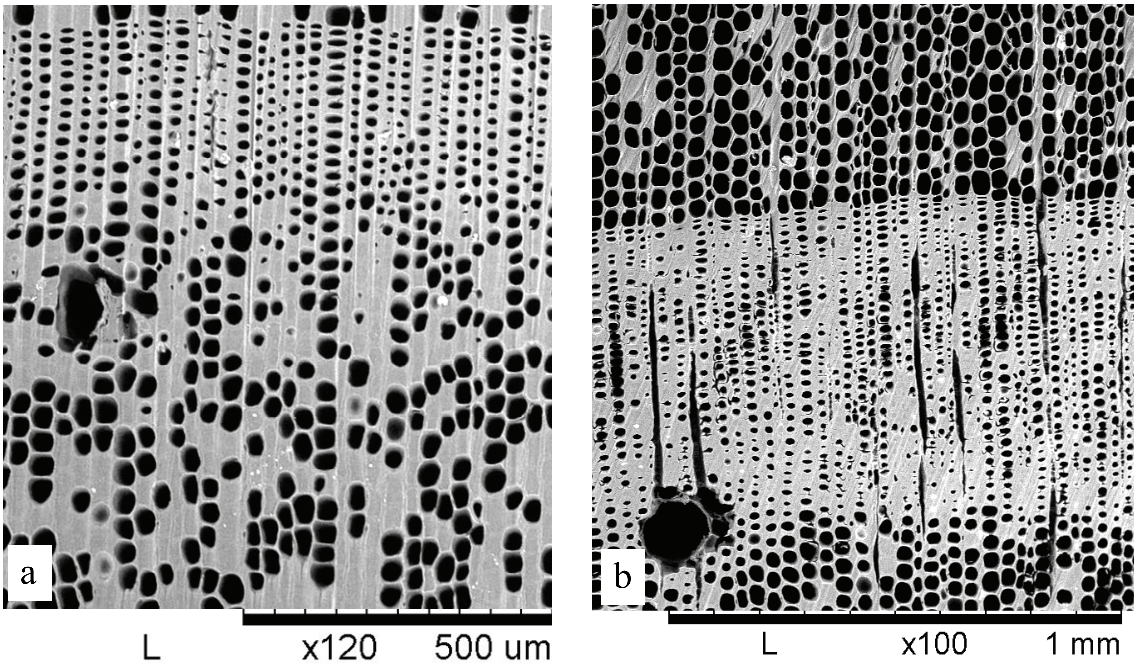

Figure 2: Micrographs showing polymer-filled cell lumen in a) high-WPG furfurylated Scots pine; and b) low-WPG furfurylated radiata and pine. Note the different length bars.

A general observation is that two types of cracks occur in the furfurylated wood samples, the first is radial oriented intercellular cracks, and the second is micro cracks in the cell wall. Figure 3 illustrates the occurrence of micro cracks in the wood cell-walls of the furfurylated radiata pine (~30% WPG) samples. As can be seen, the micro cracks in the cell-walls are oriented both tangentially and radially with respects to the tracheid cell-wall, even though the tangential cracks are more pronounced. Similar tangential cell-wall cracks could also be observed in the acetylated Scots pine samples, see Figure 4. The furfurylated Scots pine (~80% WPG) samples showed less noticeable cell-wall cracks compared with the furfurylated and acetylated Scots pine samples. On the contrary, the high-WPG furfurylated samples showed more frequent and larger radial oriented inter cellular cracks (similar to drying cracks).

Furfurylated radiata pine latewood *Furfurylated radiata pine earlywood*

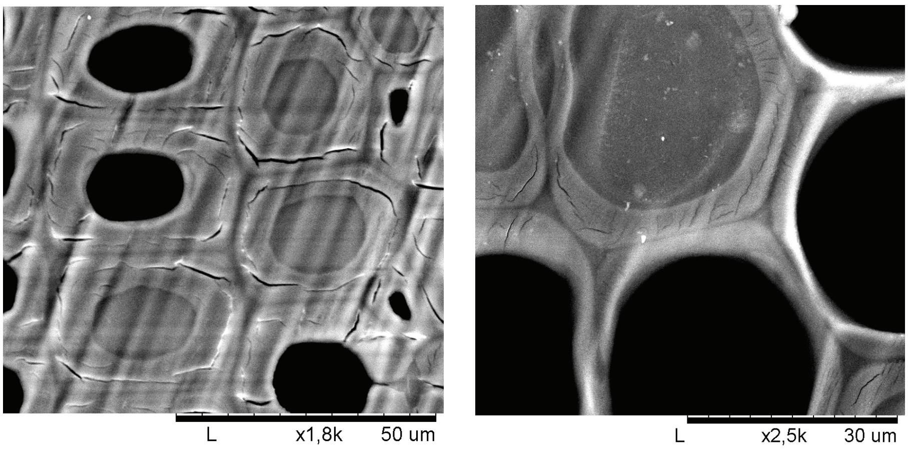

Figure 3: Micrographs showing micro cracks in the wood cell-walls in furfurylated radiata pine latewood (left) and earlywood (right). Wpg ≈ 30%. Note the different length bars.

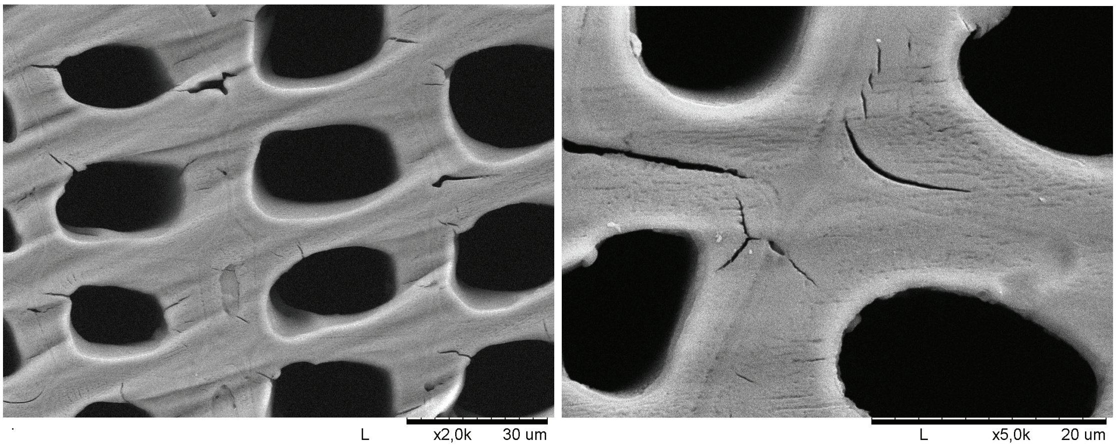

Figure 4: Micrographs showing micro cracks in the wood cell-walls in acetylated Scots pine latewood at two different magnifications.

One evident drawback with the laser ablation technique as applied in this study, i.e. for sample preparation, or "cutting" of thin sections, can be seen in Figures 3 and 4 as the diagonal oriented "lines" or "traces" in the surfaces. These artefacts arise from the removed material during the ablation process, and it is obvious that the wider section being prepared, the more severe "tracers" arise at the edge of the sample closest to the laser beam source. In addition, if UV resistant materials such as UV reflecting additives are present in the sample being prepared, this also give rise to more severe "traces". In the heat treated birch samples no obvious alterations of the micromorphology due to the heat treatment process could be observed. In the heat treated spruce samples, however, cell-wall delamination could be observed, especially in earlywood zones. Figure 5a shows an annual ring border where the earlywood region (upper part) show some cell-wall delamination and the latewood region (bottom part) show cracks through the cell-walls. Figure 5b show cell-wall delamination in the earlywood more pronounced compared with Figure 5a.

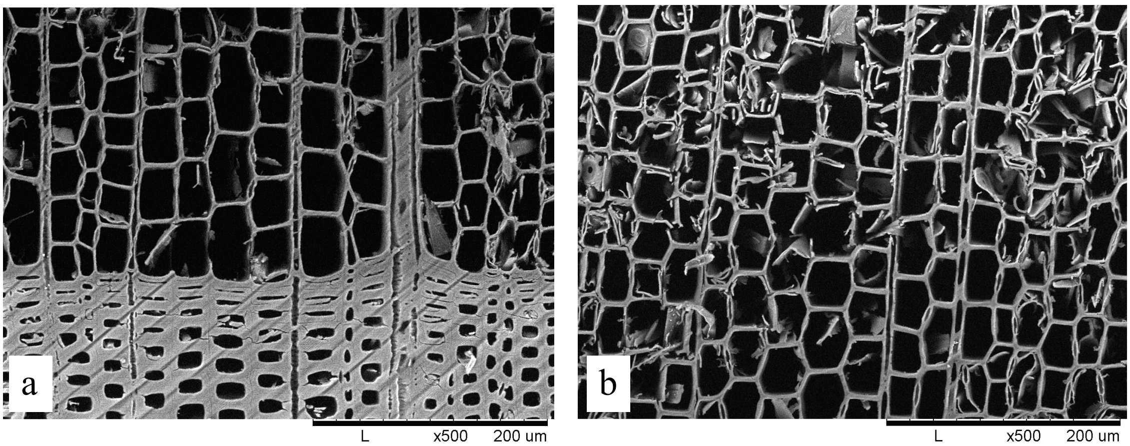

Figure 5: Micrographs showing cell-wall delamination in thermally modified spruce, a) annual ring border, b) earlywood region.

Future studies is suggested to involve a combination of micromorphological studies and *in-situ* micro mechanical analysis where laser ablated cross sections of modified wood samples could be tested in a micro-tensile test stage mounted in a SEM. This type of analysis of micro mechanical properties transverse the fibre direction could ad important information about *e.g.* early stages of chemical degradation of the wood polymers in heat treated wood.

CONCLUSIONS

This paper demonstrates that UV-laser ablation is a useful and effective surface preparation tool for micromorphological studies of modified wood and wood composites. The method can clearly reveal micro structural features such as polymer-filled lumen in the furfurylated wood as well as micro cracks in the cell-walls of the modified wood samples.

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