THESIS

Influence of Aqueous Solutions of Organic Substances on Structure and Properties of Pinewood (*Pinus sylvestris*)

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any degree or examination.

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DOKTORITÖÖ

Orgaaniliste ainete vesilahuste mõju männipuidu (*Pinus sylvestris*) struktuurile ja omadustele

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List of publications

This thesis is based on the following publications which are referred to in the text by their assigned Roman numerals **I –III**:

I **P. Meier**, T. Kaps, U. Kallavus. 2005. Swelling of Pinewood (*Pinus Sylvestris*) in Binary Aqueous Solutions of Organic Substances. – Materials Science *(Medžiagotyra)*, 11, 140–145 (ISSN 1392-1320)

II **P. Meier**, U. Kallavus, A. Rohumaa, and T. Kaps. 2006. Multiple Swelling of Pinewood *(Pinus Sylvestris)* in Binary and Ternary Mixtures of Ethanol, Acetone and Water. – Materials Science *(Medžiagotyra)*, 12, 25–30 (ISSN 1392-1320)

III **P. Meier**, E. Stöör, T. Kaps, U. Kallavus. 2006. Mechanical properties of pinewood (*Pinus Sylvestris*) swollen in organic liquids. – Proceedings of Estonian Academy of Sciences. Engineering, 12, 125–133 (ISSN 1406-0175)

Reprints of papers I – III were made with permission from the publishers.

Other publications:

IV **P. Meier**, T. Kaps, U. Kallavus. 2006. Behaviour of Pinewood (*Pinus Sylvestris*) in Various Mixtures. **–** *In:* Proc: 2nd International Conference SHARING, Berlin: Walter de Gruyter, 515–521

V Kallavus, U., **Meier, P.**, Kaps, T., Niitsoo, J., Nisumaa, R., Traksmaa, R. X-ray diffraction study of pinewood *(Pinus Sylvestris)* swollen in mixtures of water and organic solvents. – Wood Material Science and Engineering (ISSN 1748-0272). *To be published.*

In addition, some selected unpublished works are presented in the thesis (Chapters 5.3 and 5.5).

Approbation

International conferences and seminars

1. Nordic-Baltic Network in Wood Science and Engineering, Stockholm, Sweden, October 30-31, 2006.

2. Baltic Polymer Symposium, Tallinn, Estonia, October 19-21, 2005

3. 2nd International Conference "SHARING", Jurmala, Latvia, May 10-14, 2005

4. FACE (Forum for Advancing Chemical Education), Barcelona, Spain, October 16-17, 2004

Author's own contribution

The research work presented in this Thesis is a result of teamwork.

In presented publications I-III the author designed and supervised the experimental study, carried out the experiments together with MSc-student and BSc-student, interpreted the obtained data and wrote the paper with co-authors.

The liquids analysis were performed in cooperation with the Department of Forest Products Technology at Helsinki University of Technology.

The SEM and X-Ray diffraction studies were performed in cooperation with the Centre for Materials Research at Tallinn University of Technology.

Abbreviations and symbols

A	absorbance
a	absorption coefficient
a_{ODD}	dimension of an oven-dried sample
a_{SD}	dimension of a swollen sample
Act	acetone
b	width of sample
CML	compound middle lamellae
CrI	crystallinity index
D	lattice spacing
DMF	dimethylformamide
DN	solvent donor number
DP	degree of polymerization
Ea	swelling activation energy
EtOH	ethanol
F	force
FSP	fibre saturation point
f	fibre saturation point
g	specific gravity
GC	gas chromatography
h	thickness of a sample
H	hydrogen
HB	hydrogen bond
HCl	chloric acid
H_2O	water
i-PrOH	isopropanol
IR	infrared
L	space between two supports
λ	X-ray wavelength
MC	moisture content
MF	molar fraction
MV	solvent molecular volume
NMR	nuclear magnet resonance
OH	hydroxyl group
$\sigma_{comp.st}$	compression strength
$\sigma_{bend.st.}$	bending strength
S	swelling of wood
SED	solvent emission directive
Sw	swelling of wood
SB	solvent basicity
TMS	trimethylsilylate
UV	ultraviolet
VOC	volatile organic compound
WD	density of wood
θ	Bragg angle

Contents

Introduction

Interaction between wood and liquids is of fundamental importance both from a scientific standpoint and in the context of commercial processes, which involve dimensional stabilization, preservation, chemical modification, the removal of extractives and pulping.

Contact of wood with a liquid usually leads to the swelling of wood. Therefore the swelling of wood has been investigated extensively for the past 80 years and many monographs and handbooks are published about wood-water relationship (Stamm 1964, Scaar 1972, Panshin 1980, Rowell 1984, Nelson 1986, Lemmetinen et al. 1987a, 1987b, Siau 1995). Swelling of wood in organic liquids has been studied since the twenties of the last century. First thorough investigation on swelling of wood in organic liquids was performed by Stamm and Nayer (Stamm 1935, Nayer and Hossfeld 1949, Kumar 1957, 1958). These studies concentrated on the swelling of wood in variety of organic liquids, which had been carefully freed of water. The latest most thoroughgoing articles about wood swelling history and swelling phenomenon are written by Mantanis et al. (Mantanis et al. 1994a, 1994b).

Determination of swelling values on macroscopical level (measuring overall dimensions) is quite simple. For that reason it has been very attractive challenge to correlate swelling behaviour of wood with other wood properties as permeability, penetration, mechanical strength (Hossfeld 1972, Banks 1980, Fukuyama and Urakami 1982, Kretschmann and Green 1996, Obataya et al. 1998, O'Leary 2001). Despite great efforts there is still no accurate information concerning the influence of organic liquids and mixtures on structure and properties of solid wood. On the other hand, the behaviour of separated wood polymers, as cellulose, hemicelluloses and lignin in organic solvents has been investigated very extensively, but information about solid wood structure and properties is lacking.

Since swelling is a complex process, which is affected by both the type of wood and the solvent substrate, therefore it is difficult to predict the influences of each of them on the swelling of wood. The most challenging objective of the wood swelling studies in organic liquids has been to find the correlation between swelling values and specific properties of swelling agents (Rowell 1984, Ishimaru and Minase 1992, Mantanis et al. 1995b, 1995a, 1995b). It must be noted that there is currently no consensus on the relative influences of different factors on wood swelling and sometimes the results and conclusions are contradictory.

For some reason studying of wood behaviour in binary mixtures has been avoided. It has been observed that the presence of water influenced significantly the swelling of wood in many organic solvents. In the field of solution chemistry, the study of water-alcohol solutions is one of the most attractive subjects. Despite a great deal of effort spanning five decades, no general consensus has been reached concerning the structural properties of liquid alcohols and their solutions with water. Therefore accurate data of interaction between wood and aqueous solutions of organic substances is lacking and published results are sometimes contradictory.

Background

In order to reduce peak ozone levels, the European Union (and many of its member states) is looking to reduce levels of nitrogen oxides and Volatile Organic Compounds (VOC) in the atmosphere. The part of the strategy is to limit emissions of solvents from some industrial processes. The Solvent Emission Directive (SED) 1999/13/EC limits the emissions of solvent, not their use. The Directive covers only industrial solvent application – it does not cover domestic use. It covers only those industries specifically listed in the SED, including wood coating, lamination and impregnation. Stricter rules obligate researchers and producers looking for new solutions, alternative environmentally friendly products, for example using

- solvents that have a lower environmental impact – less photo-reactive (low VOC),
- silicone or UV curing technology, coating without solvents (solventless),
- water based products.

Aim of the study

The main goal of this study was to investigate the influence of aqueous solutions of organic substances on structure and properties of pinewood. Pine (*Pinus sylvestris*) was selected as a typical representative of softwood. Only the sapwood of pine was studied. Organic solvents (ethanol, acetone and dimethylformamide) were selected as model substances and representatives of constituents of wood preservative and coating materials.

Wood is a natural composite, which has a hierarchical structure from macro to the molecular scale. Due to the structure of wood, the swelling process has to be studied on three different levels. These are macromolecular (cell wall polymers), microscopic (cell wall) and macroscopic (overall dimensions). The aim of this study was to investigate interaction between pinewood and different liquids on macroscopic and microscopic level. Macroscopic and microscopic level of understanding the wood-liquid interaction is sufficient for many bulk engineering and industrial applications. It can be seen from the literature that there is no accurate data of swelling of wood in binary mixtures, and especially in aqueous solutions of organic substances.

Specific objectives of this study were:

- to determine the swelling values of wood swollen in aqueous solutions with different concentrations;
- to ascertain the influence of liquids on wood cell structure;
- to determine the changes in chemical composition of wood during the swelling process;
- to determine the influence of liquids on mechanical properties, especially the elasticity of wood;
- to investigate the changes in cellulose index of crystallinity to clarify the affect of binary mixtures on the wood structure and properties.

The scheme of this study is presented in Figure 1.

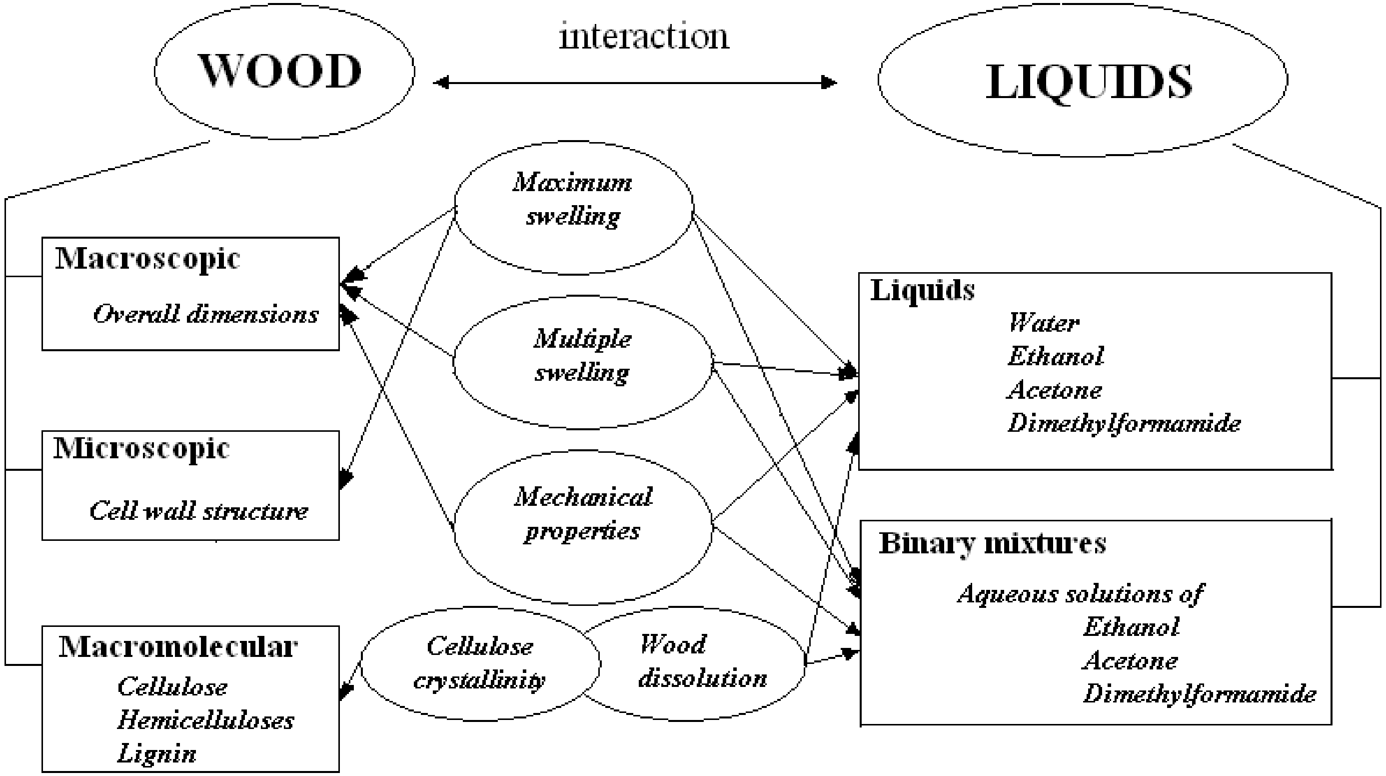

Figure 1. Scheme of the study

1. Swelling of wood

Wood is a hydrophilic material, very sensitive to water and other liquids. The changes in the H-bonding system, caused by the liquids uptake by the cell wall, usually leads to changes in the physical and mechanical properties of wood.

Swelling may be defined as the increase in the dimensions of wood per unit of dimensions of the starting material, accompanying adsorption of an adsorbate, held in naturally formed solid solution. It was suggested that adsorption is a physiochemical process, which involves enormous forces. It is only when the adsorbate is taken up spontaneously, as solid solutions, that cause the dimensions to increase. When an adsorbate is held only on pre-existing surfaces, or within permanently existing pores of a solid, no dimensional changes occur with different moisture content. Therefore, it is necessary for the adsorbate to have a real affinity with the adsorbent for swelling to occur (Morisato et al. 1997, 2002).

It is generally accepted that the competitive process of adsorption by H-bonding, and the breaking of internal hydrogen-bonds among molecules of wood constituents, play the dominant role in the whole swelling process of wood.

As wood is an anisotropic material, the swelling has to be investigated in radial, tangential and longitudinal directions. It is well known that longitudinal swelling of wood is inconsiderable compared to transverse swelling, and even swelling in radial and tangential directions are different (Ishimaru and Adachi 1988, Ishimaru and Maruto 1996, Ishimaru and Iido 2001, Yamamoto et al. 1999, 2001).

1.1. Influence of wood properties on swelling

As a result of extensive investigations it was concluded that the swelling of wood is influenced by the density of the wood, the percentage of late- and earlywood, extractives, the duration and method of drying, the microscopic and macroscopic cracks in the wood (Stamm 1964, Rowell 1984, Mantanis 1994a).

Density/ specific gravity

There has been found a clear correlation between the shrinking and swelling of wood with specific gravity (Stamm 1964)

$$S = f \times g , \qquad (1.1)$$

where S is the total volumetric shrinkage from green to the oven-dry condition on a percentage basis, and f is the fibre saturation point on a percentage volume per unit weight basis, and g is the specific gravity of the wood on a swollen volume basis.

In another research (Mantanis et al. 1995b) it was found that the best predictive model for the maximum tangential swelling of wood in organic liquids is that, which includes three variables – the solvent basicity (*SB*), the solvent molecular volume (*MV*), and the density of wood species (*WD*):

$$\boldsymbol{S = 2.27 + 0.316SB - 0.0426MV + 4.92WD} \qquad (1.2)$$

It should be also noted that the addition of the H-bonding parameter into this statistical model Eq. (1.2) did not significantly improve the fit.

Extractives

In general, removal of extractives has been reported to enhance swelling significantly especially in species, which have a large percentage of extractives (i.e., pines and another conifers). Extractives (terpenes, fats, phenols, fatty acids, tannins, etc.) are not considered to be structural components of wood. Generally, the average percent of the extractives in wood varies from 2 to 10% with the exception of some tropical wood species (20-25%).

Species high in extractives content shrink and swell less, because of the bulking action of the extractives in the cell wall (Stamm 1964).

It was found that the weight losses and the tangential dimensional changes take place in the wood samples after extraction (Rowell 1984). Comparing different extraction methods, the procedure with 80% ethyl alcohol for two hours was selected, because the extractive removal (2-4%) was sufficiently large to be representative of the range of extractives in the wood, but the dimensional changes were minimal. However, it was revealed in the same research that a significant quantity of sugar was removed in the procedure. The sugars were derived primarily from the hemicelluloses in the cell wall, which implies that the cell wall structure had been disrupted in the extraction procedure.

It is evident that the extractives and their removal can considerably influence the rate and maximum swelling of wood. Indeed, the rate of swelling of wood increased considerably after removal of extractives and the maximum equilibrium swelling generally increased on the average by 5-10% (Rowell 1984, Mantanis 1994b).

1.2. Influence of temperature on swelling

Temperature was found to have remarkable effect on wood swelling in water and series of organic solvents (Rowell 1984, Meijer 1996).

Elevating the water temperature above room temperature increased significantly the rate of swelling of wood. The activation energies of the wood swelling in water have been accurately evaluated (Mantanis et al. 1994a).

Some solvents, which did not swell wood at room temperature, were found to swell wood considerably at elevated temperatures. It was concluded that swelling is a bimolecular reaction merely requiring the collision of the solvent molecules with wood. The rate of swelling in organic liquids showed a strong dependence on temperature, which closely obeyed the classical Arhenius equation. Wood (*Scots pine*) swelling activation energies were calculated for a few solvents such as pyridine, acetone, quinoline and pentanol.

1.3. Influence of properties of organic liquids on swelling

The interaction between wood and organic liquids, especially the swelling of wood in organic liquids, has been investigated from various viewpoints over decades. The results of studies have been discussed in terms of the activation energy of swelling, the cohesive energy density, molecular weight, molar volume, the size of the molecule of the liquids (Nayer and Hossfeld 1949, Kajita et al. 1979, Mantanis et al. 1994b, Morisato et al. 1997).

The maximum swelling of wood in organic solvents was reported to be predominantly influenced by three solvent properties, **solvent basicity, molar volume, and hydrogen bonding capability.**

- A correlation was found between the maximum tangential swelling and the solvent donor number. Donor number (DN) was introduced to describe the nucleophilic behaviour or donicity of a particular solvent (**solvent basicity**). The greatest interaction for wood samples occurs with the basic probe, formamide, while lower readings are obtained with the acidic probe, ethylene glycol. This relationship was expected, since wood has an acidic character by nature (Wood pH = 4.0 – 6.0).

- In general, all the liquids, with a **molar volume** greater than 100 ml/mol or with a small hydrogen bonding parameter, caused very little equilibrium swelling.

- The swelling behaviour of wood is fairly predictable from the intensity of the **hydrogen bonding** capability of the swelling solvent. A bimolecular process is most likely, whereby the solvent forms a

> transition state, then collapses to give a molecule of liquid attached by a hydrogen bond of wood. In general, liquids with a strong hydrogen bonding parameter (HB), would be expected to swell wood to the greatest extent.

In many cases, data on swelling in solvents other than water is given relative to the swelling in water, so that the value of water is set at a value of 1, 10, or 100 and all other solvents are reported above or below this value. Some solvents do swell wood better than water due to several factors, including extractive removal, plasticization, softening, or solubilization of one or more of the cell wall polymers (usually lignin or hemicelluloses).

None of the typical solvent properties, such as solubility parameter, dielectric constant, dipole moment, and surface tension, showed any consistent correlation with the maximum swelling of wood

1.4. Swelling of wood in binary mixtures

The presence of water has been detected to influence significantly the swelling of wood in many organic solvents. The enhanced swelling of wood in binary mixtures has been explained from the standpoint of the activity of each constituent, i.e. a positive deviation of the activity of a constituent from the ideal solution means the molecules have a higher secedeability from the cohesion force in the mixture compared to the pure liquid. Thus the constituent has a greater chance to attack adsorption sites responsible for the swelling of wood than that expected in pure concentration.

A few studies (Johns et al. 1974, Ishimaru and Sakai 1988, Guyer and Hossfeld 1990, Sakai and Ishimaru 1992a, 1992b) suggest that some binary mixtures of liquids can produce more swelling than either component alone. This synergistic effect appeared to be particularly notable when water was one of the liquids.

The nature of liquid water and the organization and interaction of water molecules within it are questions that have attracted the interest of chemists for many years. A variety of techniques, including infrared absorption, neutron scattering, and nuclear magnetic resonance, have been used to probe the microscopic structure of water. The information obtained from these theoretical calculations has led to the development of about twenty “models” that attempt to explain the structure and behaviour of water. More recently, computer simulations of various kinds have been employed to explore how well these models are able to predict the observed physical properties of water (Guo et al. 2003). However, the following facts are well established:

- H_2O molecules attract each other through the special type of dipole-dipole interaction known as hydrogen bonding;
- a hydrogen-bonded cluster in which four water molecules are located at the corners of an imaginary tetrahedron is an especially favourable configuration, but
- the molecules undergo rapid thermal motions on a time scale of picoseconds, so the lifetime of any specific clustered configuration will be fleetingly brief.

Understanding the mixing state of the molecular components in alcohol-water solutions is currently a considerable challenge in the area of the physical chemistry and chemical physics of liquid systems. Despite a great deal of effort spanning five decades, no general consensus has been reached concerning the structural properties of liquid alcohols and their solutions with water. Already for the simplest system, pure methanol, contradicting conclusions have been reached even applying the same experimental techniques (Guyer and Hossfeld 1990, Soper and Finney 1993). The early hypothesis of cyclic structures has both been supported and contested.

In water-alcohol mixtures, the interaction through hydrogen bonding should operate with water-water, water-alcohol, and alcohol-alcohol molecules (Guo et al. 2002, 2004, Dixit et al. 2002, Bowron and Moreno 2003, Nose et al. 2005).

The properties of alcohol-water mixtures depend strongly on the alcohol concentration because of the bifunctional nature of the solute. In the low alcohol concentration region the trends in the thermodynamic properties, shown by the series methanol, ethanol, propanol, and tertiary butanol, suggest that the interaction between the alkyl groups and water is more relevant, and that it is related to the structural characteristics of liquid water. The low concentration of alcohol is seen as contributing to enhanced H-bonding in water. The average water structure in the alcohol-water mixtures is not significantly different from pure water, although it is possible that any very small changes could have been masked by the $OH_{alcohol}$-H_2O interaction.

Spectral studies of aqueous methanol solutions in the near infra-red region have shown that pure methanol is almost entirely associated in cycle tetramers. As water is added to methanol, the water molecules are believed to form H-bonds with the polar portion of methanol, and thereby alter the water structure. In dilute solutions of water in methanol, it was shown that the strength of the water-methanol H-bond was greater than water-water H-bond (Guyer and Hossfeld 1990).

Reports in the literature, concerning aqueous alcohol solutions, point to two concentration ranges of interest:

1) in dilute solutions of alcohol in water, the alcohol appears to act as a structure former by increasing the ordering of the water molecules around them;
2) in dilute solutions of water in alcohol, the evidence suggests that the water may cause a disruption of the alcohol aggregates with the formation of water-alcohol association complexes, which again reduces the concentration of monomeric, or free, water in a solution that is available for reaction with wood substrate.

Neutron diffraction data provides structure information concerned with water cages around hydrophobic headgroups in solution. The theory, that describes the anomalous thermodynamics of water-alcohol systems to “water iceberg formation”, has been shown to be incorrect. The recent neutron data show that both water and methanol retain their hydrogen network to some degree, and suggest that the lower-than-expected increase of entropy is most likely due to incomplete mixing of water and methanol at molecular level. It was not possible to establish from one single study whether or not this incomplete mixing on the microscopic scale was unique to the methanol-water system; however, other work on concentrated tertiary butanol-water solution provides support to the idea that this phenomenon may be ubiquitous to the alcohol-water system.

However, conclusions drawn from the recent experimental studies of alcohol-water mixtures are conflicting (Soper and Finney 1993, Turner and Soper 1994, Dixit et al. 2002, Guo et al. 2002, 2003, Bowron and Moreno 2003).

Binary systems were found to behave strangely and, therefore, cannot necessarily be the basis for generalisation with respect to other wood species and liquids. It can be concluded that the ability of a liquid to swell the wood cell wall, is dependent not only on the interactions of the liquid with the cell wall but also on interactions of the liquid with primary, secondary bound, free water adsorbed by wood and the bulk water/liquid retained in the cell lumen.

2. Swelling of cell wall

Numerous studies have introduced several suggestions as possible mechanisms by which water or water vapour is taken up by the cell walls in wood. These include the surface adsorption theory, the capillary condensation theory, the solid solution theory, polarisation theory, a two-phase mechanism and the cluster theory (Stamm 1964, Banks and Leavy1980, Hartley et al. 1992).

In general shrinkage and swelling of wood is caused by the loss or gain of liquid molecules in the cell walls, which are hydrogen bonded to adsorption sites of cellulose molecules, that make up the microfibrils in wood.

In the swelling of wood in liquids with small molecular sizes and functional groups capable of H-bonding, such as water, the adsorption is thought to occur in the following order:

1) the adsorbate molecules adsorb onto free hydroxyl groups in the pre-existing cavity and/or surface hydroxyl groups loosely bonded to each other in the cell walls, and
2) as the swelling proceeds, the neighbouring H-bonds are broken and new adsorption sites appear, which leads to an increased adsorption

It is generally accepted that the cooperative processes of the adsorption by H-bonding and breaking of internal H-bonds play a dominant role in the whole swelling process of wood. Therefore, the swelling phenomenon of wood can be best understood by separately evaluating the adsorption behaviour of liquids on the pre-swollen and dried wood.

Wood changes dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the accessible cellulose, non-crystalline cellulose, lignin, and surface of crystalline cellulose also have roles to play. Moisture swells the cell wall, which expands until it is saturated with water (fibre saturation point, FSP). Beyond this saturation point, moisture exists as free water in the void structure and does not contribute to further swelling. This process is reversible, and the fibre shrinks as it loses moisture below the FSP (Scaar 1972, Siau 1995, Berry and Roderick 2005).

Cell wall elastic limits

The orientation of the cell wall polymers in the S1 layer determines the extent of swelling of wood in water or other solvent (Rowell 1984). Swelling from the dry state to the water saturation state continues until the cross banding of the cell wall polymers in the S1 layer restricts further swelling. This point is defined as the elastic limit of the cell wall.

2.1. Swelling and dissolution of cellulose

The chemical composition of wood is complex. Wood consists of cellulose, hemicelluloses, lignin and low molecular mass compounds. Cellulose is the main polymeric component of wood cell wall. Cellulose consists of anhydro-D-glucopyranose units linked by β-1, 4-glycosidic bonds to form linear polymeric chains. Cellulose forms partially crystalline microfibrils, which are oriented helically around the cell axis. Hemicelluloses are branched heteropolysaccharides, which consist of different monosaccharide units. Lignin is a complex heterogeneous macromolecule. In wood, the structure of hemicelluloses and lignin is amorphous.

Liquids capable of swelling wood are adsorbed on and in the cell wall by polar functional groups. The hydroxyl groups making up cellulose and hemicelluloses chains are considered to be the main polar functional group found in wood (Stamm 1964, Rowell 1984, Fengel and Wegener 1989, Sjöström 1993).

Liquids that produce significant swelling are those which should be capable of forming H-bonded complexes with the wood molecules (Nayer and Hossfeld 1949, Kajita et al. 1979, Mantanis 1994b, Tanaka et al. 2004).

Swelling

Approximately 40-45% of the dry substance in wood is cellulose; the cellulose is located predominantly in the secondary cell wall. Bundles of cellulose molecules are aggregated together in the form of microfibrils in which highly ordered (crystalline) regions exist with less ordered (amorphous) regions.

Cellulose is insoluble in most solvents because of its crystalline nature; however, both intracrystalline and intercrystalline swelling is possible in certain solvents (Krassig, 1993, Klemm et al. 1998, 2005).

Swelling in aqueous media can occur in the easily accessible regions of cellulose only, or can affect the crystalline regions too. In both cases intermolecular bonds between the polymer chains are broken to a variable extent, but the intermolecular cohesion between the polymer chains is still maintained even in the case of the intracrystalline swelling.

If swelling occurs in the easily accessible regions (intercrystalline swelling), the increase in weight and volume of the sample results from a filling of the pore system by the swelling medium, combined with a rupture of interfibrillar bonds, and from the uptake of a swelling agent.

In the case of intracrystalline swelling, usually an additional increase in lattice dimensions of the crystalline regions takes place, often resulting in an increase of one of the lattice spacing due to a so-called layer lattice reaction of the swelling agent with the cellulose moiety.

Cellulose-water interaction can be understood as a competition of H-bond formation between hydroxyl groups of the polymer and H-bond formation between one OH group of a cellulose chain and a water molecule or a water cluster.

In addition, strong similarities were found between wood and cellulose maximum swelling behaviour in various organic solvents classes.

Dissolution

The dissolution or at least a considerable limited swelling of the cellulose moiety is an indispensable prerequisite for a subsequent controlled cellulose functionalization (Klemm et al. 1998). After a limited swelling, the gross structure of the cellulose sample as a moiety of particles, or fibres, or as a film, is largely maintained despite an increase in sample volume due to uptake of swelling agent and significant changes of the physical properties. On dissolution a transition from a two-phase system to a one-phase system takes place, and the original supramolecular structure of the sample is destroyed.

Despite these differences, the phenomena of swelling and dissolution have many common features, especially from the physiochemical point of view: in both cases the intermolecular forces between the macromolecules are overcome by an in summa stronger interaction leading to a loosening or even an elimination of cellulose supramolecular structure. Both the processes of swelling and dissolution serve the purpose of enhancing the accessibility of the cellulosic hydroxyl groups for a subsequent reaction. Furthermore, there is no clear cut borderline between swelling and dissolution process, and the same system can act either as a swelling agent or as a solvent depending on the DP and the structure of the cellulose sample (Krassig et al. 1993, Sturcova et al. 2004).

With regard to cellulose functionalization, it should be mentioned that swelling and dissolution may occur simultaneously during the intended reaction in the reaction medium. But more often in the organic chemistry of cellulose, a two-step process is preferred, with the first step consisting of a so-called activation, i.e. loosening of cellulose physical structure by swelling, followed by the second step, i.e. the intended reaction, proceeding either with the swollen sample in a heterogeneous manner, or together with dissolution.

2.2. Determination of cellulose crystallinity

To determine the cellulose crystallinity in wood fibres, accurate determination of the cellulose content is needed, as cellulose is expected to be the only crystalline constituent.

X-ray powder diffraction is an obvious method to study the wood sample crystallinity due to the diffraction peaks from cellulose crystals (Paakkari and Serimaa 1984, Nishiyama et al. 2002, 2003, Andersson et al. 2003, 2004, Abe and Yamamoto 2005, Garvey et al. 2005). However, all materials give rise to X-ray scattering, also the amorphous part of a sample. Hemicelluloses and lignin have been measured to have diffractograms similar to amorphous cellulose giving wide unspecific peaks.

Determination of the sample crystallinity is thus a problem of separating the amorphous from the pure crystalline part of a powder diffraction pattern. With well-crystallized samples, i.e. with large enough crystallites, this is rather simple as such crystallites give sharp diffraction peaks, which can be easily separated from the amorphous background. In the case of cellulose, the crystallites are very small, typically 20-50 Å in diameter, which will cause considerable peak broadening and serious peak overlap. Consequently, the separation of crystalline from amorphous scattering is no longer trivial.

The cellulose crystallinity is defined as 'g crystalline cellulose / 100 g cellulose', and can be calculated as the ratio of the sample crystallinity to the cellulose content of the sample.

There are different methods to assess the crystalline part of cellulose diffraction pattern in order to determine the sample crystallinity:

1) *Segal method*, based on the intensity measured at two points in the diffractogram;
2) *Ruland-Vunk method*, based on a separate measurement of an amorphous standard scaled to the diffraction pattern;
3) *Rietveld refinement method,* based on refinements of the crystal structure, peak parameters and background;
4) *Debye calculation method*, where the crystalline scattering is calculated based on the crystal structure and crystallite size.

3. Mechanical properties of swollen wood

The mechanical properties of wood composites are the reflection of their material organization.

The changes in the H-bonding system, caused by the liquids uptake by the cell wall, usually leads to changes in the physical and mechanical properties of wood (Schneider et al. 1991, Zhou 1991, Kretschmann and Green 1996, Ishimaru and Minase 2001, Ishimaru et al. 2001). It is known that strong relation exists between the strength of the wood and moisture content (MC) below the fibre saturation point (FSP). When the moisture content is above the FSP, the changes in mechanical properties are inconsiderable.

It has long been established that mechanical properties of wood vary in its moisture content (Panshin 1980, Bodig and Jayne 1982, Siau 1995, Obataya 1998). In this regard, it has been reported that the mechanical properties of wood swollen in various organic liquids differ from those swollen to the same degree by moisture; i.e., the modulus of elasticity and rupture of wood swollen in organic liquids are generally higher than those of the wood swollen by moisture. These differences in mechanical properties between organic liquid swollen wood and moisture-swollen wood are attributable to the difference in the number of broken hydrogen bonds between molecules of wood constituents, which are based on the difference in molecular sizes among the liquids, the differences in the adsorptive forces on wood constituents, and the differences in the cohesive forces among the liquid molecules.

It has been reported that the dynamic loss modulus of wood in various swelling states showed a close correlation between the modulus of rupture and explained this results using a simple viscoelastic model in which the mechanical properties of wood in various swelling states were related to the packing effect by the adsorption of the swelling liquids, differences in number of broken hydrogen bonds between the molecules of wood constituents, the cohesion forces of the liquids, the adsorption forces between the liquids and wood, and the temperature dependence of the latter two properties.

4. Materials and methods

4.1 Materials

4.1.1. Wood samples

Sapwood samples of pine (*Pinus sylvestris*) as typical representative of softwood were selected with clear grains and free from defects. The samples were cut from green wood in following forms:

- 20 × 20 × 10 mm (radial × tangential × longitudinal), for the swelling test (altogether 700 specimens)
- 10 × 10 × 200 mm, for the static bending test (altogether 300 specimens)
- 20 × 20 × 30 mm, for the compression strength test (altogether 300 specimens)

All samples were oven dried at 103 °C to constant weight. The density of pinewood varied from 0.40 to 0.55 g/cm^3.

4.1.2. Liquids

Distilled water and organic solvents were used in this study. Organic solvents were selected as representatives of different chemical classes and as model substances in wood coating materials and preservatives. Ethanol (EtOH) is alcohol, i.e. weakly acidic, acetone (Act) is an aprotic ketone and dimethylformamide (DMF) is an aprotic base amine.

The aqueous solutions of organic solvents for swelling tests were prepared in different concentrations (MF 0.1 – 0.9).

4.2. Study methods

4.2.1. Swelling of wood

Samples of pine sapwood were prepared, as described above, for treatment with each liquid - water, ethanol and acetone, aqueous solutions of these solvents and ternary mixtures at different concentrations. All experiments were performed at room temperature. All dimensional measurements were made with a Vernier calliper, accurate to ± 0.05 mm. The oven-dried weights and radial, tangential and longitudinal dimensions were measured as quickly as possible (to avoid humidity uptake from the air) and samples were immediately immersed in the swelling agents and containers were sealed. The swelling of wood in the liquids was determined in sealed containers after 90 days.

The percentage swelling was calculated applying the following equation:

$$Sw = \frac{a_{SD} - a_{ODD}}{a_{ODD}} \times 100, \qquad (4.1)$$

where Sw is the percentage swelling, a_{SD} is the dimension of a swollen sample and a_{ODD} is the dimension of an oven-dried sample.

In order to study the multiple swelling the samples were oven-dried again at 103 °C and placed in the containers for 60 days. This procedure and the measurements described above were repeated three times.

Re-swelling was performed in two different modes. In order to conduct second cycle of swelling on all the samples new solutions were prepared. Selected samples were swelled in same solutions (EtOH 0.5; Act 0.5). In order to perform third cycle of swelling new solutions were prepared.

4.2.2. Microscopy study

Investigation of cell wall structure was carried out with the scanning electron microscope JEOL JSM 840A at the 15 kV. Small sticks from the swelled wood blocks were cut out (3x3x7mm), frozen at the temperature of liquid nitrogen. One end of the stick was cut flat by cryoultramicrotome using water as intermediate filling. The samples were air dried and attached to the stubs with double-sided adhesive tape. Then the samples were coated with the gold by ion sputtering.

4.2.3. Mechanical properties of swollen wood

The static bending test was performed in the tangential direction of wood fibres under the following conditions: span 90 mm of central loading and down-speed of the cross-head 10 mm/min. The tests were stopped when the samples started to break. The bending and compression strength were calculated using conventional methods.

For calculating the bending strength, the following equation was used:

$$\sigma_{bend.st} = \frac{3F_{\max}L}{2bh^2}, \qquad (4.2)$$

where $\sigma_{bend.st.}$ is the bending strength, F is the maximum force, L is the space between two supports, b is the width of the a sample and h is the thickness of a sample.

The compression test was performed in the longitudinal direction of wood with down-speed 10 mm/min. The tests were stopped when the samples started to break. For calculating the compression strength $\sigma_{comp.st.}$, the following equation was used:

$$\sigma_{comp.st.} = \frac{F}{ab}, \qquad (4.3)$$

where a and b are the cross-sectional dimensions of the sample.

4.2.4. Cellulose crystallinity

The most used physical methods for finding cellulose characteristics are: small and wide-angle X-rays diffraction, electron microscopy, IR spectroscopy and more recently nuclear magnetic resonance (NMR) (Paakkari and Serimaa 1984, Fink et al. 1995, Liitiä 2002, Åkerholm et al. 2004). In general, data obtained through a single method, does not lead to accurate information concerning celluloses structure, crystallinity or microfibrals dimensions. Due to this reason many methods or combined methods are preferred.

X-ray diffraction experiments were performed using Bruker D5005 diffractometer at 40KV and 40mA.

The degree of crystallinity of swollen pinewood was determined from the ratio of the integral intensity of crystalline portions to the total intensity of the sample over the range from $2\theta = 7$ to 42. The relative value of crystallinity CrI_R was determined from the crystallinity, where CrI and CrI_0 were the crystallinities of treated and oven-dry wood cellulose, respectively:

$$CrI_R = \frac{CrI}{CrI_0}. \tag{4.4}$$

The lattice spacing (D) was expressed by the conventional Bragg equation as follows:

$$D = \frac{\lambda}{2 \cdot \sin\theta}, \tag{4.5}$$

where D is a lattice spacing, λ is the X-ray wavelength of the incident beam (in this case Cu K_α 0,154 nm), and θ is the Bragg angle.

4.2.5. Liquids study methods

Some liquids were studied after first swelling cycle (90 days) to determine possible wood constituents dissolved into the liquids during swelling process. Following swelling agents were studied: water, ethanol (96%), acetone, DMF, ethanol- water (MF 0.5) and acetone-water (MF 0.5)

Lignin

The amount of dissolved lignin was determined from the UV absorption value at 280 nm with UNICAM 5625 UV-Vis spectrometer. The amount of dissolved lignin was calculated by Lambert-Beer law using the following equation:

$$c = A/(ab), \tag{4.6}$$

where c is the amount of lignin in the solution (g/l), A is the measured absorbance (no units), a is the absorption coefficient (17.8) from literature ($l \times g^{-1} \times cm^{-1}$) and b is the path length of the cuvette (cm).

Carbohydrates

The gas chromatographic (GC) and mass-spectroscopy analysis were performed with Fisous MD 800 Shimadzu.

Traditionally the total hydrolysis of carbohydrates was done by aqueous mineral acid solutions. The method is convenient when analyzing the neutral monosaccharide composition of carbohydrates. Also it is possible to determine the native uronic acid groups of polysaccharides with the methanolysis-GC method.

The determination of carbohydrates was performed by methanolysis and gaschromatography. This method is used to determine the amount and composition of carbohydrates, present mainly in hemicelluloses and pectins. Crystalline cellulose is resistant towards this acidolysis, which is the reason that limits the utility to some extent. It is also not possible to avoid some degradation of uronic acids, although the degradation occurs to a reasonable degree (Holmbom and Örså, 1993).

The acidolysis was performed with 2M solution of HCl in anhydrous methanol. The methyl glycoside esters of the monosaccharides were then analysed by GC as their per(trimethylsilylated) (TMS) derivates.

5. Results and discussion

5.1. Swelling of wood in binary mixtures (Papers I, II)

The use of binary solutions leads to a three-component system – liquid 1, liquid 2 and the cell wall. Thus it is more difficult to understand the interaction between the binary solutions and wood. Swelling in organic solvent-water mixtures is substantiated to discuss from three different aspects: swelling in water, swelling in organic liquids, and swelling in binary mixtures.

Swelling of wood in water has been investigated extensively from various standpoints. Swelling in organic solvents has also been studied for a long time, but compared to the works of swelling in water, the results have been more indistinct and sometimes contradictory. The first problem in many researches dealing with swelling in organic liquids has been to determine the "pureness" of a solvent – is it really anhydrous or includes water? It has been proved that the presence of water in liquids changes tremendously the swelling values (Hossfeld, 1972, Guyer and Hossfeld 1990).

In general the correlation between wood swelling and liquid properties is not always clear, it is generally accepted that the swelling of wood involves competitive processes of the adsorption by hydrogen bonding, and the scission of internal H-bonds between the amorphous molecules of wood constituents; therefore it depends on the H-bonding properties of a liquid (Mantanis 1994a, 1995c, Bochek 2003).

Organic solvents used in this study were selected as representatives of different chemical classes (except two alcohols) and have different properties, such as molecular weight, molar volume, dipole moment, dielectric constant, solubility parameter, hydrogen bonding parameter, and basicity.

It is necessary to specify that the purpose of this study was not to make generalizations for all wood species and organic solvents. The earlier attempts of several researches have been unsuccessful and therefore, it is reasonable to discuss separately the influence of every liquid (also binary mixtures) to the wood.

It has been established that wood swelling in organic liquids is most affected by three liquid parameters – hydrogen bonding capability, solvent basicity and molar volume. From this aspect all solvents have good "credit" as swelling agents.

It is accepted that organic solvents are divided into five groups by their swelling ability (Mantanis et al 1994b). Water and ethanol belong to class I, acetone and dimethylformamide to class II. All swelling agents used in this study have low molar volume and high hydrogen bonding parameter with the exception of the acetone (medium hydrogen bonding parameter).

Comparing swelling values of pure liquids wood swells in the DMF more than in water, contrarily to alcohols and acetone (Figs. 5.1 and 5.2). These results are in accordance with other researches (Neyer 1949, Stamm 1964, Mantanis et al. 1994b). It is known that liquids that produce significant swelling are those, which should be capable of forming H-bonded complexes with wood molecules.

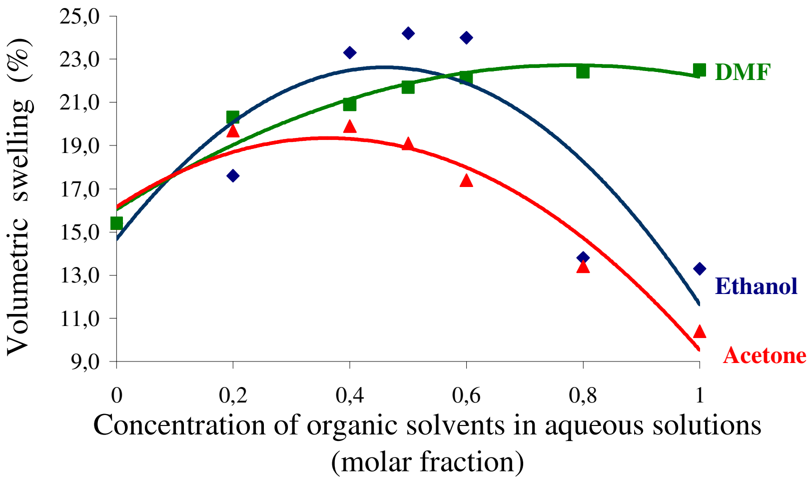

Figure 5.1. Volumetric swelling of pinewood in aqueous solutions

Interaction between wood and binary alcohol-water systems have been discussed based on anomalous properties of these systems (Guyer and Hossfeld 1990, Sakai and Ishimaru 1992), especially on the assumption of non-idealites of binary mixtures. It must be noted that the results of this study will be discussed in the context of reports of other works relating to the structured nature of water-solvents binary systems (Dixit et al. 2002, Guo et al. 2002, 2004, Bowron and Moreno 2003, Nose 2005).

Swelling of wood in the DMF-water mixtures differs from others mixtures used in current study. The maximum swelling values increased with increasing the concentration of the DMF in mixtures (Fig. 5.1). Already at the low concentration of the DMF (MF 0.2) the swelling values were remarkably higher than in water. Dimethylformamide is probably the dominant constituent in binary mixtures with water responsible for wood swelling. It is also known that the rate of swelling in the DMF is faster than in water (Mantanis 1994b).

Some similarities exist between the swelling behaviour in alcohols and acetone, but the influence of them on the wood structure must be discussed separately because of the different structure of each organic solvent.

Swelling of wood in alcohol-water mixtures, especially in methanol-water mixtures, has been more investigated topic compared to the other binary mixtures (Guyer and Hossfeld 1990, Soper 1993, Meijer 1996, O’Leary 2001). Also the structure of alcohol aqueous solutions have been investigated applying various techniques and methods. Despite a great deal of effort spanning four decades, no general consensus has been reached concerning the structural properties of liquid alcohols and their solutions with water.

The eccentricities of aqueous solutions are closely tied to the structure and dynamics of a liquid. For instance, the dynamics of water is slowed down markedly as a solute is added, as manifested by variety of dynamical measures. For instance, the diffusion coefficients and the electrical behaviour of water all became more sluggish upon mixing.

Generally in water-alcohol mixtures, the interaction through H-bonding should operate with water-water, water-alcohol, and alcohol-alcohol molecules (Dixit 2002, Guo et al. 2002, Bowron and Moreno 2003).

As seen from the Figure 5.1 some binary mixtures of alcohol and acetone produce more swelling than either component alone. The swelling values depend on the concentration of mixtures.

Swelling of wood depends on the amount of water in alcohol-water binary mixtures. Reports in the literature concerning aqueous alcohol solutions point out two concentration ranges of interest in interpreting the results of this study. First, in dilute solutions of alcohol in water, the alcohol appears to act as a structure former by increasing the ordering of the water molecules around them. This tends to shift the equilibrium to one with higher concentration of structured water and a lower concentration of monomeric water. And second, in dilute solutions of water in alcohol, the evidence suggests that the water may cause a disruption of the alcohol aggregates with the formation of water–alcohol association complexes, which again reduces the concentration of monomeric, or free water, water in solution that is available for reaction with wood substances (Dixit 2002, Guo et al. 2002, 2003).

Binary mixtures with concentration of alcohol 0.1-0.6 produce hyperswelling of wood. The greatest value of swelling was observed in ethanol-water mixture (MF 0.5), volumetric swelling 24.2% and tangential swelling 12.9%. The volumetric swelling in water was 15.4% and in ethanol 13.3%.

Wood swells in some binary mixtures (MF of alcohol 0.8-0.9) less than in water, but still more than in pure solvents. The presence of water in alcohol-water and acetone-water binary mixtures acts probably as a promoter for the swelling process

The swelling of wood in binary solutions of water and alcohol is dependent upon binary solution composition, and it can be a very slow process. The degree of swelling of wood by the binary system appears to result from the competition between alcohol and wood for water. This suggests that wood swelling may be largely controlled by the free or unassimilated water in the system.

The transverse swelling anisotropy in wood was confirmed with this study. The ratio between tangential and radial swelling was approximately 2:1. The factors, considered to be of primary importance for transverse swelling anisotropy, are interaction between earlywood and latewood, restriction of radial swelling by ray tissues, differences in microfibral orientation in the tangential and radial cell walls, differences in chemical composition in tangential and radial cell walls, and differences in the sum of cell wall thicknesses in the tangential and radial directions. The volumetric swelling curves were similar to those, obtained from the tangential and radial swelling, which leads to the conclusion that the synergistic effect emerges in both transverse directions.

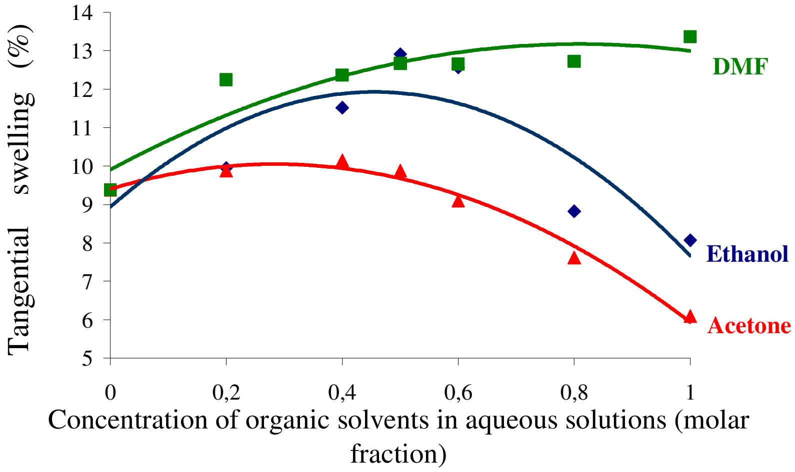

Figure 5.2. Tangential swelling of pinewood in aqueous solutions

Longitudinal swelling of pinewood was less than 1% and therefore it can be neglected.

Binary systems were found to behave strangely and therefore, cannot necessarily be the basis for generalisations with respect to other wood species and liquids. The ability of a liquid to swell the wood cell wall is dependent not only on the interactions of the liquid with the cell wall, but also with the interactions of fluid with primary, secondary bound, free water absorbed by wood, and the bulk water/liquid retained in the cell lumen.

The swelling of wood is closely related to the dissolution of wood matter. In principal the wood matter is not easily subjected to the impact of neutral organic solvents at normal temperature, or even to the impact of cold water (Sjöström 1993, Oguchi et al. 1995). These solvents only excrete a part of extractives. In bulk wood the reaction occurs very slowly compared to the milled wood, where the specific area of the reaction is much larger.

According to the literature neutral organic solvents do not have significant effect on wood (Fengel and Wegener 1989) up to 100 °C. Ethanol has a noticeable degradable effect on lignin only at temperatures above 150 °C dissolving considerable part of it. The mixtures of water-alcohol have more severe effect on lignin solubility. The swelling of wood in ethanol (96%) without any rising of temperature already caused the weakening of bonds between the CML and S1 and the detachment of cells due to the forces during the sectioning of samples (Fig. 5.3).

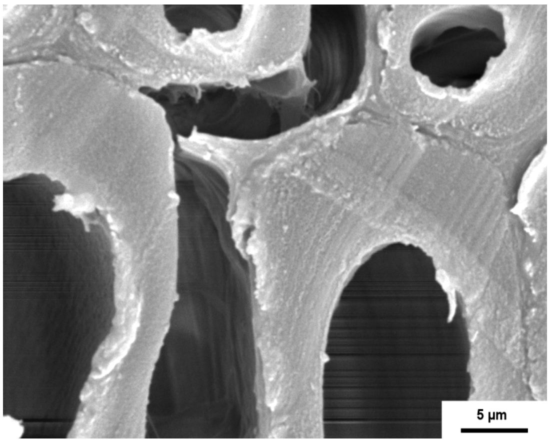

Figure 5.3. The SEM micrograph of the cross section of pinewood swelled in ethanol (96%)

The swelling of wood in ethanol-water mixtures has a dramatic effect on wood structure. The wood cells (Figs. 5.4 and 5.5) were separated from each other and the liberated CML was hanging between the detached cells.

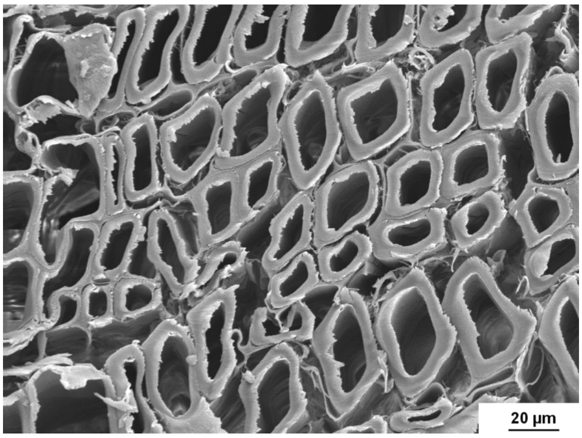

Figure 5.4. The SEM micrograph of the cross section of pinewood swelled in ethanol-water (MF 0.5)

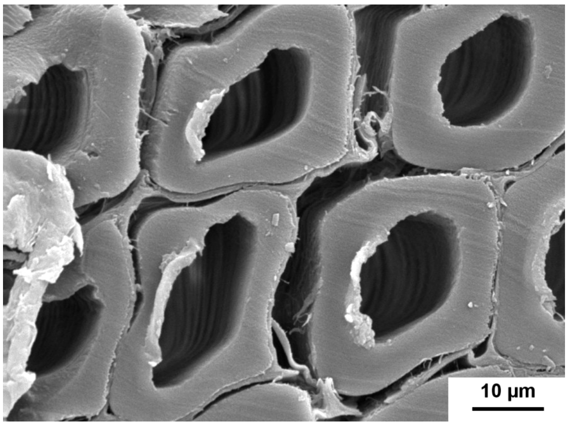

Figure 5.5. The SEM micrograph of the cross section of pinewood swelled in ethanol-water (MF 0.5)

The ethanol-water mixture dissolved a part of lignin from the CML and released individual cells at sectioning. The shape of cells was distorted, indicating the decay in wood cell wall rigidity and the mass loss of the whole cell walls.

It is known that acetone is better solvent for separated lignin than ethanol, especially for the high molecular fragments. One of the factors in swelling of lignin in solvents is the ability of the solvent to generate hydrogen bonds.

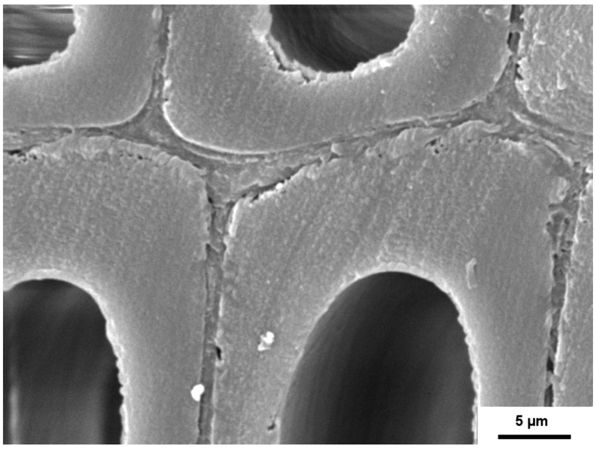

Figure 5.6. The SEM micrograph of the cross section of pinewood swelled in acetone

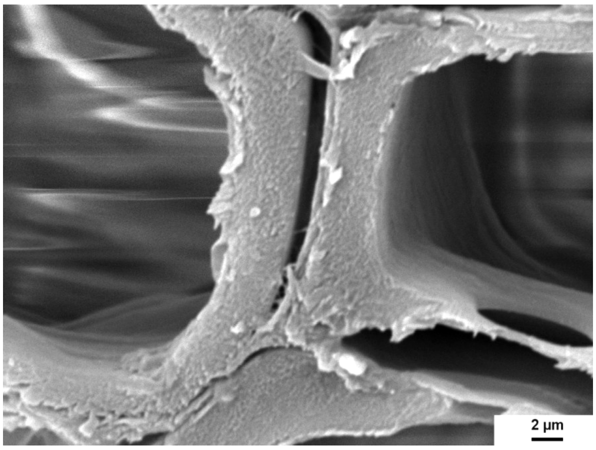

Figure 5.7. The SEM micrograph of the cross section of pinewood swelled in acetone – water (MF 0.5)

As it is seen from the Figures 5.6 and 5.7, acetone and acetone-water mixture have a very mild effect on the cell wall structure, and its bonding to the CML. Here the lignin, sensitive to the acetone, is not directly accessible and the water does not play the role of preliminary swelling.

The DMF has an interesting and different from previous solvents influence on the cell wall layers and CML. In the Figure 5.8 it is visible that swelling in the DMF opened up the location of the primary wall layer and S3 layer.

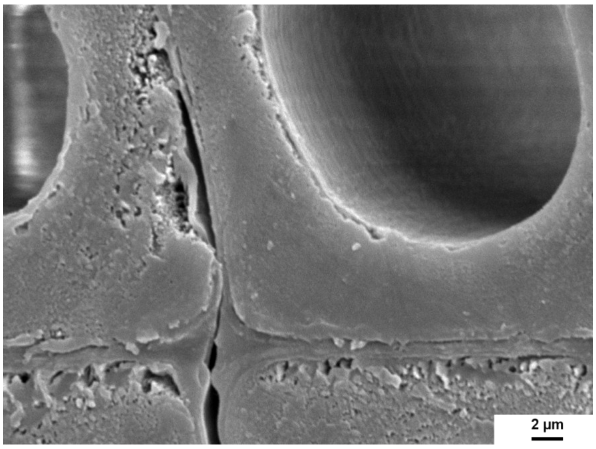

Figure 5.8. The SEM micrograph of the cross section of pinewood swelled in DMF

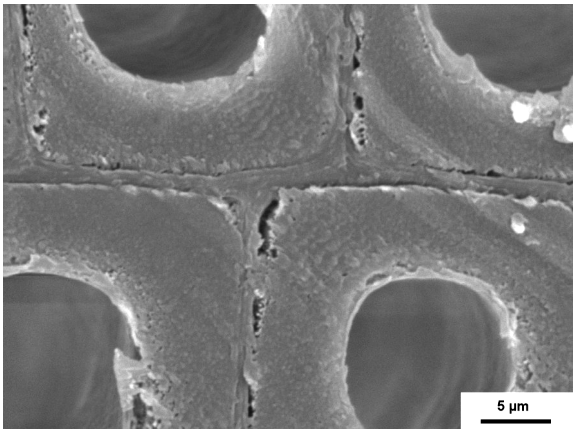

Figure 5.9. The SEM micrograph of the cross section of pinewood swelled in the DMF – water (MF 0.5)

The DMF is known as a solvent for both lignin and cellulose. There is no substantial difference in the influence on the cell structure between the pure DMF and its mixture with water (Figs. 5.8 and 5.9).

5.2. Multiple swelling of wood (Paper II)

From the view point of re-swelling it is equally essential which solutions are applied during the subsequent cycles. In current research for every cycle of swelling (altogether 3 drying-swelling cycles) in ethanol-water and acetone-water mixtures new solutions were prepared. For comparative tests some specimens were swollen in the same mixtures.

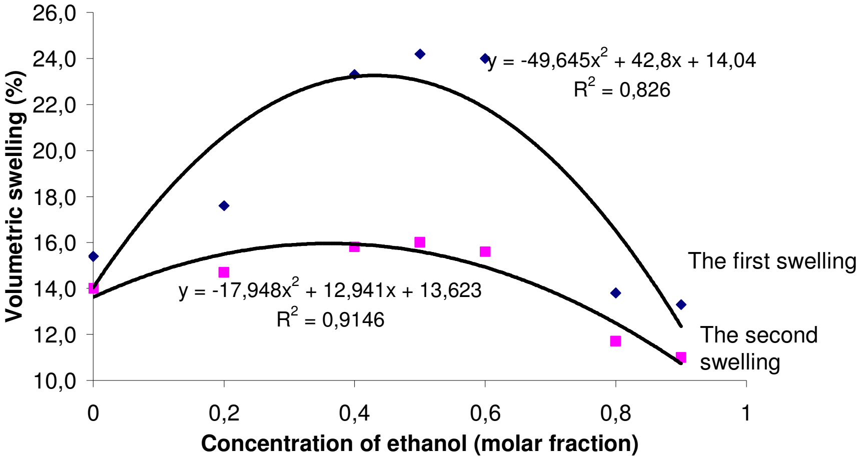

Figure 5.10. Repeated swelling of pine sapwood in aqueous solutions of ethanol (new solutions)

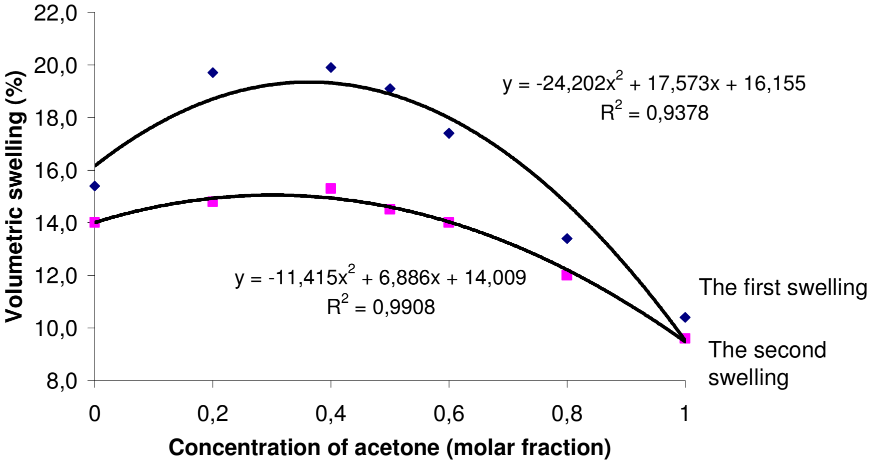

Figure 5.11. Repeated swelling of pine sapwood in aqueous solutions of acetone (new solutions)

Noticeable damping in swelling values occurred already after the second swelling cycle, especially in the case of aqueous solutions of ethanol (MF 0.4-0.6) and acetone (MF 0.2-0.5) as seen in Figures 5.10 and 5.11.

The overall dimensions of specimens after drying, followed by swelling, were higher than the initial and previous one (Fig. 5.12). The behaviour of wood in ethanol and acetone was quite similar. Most substantial changes occurred in aqueous solutions of both solvents (MF 0.5) and least significant changes in pure solvents. After the first cycle of swelling in ethanol aqueous solution (MF 0.5) and drying absolutely dry the measurements of samples were 3% larger and after second cycle 5% larger compared to their initial values. The values with acetone aqueous solution (MF 0.5) were respectively 2% and 3%.

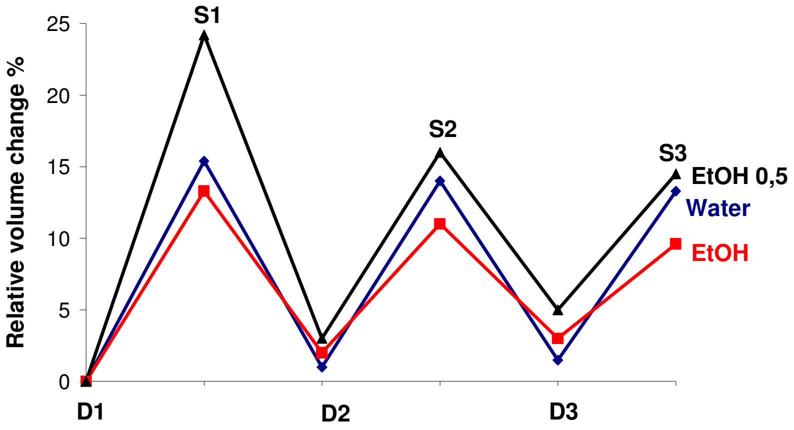

Figure 5.12. Cyclic swelling of pinewood in water, ethanol and ethanol aqueous solutions (MF of ethanol 0.5), where S1, S2, S3 are the swelling cycles and D1, D2 and D3 the drying cycles

If re-swelling caused the measurements of samples to enlarge after every swelling-drying cycle in absolutely dry state, reverse phenomenon occurred with wood mass. After swelling wood in water, the mass in absolutely dry state (so called initial mass) remained stable also after consecutive swelling-drying cycles. Changes in wood initial mass occurred after swelling in ethanol and acetone and their aqueous solutions. Swelling in ethanol and acetone caused the mass of absolutely dry wood to decrease 2-4% after first swelling-drying cycle. In case of acetone and ethanol aqueous solutions the change in mass was respectively 3-5%.

The comparative tests in new and same liquids showed considerable differences in maximum swelling values after 90 days of swelling. The data is presented in Table 5.1. It is obvious, that using the same solutions in re-swelling caused the values to decrease about 50% compared to the values, which had been achieved after swelling in new solution (Table 5.1).

Table 5.1. Tangential swelling after second cycle

	Tangential swelling, %	
	New mixture	Same mixture
Ethanol	3.6	1.9
Ethanol-water (MF 0.5)	5.3	2.5
Acetone	3.9	1.5
Acetone-water (MF 0.5)	4.9	1.8

The results of comparative tests results indicated once more to the changes in both, wood and liquids structure.

In Figure 5.13 it is visible that in pure ethanol (96%) the latewood cells are so tremendously swelled, that the normal matrix of cells has been completely distorted. The single swelling in ethanol did not generate a similar effect (see Fig. 5.3).

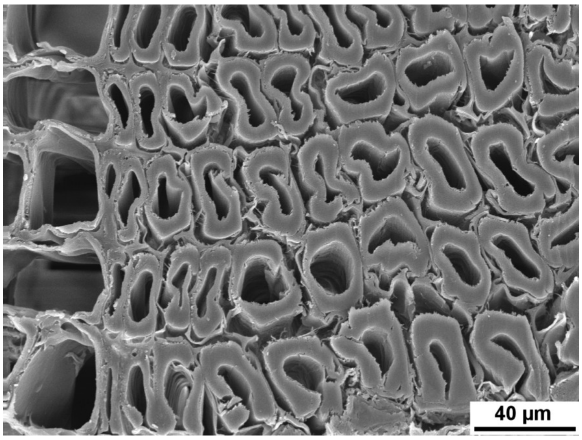

Figure 5.13. The SEM micrograph of the cross section of pinewood swelled twice in ethanol (96%)

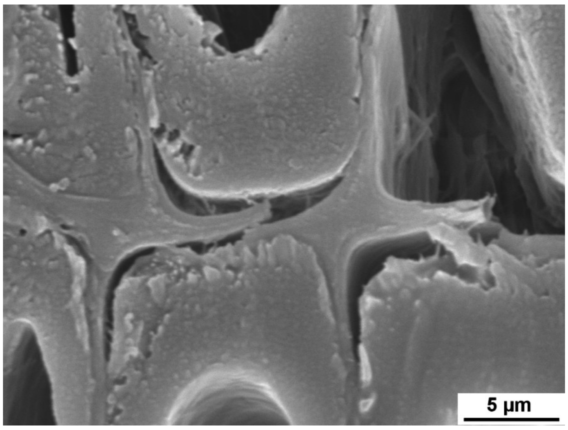

Figure 5.14. The SEM micrograph of the cross section of pinewood swelled twice in ethanol (96%)

The close view of the cross-section of latewood cells swelled in pure ethanol showed the deliberation and disruption of the CML (Fig. 5.14). This evidence is essentially different from the first swelling of pine in pure ethanol. Presumably this effect was caused by the excess water (4%) in ethanol that stimulated this remarkable swelling of wood cells.

The last statement was additionally confirmed investigating the cross section of the pine wood cells after multiple swelling in the mixture of ethanol-water (Figs. 5.15 and 5.16).

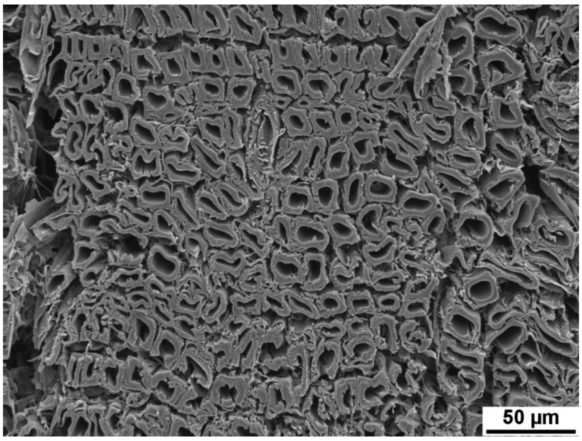

Figure 5.15. The SEM micrograph of the cross section of pinewood swelled twice in ethanol – water (MF 0.5)

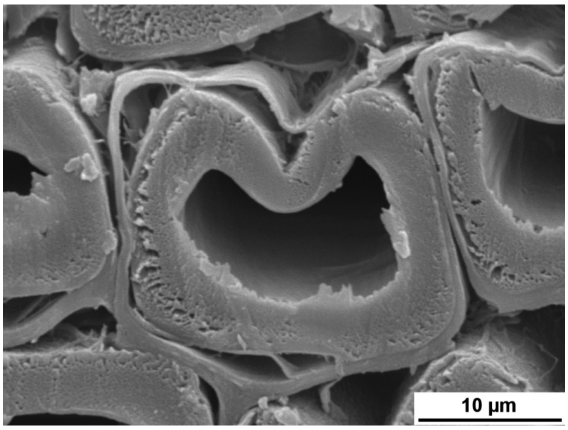

Figure 5.16. The SEM micrograph of the cross section of pinewood swelled twice in ethanol – water (MF 0.5)

In Figure 5.16 the disruption of wood architecture due to the swelling in ethanol-water is very similar to Figure 5.15. Only the swelling rate is more expressive and the cell walls more distended. Therefore the influence of this small amount of water (4%) in ethanol was revealed only after the multiple swelling.

Additionally the close-up view of the cell apexes showed deeper impact of the water in ethanol-water mixture. In Figure 5.16 it is visible that the CML is unbroken, but mostly separated from the cell walls.

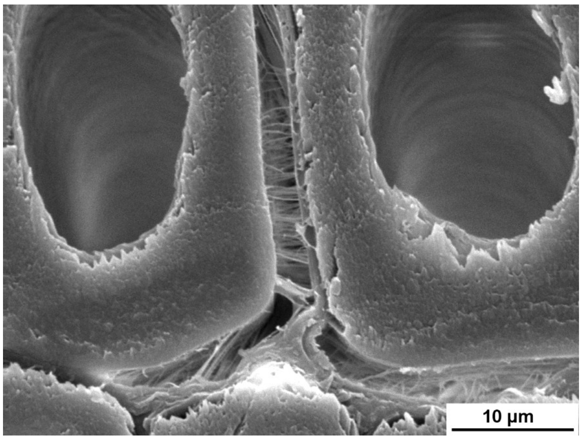

Figure 5.17. The SEM micrograph of the cross section of pinewood swelled twice in acetone

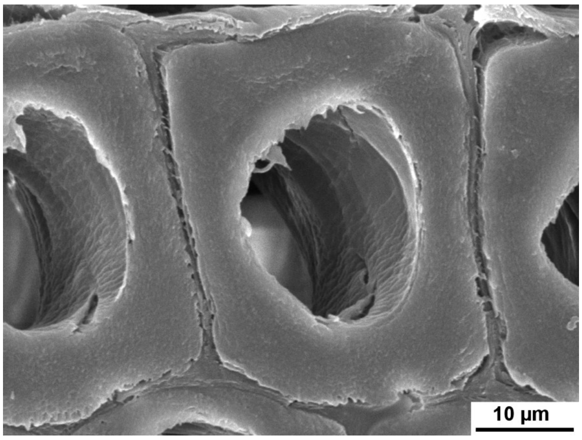

Figure 5.18. The SEM micrograph of the cross section of pinewood swelled twice in acetone – water

Acetone is known to be a better solvent for separated lignin than ethanol, especially for the high molecular fragments. Here lignin is not directly affected by the acetone. As it is seen from Figure 5.17 acetone has a mild effect on the cell wall structure and it's bonding to the CML. After the mechanical damage caused by the movement of cutting knife edge, the fibrillar bonds between wood cell wall and the CML were still present.

Considerable effect, compared to the single swelling, appeared during the multiple swelling of the pinewood in the mixture of acetone-water (Fig. 5.18). When single swelling did not reveal any substantial change in the wood structure, the multiple swelling caused noticeable swelling of the S3 layer of the cell wall. Consequently, during the multiple swelling the water performed the role of preliminary swelling of S3 and opened lignin upon the impact of acetone.

5.3. Dissolution of wood matter during swelling

Measurements on macroscopic level and investigations of wood cell structure on microscopic level led to the necessity of determination of wood matter dissolution during the swelling process.

Unextracted wood was used for swelling experiments in this study. The amount of extractives in wood was determined with a separate test and it was approximately 2.2 %. Extractives (usually comprise 1-5% of the wood) are non-cell wall components and can be removed using various solvents, e.g. acetone, ethanol, water (Rowell 1984, Sjöström 1993).

The analyses of liquids after 90 days of swelling identified small amount of resin acids in swelling agents. Acetone and the DMF removed more extractives compared to others liquids. The amount of resin acids determined with GC MS was approximately 0.17 g/l in acetone as well in the DMF. Ethanol and ethanol-water mixtures removed small amount of resin acids, correspondingly 0.07 and 0.03 g/l. The influence of acetone-water mixture was inconsiderable – 0.008 g/l and the amount of resin acids in water was 0. In general, removal of extractives has been reported to enhance swelling significantly especially in species, which have a large percentage of extractives. It was found for example that, in case of wood swelling in acetone and water, an increase in the amount of extractives in wood generally causes a decrease in the wood swelling activation energy (Ea). On the other hand, no correlation has been found between Ea and the content of extractives in the case of wood swelling in ethanol (Mantanis 1994a). There is no direct correlation between swelling values and the amount of removed extractives during swelling process in current research. Apparently the removal of extractives by strong solvents as acetone and dimethylformamide can contribute to the increase of swelling values in small range, but it definitely does not explain the hyperswelling in binary mixtures.

As the swelling of wood in organic solvents is closely related to the dissolution of wood matter, it is important to determine also the extent of wood constituents dissolved into the liquids after swelling process. It is obvious that during the swelling process wood samples lost some weight, which was determined after the first swelling-drying cycle by weighing the samples. Also the SEM micrographs showed changes in cell wall structure

Using organic solvents leads to the removing of wood constituents and extractives from the wood samples. It is reasoned that strong solvents as acetone, dimethylformamide, and also ethanol have greater affect on the cell wall structure than water.

Acetone and the DMF dissolved more lignin compared to other liquids (Fig. 5.19). The amount of lignin determined by UV absorption spectroscopy was in acetone 3.31 g/l and in the DMF 2.33 g/l. The quantity of lignin dissolved by the other liquids was considerably less (< 0.5 g/l).

It appears that the sugars were derived primarily from the hemicelluloses in the cell wall, which also implies that the cell wall has been somewhat disrupted (Chapter 5.1) in the swelling process. Thus the whole internal structure of the cell wall probably disrupted, the network of secondary bonds decreased, and the overall cell structure was in a more loosely bonded state.

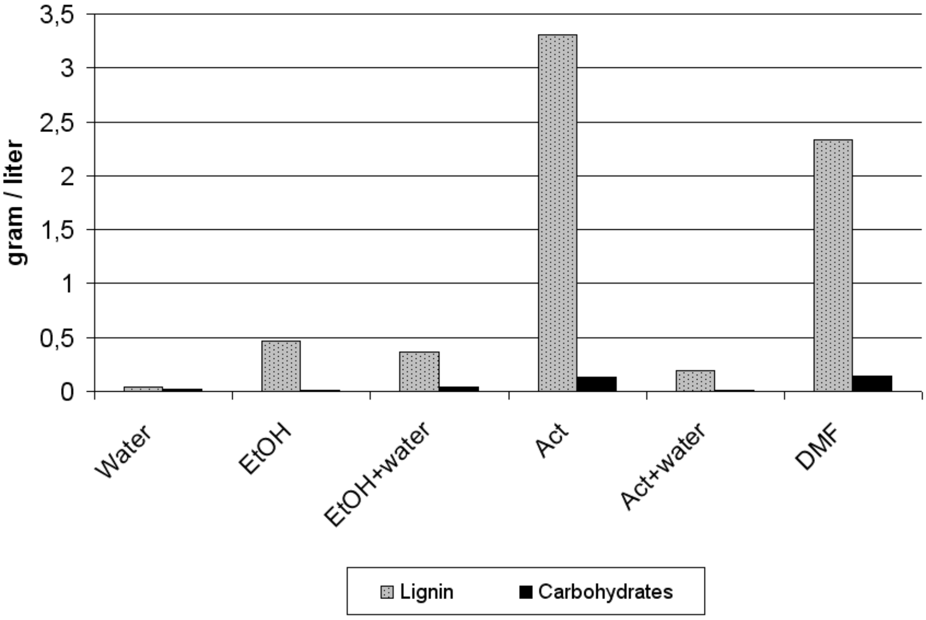

Figure 5.19. The distribution of wood constituents in liquids

Very small quantities of carbohydrates were also detected in liquids. It is obvious that used liquids can not affect cellulose and hemicelluloses in wood cell at the room temperature. The SEM micrographs showed the same trend.

5.4. Mechanical properties of swollen wood (Paper III)

The fibrous nature of wood strongly influences its mechanical properties. It is well known that changes in the moisture content below the FSP have very strong influence on the strength properties of wood (Scaar 1972, Siau 1995). When the MC is above the FSP, the changes in mechanical properties are inconsiderable.

The goal of the study was not to determine the absolute values of mechanical properties, but to compare the influence of different liquids on the strength of wood. Therefore all experiments were carried out in the same conditions. The influence of different organic liquids on mechanical properties of wood, especially in the maximum saturated condition of wood, would give additional information for clarifying the phenomenon of hyperswelling.

Both, compression strength along the grain and static bending strength in tangential direction of swollen pine sapwood appeared to be strongly related to the swelling of wood. As seen from the Figure 5.20 the presence of water in acetone and ethanol aqueous solutions had significant influence on the strength properties of wood. The difference of strength properties of wood swollen in these liquids is small and differs significantly from values given by acetone and ethanol (96%).

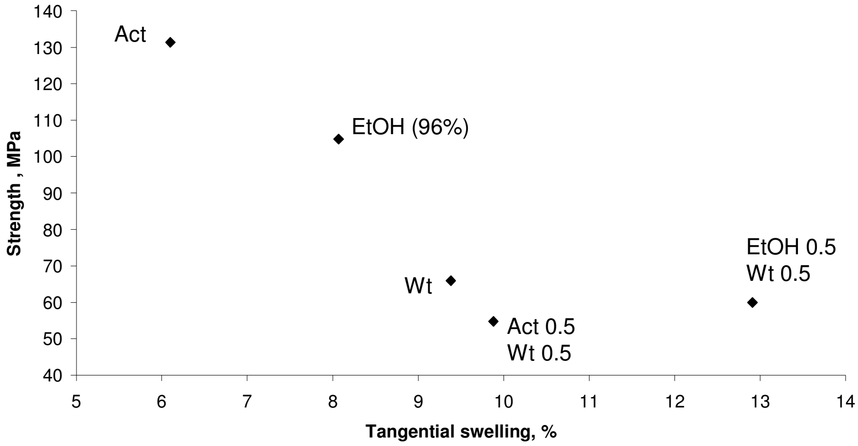

Figure 5.20. Bending strength in tangential direction as a function of the percentage of swelling and of the liquid

The deflection in the static bending test was also measured (Fig. 5.21). A strong correlation existed between the tangential swelling of wood and its deflection. The biggest deflection was caused by ethanol-water mixture (MF 0.5) and had therefore better elastic properties compared to the wood, swollen in other liquids used in this study. Microscopy study showed that ethanol-water mixtures had great influence on wood structure. The wood cells were separated from each other and the liberated CML was hanging between the detached cells (Chapter 5.1).

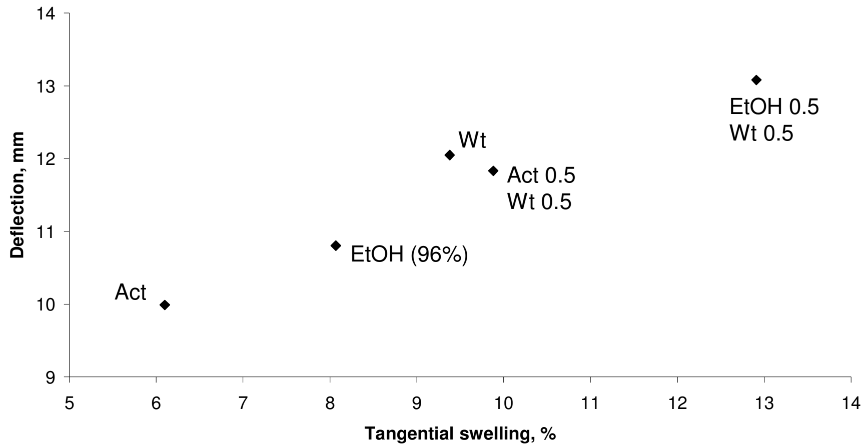

Figure 5.21. Deflection as a function of the percentage of tangential swelling and of the liquid

5.5. Structure of cellulose after swelling

Wood cell wall is a multilayered web of hydrogen-bonded semicrystalline composites. The constituents of wood fibres are essentially amorphous, except cellulose, which consists of both amorphous and crystalline regions. Wide angle X-ray diffraction reveals that the diffraction from solid wood is a combination of size and strain broadened Bragg peaks from cellulose I crystals superimposed over an amorphous background.

To determine the cellulose crystallinity in wood, it is necessary to take into consideration the impact of the whole wood material, as it gives the rise to scattering of the X-rays, and modifies the shape of diffraction pattern. Equally important factor is the orientation of solid wood sample towards the X-ray beam. Therefore, to extract the information on cellulose crystallinity from the diffraction pattern, it requires proper differentiation of the non-crystalline part of the sample.

In some works (Andersson et al 2004, Thygesen et al. 2005) the hemicelluloses and sulphate lignin have been considered as a reasonable measure for the amorphous part of the wood material, to be accordingly scaled down and fitted to the measured X-ray pattern. In this work standard Klason lignin was prepared using the same wood source as for swelling experiments.

Swelling of the wood cell wall amorphous matrix should have certain influence on the cellulose unit cell structure, as it is densely packed into this matrix. Crystalline cellulose in not permeable by water, but dry amorphous cellulose absorbs water in considerable extent. Therefore, it could be foreseen that in the process of swelling, when large amount of liquid is transformed into the cell wall, the crystal structure of cellulose could change the dimensions of its unit cell. To take it into account the swelling of the amorphous sample, prepared from Klason lignin, was measured at different swelling durations (Fig. 5.22) and the shift of the diffraction pattern maximum was calculated (Fig.5.23). A distinct change occurred in the shape and maximum location of the diffraction pattern (Fig.5.22) and this was taken into account in the evaluation of index of crystallinity of wood cellulose swollen at different durations.

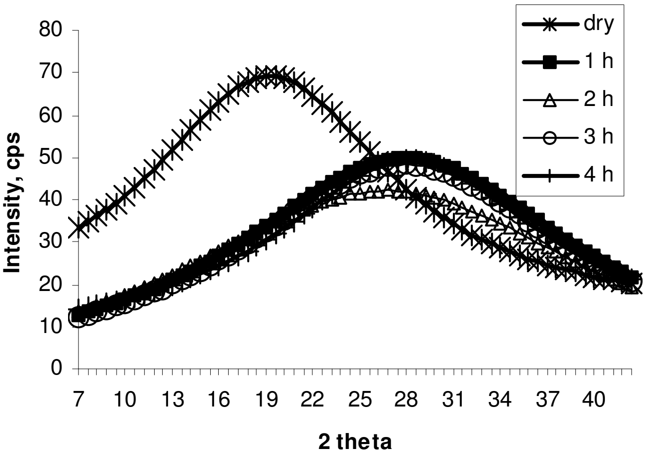

Figure 5.22. Drift of the amorphous model compound (Klason lignin) diffraction pattern shape according to the swelling time of the wood sample.

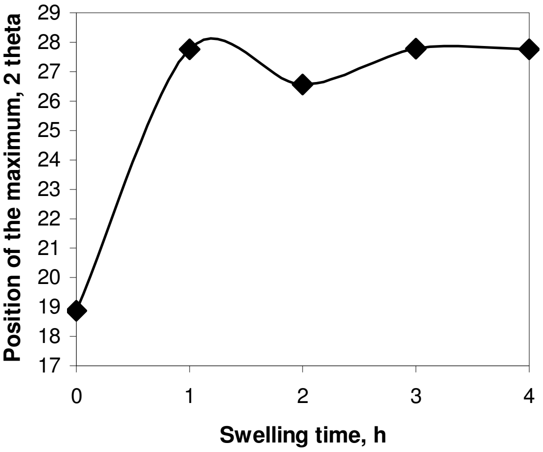

Figure 5.23. Dependence of the maximum of the amorphous share of the diffraction pattern of swelled wood (Klason lignin).

Due to the intraplanar hydrogen bonds, formed primarily between adjacent cellulose molecules in the cellulose in the same 002 lattice planes, a sheet –like structure is conceived. In the X-ray pattern recorded from the wood, only the peak corresponding to the (002) crystal plane (Fig.5.24) is well detected, as the amorphous matrix shrouds other less distinctive peaks. For this reason the alteration of the crystal structure in 002 lattice plane will be discussed.

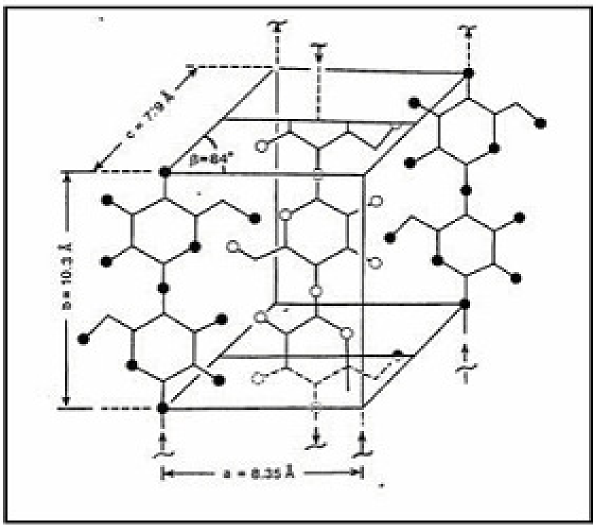

Figure 5.24. The structure of a unit cell of cellulose by Meyer and Mischin
http://web.utk.edu/~mse/pages/Textiles/Rayon%20fibers.htm

According to the Equation (4.5), a shift of the (002) peak towards higher 2θ values means that in wood cellulose the lattice spacing in the (002) plane is decreasing. The plane (002) is perpendicular to the cellulose molecule chain's direction (Fig. 5.24) and represents the distance between them. Therefore the decrease of the lattice space in this direction conducts to the aim that in swelling of wood the highly ordered regions in cellulose microfibrils ought to shrink while the cell wall expands.

When water is introduced into wood, it is contained both within the cell wall and within the cell opening called lumen. When wood saturated by water dries, most of the water in the opening is removed before the water tied inside the cell wall. This is because it takes less energy to remove the loosely held water in the openings of the cells. The level of moisture in wood, at which all lumens are void of water, and the cell wall remains saturated, is called the "fibre saturation point" (FSP). The fibre saturation point is also often considered as the moisture content, below which the physical and mechanical properties of wood begin to change as a function of moisture content. In absorption process it is difficult to distinguish by the moisture content measurements (Figs. 5.27 and 5.28) when the FSP is attained, because filling of lumens and absorption into the cell wall occur simultaneously. The situation becomes more complicated when water is mixed with organic solvents. Therefore measuring the shift of the (002) peak in the X-ray diffraction pattern and the relative index of crystallinity enables more detailed information about the ongoing processes in the cell wall.

In Figures 5.25 and 5.26 the shift of the peak position in the (002) plane during swelling of wood in various solutions was recorded over long (Fig. 5.25) and short swelling times (Fig. 5.26). Different solutions have distinctive effect on the swelling behaviour.

According to the Figure5.26 in first two hours all the swelling agents, except acetone, caused the shift of the (002) peak towards higher 2θ values that corresponds to the shrinking of cellulose microfibrils. The most noticeable jump up in the peak position was measured for the acetone-water medium. This is in a significant correlation with the fast uptake of the same liquid in first two hours (Fig. 5.26). As it is seen in Figure 5.28 acetone is absorbed into wood with the minimum rate and the crystal structure of cellulose is not yet affected.

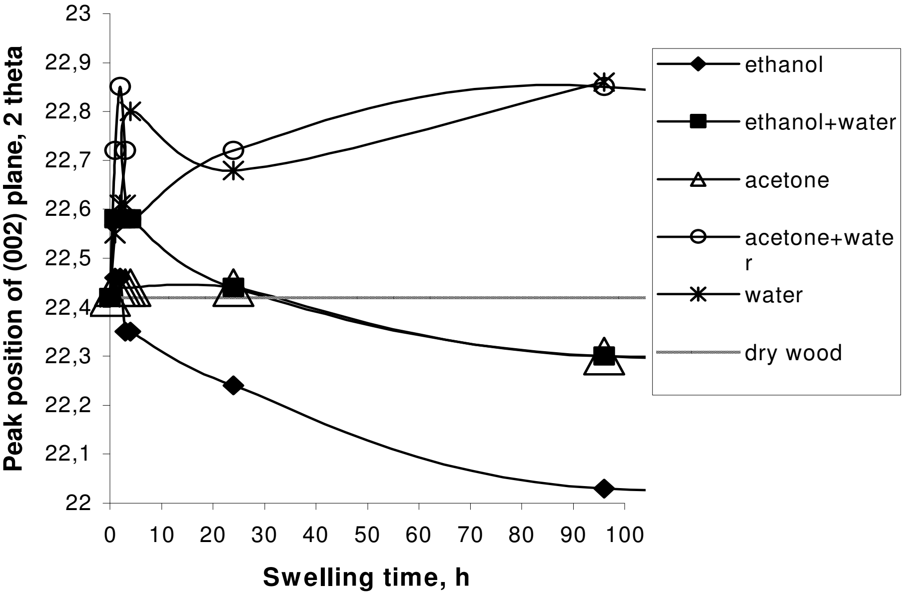

Figure 5.25. Shift of the peak position in the (002) plane during swelling of wood in various solutions

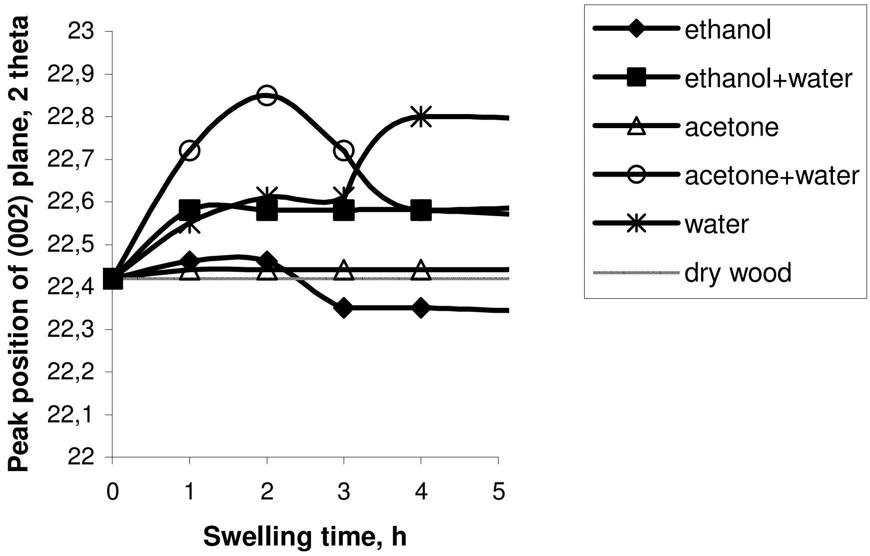

Figure 5.26. Shift of the peak position in the (002) plane during swelling of wood in various solutions

After 3 hours, a drop in the peak position of the (002) plane towards lower 2θ values appeared for the wood sample swollen in ethanol, while the solution uptake (Figure 5.28) gradually grew. The unit cell of cellulose acted in an elastic way, and the microfibrils started to restore their initial shape. The main amount of solution was absorbed through openings. Samples swollen in ethanol-water, acetone and water remained steady. The solution absorbance occurred mainly by openings. Curve for the peak position of the (002) plane for acetone-water showed a sharp drop below the position of the (002) plane for the dry wood. This probably indicates a step in the unit cell deformation, when the dimension in (002) plane temporarily increased. At the same time the uptake of the solution grew steadily. This indicates the beginning of chemical reaction between cellulose and acetone that caused the swelling of the unit cell in the (002) plane.

After 4 hours of swelling in different media, the peak position of the (002) plane stayed steady for wood swollen in acetone, ethanol and ethanol-water. Curve for acetone-water continued to drop and accordingly the unit cell of cellulose grew larger in (002) plane. The amount of ethanol-water solution absorbed into wood grew faster than other swelling agents (Fig. 5.28). For the water it is a time to shrink the unit cell as the water curve started to rise (Figure 5.26). At the same time water uptake by wood had the minimal growth rate compared to other swelling media (Fig. 5.28).

After 24 hours the main tendencies of the cellulose in impact to wood was revealed (Fig. 5.25). In ethanol the drop in the position of the (002) plane towards lower 2θ values was remarkably far from the (002) plane position of the oven-dry wood. This shows continuing enlargement of the cellulose unit cell in the (002) plane due to the chemical reaction. Surprisingly, the ethanol uptake by wood remains smallest of all the other swelling media (Fig.5.27). Acetone and ethanol-water mixture showed the tendency to increase the unit cell dimensions of cellulose, but not to that extent as pure ethanol. Curves for water and acetone-water directed upwards after the water curve passed the minimum. The microfibrils in these solutions continued to shrink.

In a longer perspective (after 96 h) of swelling the distance between cellulose chains decreased only in wood swollen in water and acetone-water mixture. Other media – ethanol, ethanol-water, and acetone altered the crystal structure of cellulose towards expansion of the unit cell in the (002) plane and therefore the chemical reaction between the wood and these media was expected. The ethanol uptake by wood still remains lowest of all the other swelling media (Fig.5.27).

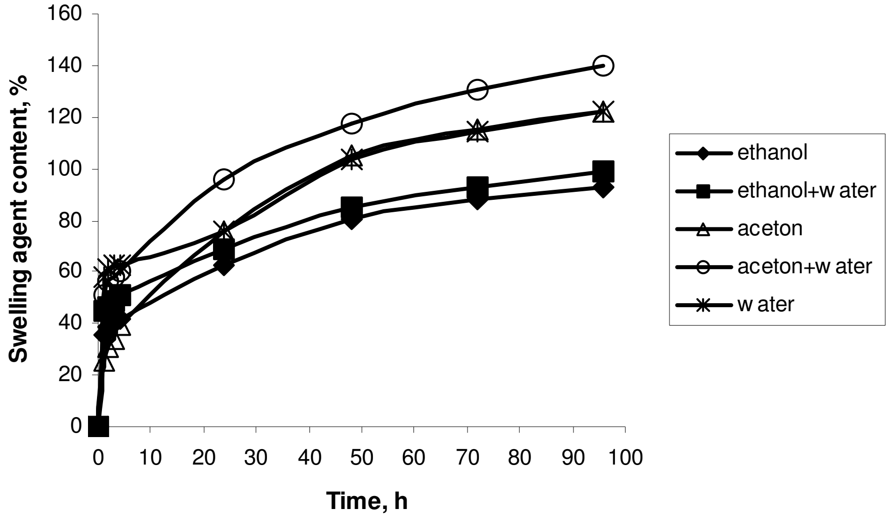

Figure 5.27. Relationship between moisture content absorbed into the wood and the swelling time

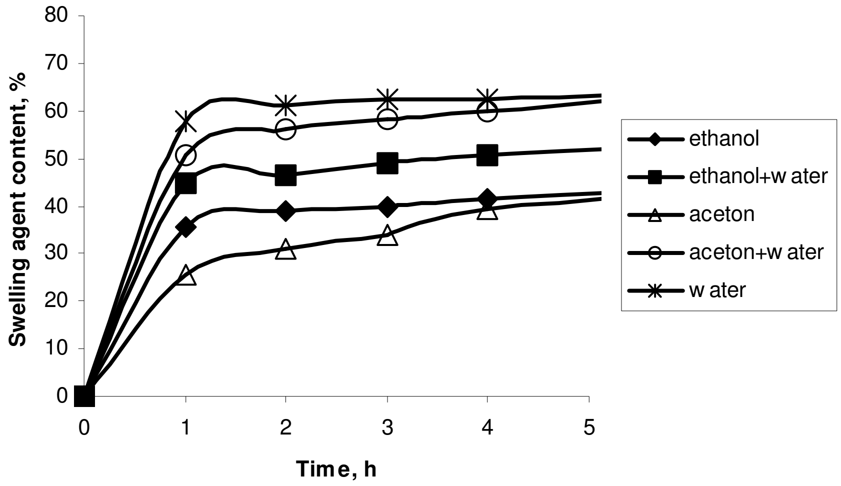

Figure 5.28. Relationship between moisture content absorbed into the wood and the swelling time.

Relaying on the changes described above, the shift of the peak according to the (002) plane towards higher 2θ values is most noticeable when the swelling was performed in pure water and acetone water mixture. Water plays important role in the swelling of amorphous part of cellulose causing the shrinkage of crystal part of cellulose chains. This conclusion is in a significant correlation with the swelling media uptake curves (Fig. 5.27), where swelling in acetone-water mixture is the utmost. At the same time it is quite intriguing, that pure acetone having the same absorbance capacity as water (Fig. 5.27), had completely opposite influence on the unit cell of crystal cellulose expanding the distance between the cellulose chains. The most drastic influence to the crystal structure of cellulose possesses ethanol expanding remarkably microcrystals. At the same time the uptake of ethanol was lowermost.

In Figures 5.29 and 5.30 dependence of the relative index of crystallinity on the swelling time is represented. Relative index of crystallinity showed the changes in the portion of crystalline cellulose over the whole matter in the sample relatively to oven –dry wood. The changes in the CrI_R (Fig. 5.30) were not so sensitive to the first hours of swelling as the shift of the peak position in the (002) plane (Fig. 5.26). All water mixtures altered the crystal structure of cellulose in the same way. The relative index of crystallinity was most drastically influenced by the swelling of the wood in pure water. It was caused by the high water uptake rate (Figs. 5.27 and 5.28) and swelling of amorphous portion of cellulose. Also swelling in acetone-water and ethanol-water altered CrI_R towards lower density of the crystal part of cellulose compared to the oven-dry wood.

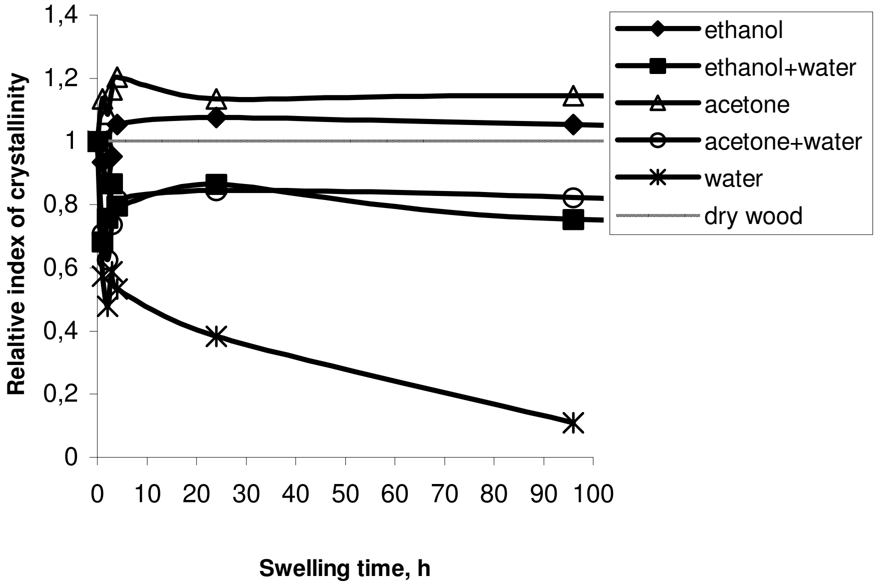

Figure 5.29. Relationship between relative index of crystallinity and the swelling time;

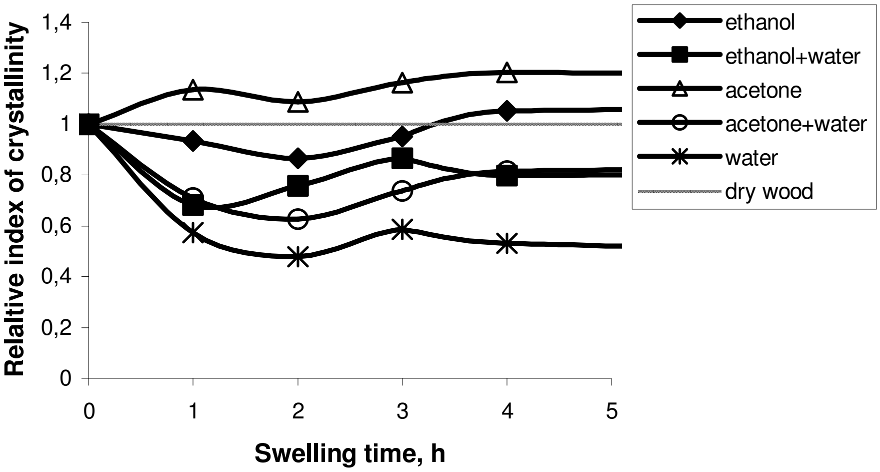

Figure 5.30. Relationship between relative index of crystallinity and the swelling time.

Only swelling the wood samples in ethanol and acetone turned cellulose more crystalline compared to the untreated wood. In this process the distance between cellulose chains in (002) plane increased.

The changes on macromolecular level in the unit cell structure of cellulose were very fast and salutatory during the first 4 hours of swelling (Fig. 5.26). On macroscopic level the changes in overall dimensions of wood were not so drastic. It is known from the literature (Ishimaru and Minase 1992, Mantanis et al. 1995a, 1995b) that liquids have a different rate and time for swelling. Water as a very fast swelling agent affects in the beginning of swelling process the amorphous part of cellulose and also hemicelluloses. Acetone contrarily seems to penetrate in the beginning of swelling process into the crystalline part of cellulose (Fig 5.26). Anyway, this phenomenon of unit cell changes during the first hours of swelling is useful.

The swelling values, SEM studies, mechanical properties of wood and liquids studies were performed after 90 days of swelling. The X-ray diffraction studies showed that changes on macromolecular level are already completed in 4 days (Fig. 5.29), but on the other hand the weight of samples continued to grow (Fig. 5.27). The elasticity of wood swollen in organic solvents and binary mixtures had very good linear correlation to the relative index of crystallinity (Fig. 5.31). The behaviour of wood in water seemed to be different compared to other liquids.

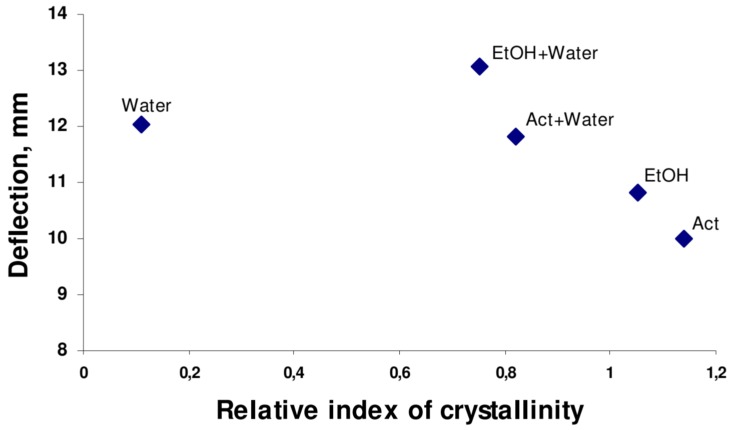

Figure 5.31. Relationship between relative index of crystallinity and the deflection.

The unique and fascinating structure of wood is the reason for different rate and duration of processes caused by the liquids on macroscopic, microscopic and macromolecular level. The dynamics of these processes is important from scientific standpoint. In industrial processes the equilibrium state of systems of wood and liquids is usually more significant.

6. Conclusions

In the present research for the first time the influence of binary mixtures of some organic substances (ethanol, acetone, dimethylformamide) and water on wood structure and properties was investigated systematically. The reciprocal influence of wood and liquids was studied on three different levels: macroscopic, microscopic and macromolecular level. It was concluded, that the influence of the liquids used in the research on wood structure and properties was different.

On **macroscopic level** the swelling values of wood in pure substances are first and foremost related to the H-bonding ability of these substances. Current results were in concordance with the previous research results that have been published on wood swelling in organic substances.

Applying both ethanol and acetone aqueous solutions caused hyperswelling – the phenomenon when solid material swells in binary mixtures more than in pure components The hyperswelling of wood in binary mixtures is triggered by the co-influence of different factors, including also the change in the chemical structure of the cell wall of wood (including the removal of extractives) and the processes occurring on macromolecular level in the cell wall.

The recently published studies have shown that besides monomolecular water and ethanol the globules (water-water, ethanol-ethanol, ethanol-water) are formed in different relations depending on the concentration of the ethanol aqueous solution on molecular level. It can be presumed that due to its measurements the components of the binary mixtures have different capability to penetrate into the cell wall and cause wood swelling.

Changes occurred in the chemical structure of the cell wall as the result of the long-term reciprocal influence of wood and liquids. On the basis of these results it was not possible to find the direct correlation between swelling values and the amount of dissolved wood matter, but it caused the decay of CML.

In case of repeated swelling of wood during every subsequent cycle the decrease in swelling characteristics occurred as well as the dimensional increase of the specimens in absolutely dry state that indicated irreversible changes in wood structure.

The **microscopy studies** of wood proved that the liquids used influenced the different layers of cell wall, first and foremost the middle lamellae of the cell wall. Swelling in the DMF opened up the location of the primary cell wall layer and secondary layer S3. Acetone and acetone-water mixtures had very mild effect on the cell wall structure and its bonding to the compound middle lamellae (CML). Swelling of wood in ethanol caused the weakening of bonds between the CML and S1 layer. Ethanol-water mixture dissolved the main part of lignin from the CML and released individual cells at sectioning.

The changes that occurred during swelling influenced also the **mechanical properties of wood** that were determined at the maximum swelling of wood. The deflection of wood in static bending was in linear correlation with the tangential swelling of wood. The wood swollen in ethanol aqueous solutions had better elastic properties compared to wood swelled in other liquids – the deflection increased 9% compared to the wood swollen in water.

The most significant changes occurred on the **macromolecular level** of wood or in the unit cell of cellulose level already in the first 4 hours. It was confirmed that the relative crystallization index of wood swollen in water (0.53) and in ethanol and acetone aqueous solutions (accordingly 0.75 and 0.82) is lower than in absolutely dry wood (1.00), that indicates to the changes in the amorphous and in crystalline part of the cellulose during the swelling process. Since the amorphous part of the cellulose was subjected to swelling, the relative increasing of this part caused also increase in volumetric swelling that appears in hyperswelling. The dynamics of these processes is important from scientific standpoint. In industrial processes the equilibrium state of systems of wood and liquids is usually more significant.

The wood treated in this way appears to behave as a novel material, where the bonds between wood fibres are considerably weakened and the elasticity of wood is increased. The acquired experimental results can be applied in different technological processes, e.g. glued-bended products and 3D veneer.

Acknowledgements

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I express warm thanks to my family for patient and kind support.

I dedicate this thesis to the memory of my father Kalev. His encouragement, support and faith have given me the strength and willpower during all these years.

Abstract

The main purpose of this study was to investigate the influence of aqueous solutions of organic substances on structure and properties of pinewood. The subject was set up by stricter rules of the Solvent Emission Directive (SED) 1999/13/EC, which obligates the producers looking for new solutions, alternative environmentally friendly products, e.g. water-based materials in wood coating, lamination and impregnation industry. Pine (*Pinus sylvestris*) was selected as typical representative of softwood. Only the sapwood of pine was studied. Organic solvents (ethanol, acetone and dimethylformamide) were selected as model substances and the representatives of constituents of wood preservative and coating materials. The reciprocal influence of wood and liquids was studied on three different levels: macroscopic, microscopic and macromolecular level.

On **macroscopic level** the volumetric swelling of wood in ethanol (13.3 %) and acetone (10.4%) after 90 days was lower and in the DMF (22.5%) higher than in water (15.4%). The swelling characteristics of wood in pure substances are first and foremost related to the H-bonding ability of these substances. Current results are in concordance with the previous research results that have been published on wood swelling in organic substances.

The recently published studies have shown that depending on the concentration of the ethanol aqueous solution globules are formed in molecular level in different relations (water-water, ethanol-ethanol, ethanol-water), monomolecular water and ethanol molecules. At the same time there is no methodology on the affect of binary mixtures on wood structure. It can be presumed that due to its measurements the components of the binary mixtures have different capability to penetrate into the cell wall and cause wood swelling. Applying both ethanol and acetone aqueous solutions caused hyperswelling – the phenomenon when solid material swells in binary mixtures more than in pure components. The deviation from additivity in ethanol aqueous solution with ethanol molar fraction 0.5 was 73% and in acetone aqueous solution at molar fraction 0.4 by 47%.

Actually hyperswelling in binary mixtures is triggered by the co-influence of different factors, including also the change in the chemical structure of the cell wall of wood (including the removal of extractives) and the processes occurring on macromolecular level in the cell wall. Changes occur in the chemical structure of the cell wall as the result of the long-term reciprocal influence of wood and liquids. The DMF dissolved notable amount of lignin (2.33 g/l) and smaller amount of carbohydrates (0.14 g/l) from the wood. The amount of removed extractives (mainly resin acids) was 0.17 g/l. Acetone dissolved the biggest amount of lignin (3.31 g/l), but the influence of acetone-water mixture (MF 0.5) was considerably smaller (0.19 g/l). Ethanol and ethanol-water mixture (MF 0.5) had quite similar ability to dissolve lignin, in

ethanol 0.47 g/l and in ethanol-water mixture 0.37 g/l. On the basis of these results it is not possible to find the direct correlation between swelling values and the amount of dissolved wood matter, but it caused the decay of CML.

The most significant changes occurred on the **macromolecular level** of wood or in the unit cell of cellulose level already in the first 4 hours. The shift of the 002 peak position in the X-ray diffraction study described most elaborately the changes in the distance between cellulose chains. It was confirmed that the relative crystallization index of wood swollen in water (0.53) and in ethanol and acetone aqueous solutions (accordingly 0.75 and 0.82) is lower than in absolutely dry wood (1.00), that indicates to the changes in the amorphous and in crystalline part of the cellulose during the swelling process. Since the amorphous part of the cellulose was subjected to swelling, the relative increasing of this part caused also increase in volumetric swelling that appears in hyperswelling.

In repeated swelling of wood the swelling characteristics depend on whether the mixture used had gone through one swelling cycle or new mixtures had been prepared with the same concentration. Using the same mixtures the swelling characteristics were nearly 2 times lower than in new mixtures. After the second cycle the tangential swelling of wood in ethanol aqueous solution (MF 0.5) was 5.3% with a new mixture, and with the old mixture 2.5%. The respective values with the acetone aqueous solutions (MF 0.5) were 4.9% and 1.8%. In case of repeated swelling of wood during every subsequent cycle the decrease in swelling characteristics occurred as well as the dimensional increase of the specimens in absolutely dry state that indicated irreversible changes in wood structure.

The **microscopy studies** of wood proved that the liquids used influenced the different layers of cell wall, first and foremost the middle lamellae of the cell wall. Swelling in the DMF opened up the location of the primary cell wall layer and secondary layer S3. Acetone and acetone-water mixtures had very mild effect on the cell wall structure and its bonding to the compound middle lamellae (CML). Swelling of wood in ethanol caused the weakening of bonds between the CML and S1 layer. Ethanol-water mixture dissolved the main part of lignin from the CML and released individual cells at sectioning.

The changes that occurred during swelling influenced also the **mechanical properties of wood** that were determined at the maximum swelling of wood. The deflection of wood in static bending was in linear correlation with the tangential swelling of wood. The wood swollen in ethanol aqueous solutions had better elastic properties compared to wood swelled in other liquids. The wood treated in this way appears to behave as a novel material, where the bonds between wood fibres are considerably weakened and the elasticity of wood is increased.

Kokkuvõte

Käesoleva töö eesmärgiks oli uurida orgaaniliste ainete vesilahuste mõju männipuidu struktuurile ja omadustele. Antud teema on valitud lähtudes EU direktiivist 1999/13/EC, mis seab ettevõtetele rangemad nõuded lenduvate orgaaniliste ühendite osas. Et antud nimistusse kuuluvad ka puidu viimistlus- ja immutusaineid tootvad ja kasutavad ettevõtted, siis sunnib see viimaseid otsima uusi keskkonna- ja inimsõbralikke lahendusi. Üheks võimaluseks on vesipõhiste viimistlus- ja immutusainete kasutamine puidutööstuses. Antud töö katseliseks osaks oli valitud mudelsüsteemid: mänd kui tüüpiline okaspuu esindaja ja orgaanilistest ainetest alkoholide, ketoonide ja lämmastikühendite tüüpilised esindajad etanool, atsetoon ja dimetüülformamiid (DMF). Männipuidus uuriti ainult maltspuidu osa.

Antud töös uuriti süstemaatiliselt mõnede orgaaniliste ainete (etanool, atsetoon, dimetüülformamiid) ja vee kaksiksegude mõju puidu struktuurile ja omadustele. Puidu ja vedelike vastasmõju uuriti kolmel erineval tasandil: makroskoopilisel, mikroskoopilisel ja makromolekulaarsel.

Makroskoopilisel tasandil oli puidu täielik mahuline pundumine etanoolis (13.3%) ja atsetoonis (10.4%) madalam ning DMF-s (22.5%) kõrgem kui vees(15.4%). Puidu pundumiskarakteristikud puhastes ainetes on eeskätt seotud nende ainete H-sidemete moodustamise võimega. Antud tulemused on kooskõlas ka eelnevate uurimustega puidu pundumise kohta orgaanilistes ainetes. Viimasel ajal publitseeritud töödes on näidatud, et sõltuvalt etanooli vesilahuse kontsentratsioonist moodustuvad molekulaarsel tasandil erinevas vahekorras gloobulid (vesi-vesi, etanool-etanool, etanool-vesi), monomolekulaarne vesi ja etanooli molekulid. Samas puudub metoodika kaksiksegude mõjust puidu struktuurile. Võib oletada, et tänu oma mõõtmetele omavad kaksiksegude koostisosad erinevat võimet tungida rakuseina ja põhjustada puidu pundumist. Nii etanooli kui ka atsetooni vesilahuste kasutamisel leidis aset hüperpundumine – nähtus, mille puhul tahke materjal pundub binaarsetes segudes rohkem kui puhastes komponentides. Kõrvalekalle aditiivsusest etanooli vesilahuses etanooli moolimurru 0.5 juures oli 73% ja atsetooni vesilahuses atsetooni moolimurru 0.4 juures 47%.

Hüperpundumise kaksiksegudes kutsub tegelikult esile erinevate tegurite koosmõju, sealjuures ka puidu rakuseina keemilise koostise muutumine (k.a. ekstraktiivainete eraldumine) ja rakuseinas makromolekulaarsel tasandil toimuvad protsessid.

Puidu ja vedelike pikaajalise vastasmõju tulemusel leidsid aset muudatused rakuseina keemilises koostises. DMF ja atsetoon lahustasid märgatava osa ligniini, vastavalt 2.33 g/l ja 3.31 g/l. Atsetooni vesilahuse (moolimurd 0.5) mõju oli tunduvalt väiksem (0.19 g/l). Etanooli ja etanooli vesilahuse (moolimurd 0.5) võime lahustada ligniini oli suhteliselt sarnane, etanoolis 0.47

g/l ja etanooli vesilahuses 0.37 g/l. Antud tulemuste põhjal ei ole võimalik leida otsest seost puidu pundumiskarakteristikute ja vedelike poolt lahustunud puitaine vahel, kuid see aitab kaasa raku vaheplaadi lagunemisele.

Suurimad muudatused puidu **makromolekulaarsel tasandil** ehk tselluloosi ühikrakus leidsid aset juba esimese 4 tunni jooksul. Puidu röntgendifraktomeetrilisel uuringul kirjeldas piigi 002 asendi muutus kõige ilmekamalt muudatusi tselluloosi lülide vahelises kauguses. Tõestati, et tselluloosi suhteline kristallisatsiooniindeks on vees (0.53) ja etanooli ning atsetooni vesilahuses (vastavalt 0.75 ja 0.82) pundunud puidul väiksem kui absoluutkuival puidul (1.00), mis näitab tselluloosi amorfse ja kristallilise osa muutustele pundumisprotsessis. Kuna pundumisele allub tselluloosi amorfne osa, siis selle osa suhteline suurenemine toob kaasa mahulise pundumise suurenemise, mis avaldub ka hüperpundumises.

Puidu korduvpunnutamisel sõltusid pundumiskarakteristikud sellest, kas kasutati ühe pundumistsükli läbinud vedelikke või valmistati sama kontsentratsiooniga uued vedelikud. Samade vedelike kasutamisel olid pundumiskarakteristikud ligi 2 korda väiksemad kui uute vedelike puhul. Puidu pundumine tangentsiaalsuunas pärast teise tsükli lõppu etanooli vesilahuses (MF 0.5) uue lahusega oli 5.3% ja vana lahusega 2.5%. Vastavad väärtused atsetooni vesilahustega (MF 0.5) olid 4.9% ja 1.8%. Puidu korduvpunnutamisel leidis iga järgneva tsükli jooksul aset nii pundumiskarakteristikute vähenemine kui ka katsekehade mõõtude suurenemine absoluutkuivas olekus, mis viitas pöördumatutele muudatustele puidu struktuuris. Puidu **mikroskoopilised uuringud** tõestasid, et kasutatud vedelikud mõjutavad erinevaid rakuseina kihte, esmajoones raku vaheplaati. Pundumine DMF-s mõjutas enim rakuseina primaarkihti ja sekundaarkihti S3. Atsetoonil ja atsetooni vesilahusel oli väga nõrk mõju rakuseinale ja vaheplaadile. Pundumine etanoolis nõrgendas sidemeid vaheplaadi ja sekundaarkihi S1 vahel. Etanooli vesilahus (moolimurd 0.5) lahustas suurema osa vaheplaadi koostises olevast ligniinist ning põhjustas rakkude eraldumise teineteisest.

Pundumise käigus aset leidnud muudatused puidu struktuuris mõjutasid ka **puidu mehaanilisi omadusi**, mis määrati puidu maksimaalselt pundunud olekus. Puidu läbipaine staatilisel paindel on lineaarses sõltuvuses puidu tangentsiaalsuunalise pundumisega. Etanooli vesilahuses pundunud puit oli parimate elastsusomadustega, võrreldes teistes vedelikes pundunud puiduga. Antud viisil käsitletud puit kujutab endast uudsete omadustega materjali, kus puidukiudude omavahelised sidemed on oluliselt nõrgenenud ja puidu elastsus suurenenud.

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Appendix A

Paper I

P. Meier, T. Kaps, U. Kallavus. 2005. Swelling of Pinewood (*Pinus Sylvestris*) in Binary Aqueous Solutions of Organic Substances. – Materials Science *(Medžiagotyra)*, 11, 140–145

Appendix A

Paper II

P. Meier, U. Kallavus, A. Rohumaa, and T. Kaps. 2006. Multiple Swelling of Pinewood *(Pinus Sylvestris)* in Binary and Ternary Mixtures of Ethanol, Acetone and Water. – Materials Science *(Medžiagotyra)*, 12, 25–30

Appendix A

Paper III

P. Meier, E. Stöör, T. Kaps, U. Kallavus. 2006. Mechanical properties of pinewood (*Pinus Sylvestris*) swollen in organic liquids. – Proceedings of Estonian Academy of Sciences. Engineering, 12, 125−133

Appendix B

Curriculum Vitae

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1990 – Engineer Diploma (Tallinn University of Technology)
1999 – Master of Science (Tallinn University of Technology)

Professional experience

1990 – 1998	Tallinn University of Technology, Chair of Woodworking, teaching assistant
1998 -	Tallinn University of Technology, Chair of Woodworking, lecturer

Further training

2003 – 2005	Helsinki University of Technology, Finland

Publications

- P. Meier, T. Kaps, U. Kallavus. 2005. Swelling of Pinewood (*Pinus Sylvestris*) in Binary Aqueous Solutions of Organic Substances. – Materials Science *(Medžiagotyra)*, 11, 140–145 (ISSN 1392-1320)
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- P. Meier, R. Reiska, J. Mikkiver. 1998. Properties and Chemical Composition of Pinewood. – 24th Estonian Chemistry Days, Tartu, 44

Appendix B

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1990 – 1998 Tallinna Tehnikaülikool, Puidutöötlemise õppetool, assistent
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Publikatsioonid

- P. Meier, U. Kallavus, A. Rohumaa, and T. Kaps. 2006. Multiple Swelling of Pinewood *(Pinus Sylvestris)* in Binary and Ternary Mixtures of Ethanol, Acetone and Water. – Materials Science *(Medžiagotyra)*, 12, 25–30 (ISSN 1392-1320)
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DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and destruction of polyethylene. 1993.
2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.
3. **Meeme Põldme**. Phase transformations in hydrothermal sintering processing of phosphate rock. 1995.
4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi apatites. 1995.
5. **Anu Hamburg**. The influence of food processing and storage on the N-nitrosamines formation and content in some Estonian foodstuffs. 1995.
6. **Ruth Kuldvee**. Computerized sampling in ion chromatography and in capillary electrophoresis. 1999.
7. **Külliki Varvas**. Enzymatic oxidation of arachidonic acid in the coral *Gersemia fruticosa*. 1999.
8. **Marina Kudrjašova**. Application of factor analysis to thermochromatography and promotion studies. 2000.
9. **Viia Lepane**. Characterization of aquatic humic substances by size exclusion chromatography and capillary electrophoresis. 2001.
10. **Andres Trikkel**. Estonian calcareous rocks and oil shale ash as sorbents for SO_2. 2001.
11. **Marina Kritševskaja**. Photocatalytic oxidation of organic pollutants in aqueous and gaseous phases. 2003.
12. **Inna Kamenev**. Aerobic bio-oxidation with ozonation in recalcitrant wastewater treatment. 2003.
13. **Janek Reinik**. Methods for purification of xylidine-polluted water. 2003.
14. **Andres Krumme**. Crystallisation behaviour of high density polyethylene blends with bimodal molar mass distribution. 2003.
15. **Anna Goi**. Advanced oxidation processes for water purification and soil remediation. 2005.