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Swelling of Pinewood (*Pinus Sylvestris)* in Binary Aqueous Solutions of Organic Substances

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Samples of pine (*Pinus Sylvestris*) sapwood were swelled in binary mixtures. Binary mixtures used in this study were aqueous solutions of ethanol, isopropanol, acetone and dimethylformamide. The tangential, radial and longitudinal swelling was measured and volumetric swelling of oven-dried samples was determined. The synergic effects of swelling in aqueous solutions were observed. The properties of binary liquid systems have a major influence on the swelling of wood. Microscopy studies of wood samples show that after swelling in water the cells are densely packed and the compound middle lamellae (CML) has arranged in a form of continuous ribbon around the cells. The swelling of wood in ethanol-water mixtures has a dramatic effect on the wood structure through dissolving a main part of lignin from CML and released individual cells at sectioning. Acetone and acetone-water mixtures have an insignificant effect on the cell wall structure and its bonding to the CML. The swelling in DMF opened up the location of the primary wall layer and S3 layer. There is no substantial difference in the influence on the cell structure between pure DMF and its mixture with water.

INTRODUCTION

The swelling of wood in liquids is of fundamental importance both from a scientific standpoint and in the context of commercial processes, which involve dimensional stabilization, chemical modification, preservation, pulping, and the removal of extractives. Since swelling is a complex process, which is affected by both the type of wood and the solvent substrate, the influence of each of them on the maximum swelling of wood is difficult to predict. The swelling of wood in aqueous solutions of organic substances is important from the point of water-born preservatives and coating materials.

Scientists have studied the phenomenon of wood swelling during last 60 years attempting to determine the factors influencing that process [1 – 4]. The results of studies have 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, the relation between adsorptivity of the liquid and wood swelling in thermodynamic basis. It has been found that swelling of wood was influenced also by the duration and method of drying, the density of the wood, the percentage of earlywood and latewood, and the microscopic and macroscopic haircheсks in the wood [1 – 3].

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. The swelling of wood in water has been investigated much more than the behavior of wood in organic solvents.

For some reason studying of wood behavior in aqueous solutions of organic substances has been avoided. This might be explained by the fact that the effect of binary mixtures of organic substances in aqueous solutions is more complex than with water alone. Solvation in aqueous solution has been a most intensive studied problem in chemical physics. The microscopic picture of water-alcohol mixture is a very important and challenging problem in chemical physics. The results of studies have been up to the present contradictious even using the same experimental techniques.

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), microscopic (cell) and macroscopic (overall dimensions). This distinction is conventional and convenient because there is no clear dividing line between these levels.

The aim of this study was to investigate interaction between wood and binary mixtures on macroscopic and microscopic level.

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

As wood is an anisotropic material the swelling has to investigate 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 [5].

EXPERIMENTAL

Materials

350 sapwood samples of pine (*Pinus Sylvestris*) as typical representatives of softwood were selected for this

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investigation. The samples were cut from green wood in the form of 20 (radial) × 20 (tangential) × 10 (longitudinal) mm pieces and oven dried at 103 °C to constant weight. The longitudinal direction was selected the shortest one to achieve complete penetration of the liquids in a reasonably short period of time. The density of pine varied from 0.4 to 0.55 g/cm^3 and the number of annual rings per cm was from 10 to 12 in the oven-dried condition. Radial, tangential and longitudinal swelling was measured.

Organic solvents used in this study were selected as representatives of different chemical classes. Ethanol (EtOH) and isopropanol (i-PrOH) are alcohols and are protic i.e. weakly acidic, acetone (Act) is an aprotic ketone and dimethylformamide (DMF) is an aprotic base amine. These organic liquids have different properties such as molecular weight, molar volume, dipole moment, dielectric constant, solubility parameter, hydrogen bonding parameter, and basicity all of the which affect wood swelling in various ways.

The aqueous solutions of organic solvents were prepared in different concentrations (molar fractions 0.2; 0.4; 0.5; 0.6; 0.8).

Methods

Ten samples of pinewood were prepared as described above for treatment with each solution – water, organic solvents and aqueous solutions of these solvents at different concentrations. All experiments were performed at ambient temperature. All dimensional measurements were made with a Vernier caliper, with accuracy 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 the containers sealed. The swelling of wood in the liquids was determined after 90 days. The percentage swelling Sw was calculated applying the equation

$$Sw = \frac{a_{SD} - a_{ODD}}{a_{ODD}} \cdot 100,$$

where a_{SD} is swollen dimension, a_{ODD} is oven-dried dimension.

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 (3 × 3 × 7 mm) and 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.

RESULTS AND DISCUSSIONS

Swelling in binary mixtures

Comparing swelling values of pure liquids wood swells in DMF more than in water contrarily to alcohols and acetone. In general, all the liquids, with molar volume greater than 100 ml/mol or with a small hydrogen bonding parameter, caused very little equilibrium swelling [2]. All swelling agents used in this study had low molar volume and high hydrogen bonding parameter with exception acetone (medium hydrogen bonding parameter).

As shown in Figure 1, some similarities exist between the swelling behavior in alcohols and acetone. A strong effect of synergy became evident at MF_{Act} 0.4 – 0.5 and MF_{Alc} 0.4 – 0.6. Totally different swelling was detected for pinewood in DMF. There is no obvious synergy and after a rapid rise in swelling values after MF_{DMF} 0.2 the rate of increase is less evident.

Interaction of wood with the binary alcohol-water systems have been discussed based on anomalous properties of these systems [6, 7]. The properties of aqueous solutions of alcohol and acetone are probably the key to explaining the synergic effects observed in this study. It is well-known that liquids having large molecular size tend to swell wood to a lesser extent. However the mechanism is not yet known although the large molecular size is thought likely to inhibit penetration of the wood structure.

Some previous studies of aqueous alcohol solutions results [9, 10] indicate that the alcohol appears to act as a structure former by increasing the ordering of the water molecules around it. This tends to shift the equilibrium to one with a higher concentration of structured water and a lower concentration of monomeric water. An increasing amount of experimental and theoretical investigation suggest that the hydrophobic headgroups of alcohol molecules in aqueous solution cluster together. However a consistent description of the details of this self-association is lacking.

X-ray emission and absorption spectroscopy techniques have been used to examine the molecular structure of liquid methanol, water, and their mixtures [8]. It was found that molecules in the pure liquid methanol predominantly persist as hydrogen-bonded chains and rings with 6 and / or 8 molecules of equal abundance. After mixing methanol and water the 6 – 8 molecule chains connected with water molecules to form bigger water / methanol clusters. These clusters are very stable, due to the hydrogen bonds that hold them together. The calculations show that when a few water molecules interact with chains, the chains start to bend over to form an open-ring structures. By adding water, the alcohol structures become more compact [8 – 10].

Furthermore, investigations indicated incomplete mixing water and alcohol at the microscopic level [8].

On the other hand the water may cause a distribution of alcohol aggregates with the formation of water – alcohol association complexes which again reduces the concentration of monomeric or free water in solution. That is available for reaction with wood substrates.

Several unsuccessful attempts have been made to relate the degree of swelling to different properties of fluids such as the dielectric constant, the dipole moment, the surface tension, but good correlations are often found within homologous series. The best results were obtained from correlating swelling with the tendency for the liquid to form hydrogen bonds [2].

Fluids capable of swelling wood are adsorbed on to and in the cell wall by polar functional groups. The hydroxyl groups existing up cellulose and hemicellulose chains are considered to be the main polar functional group found in wood. Liquids, which should be capable of

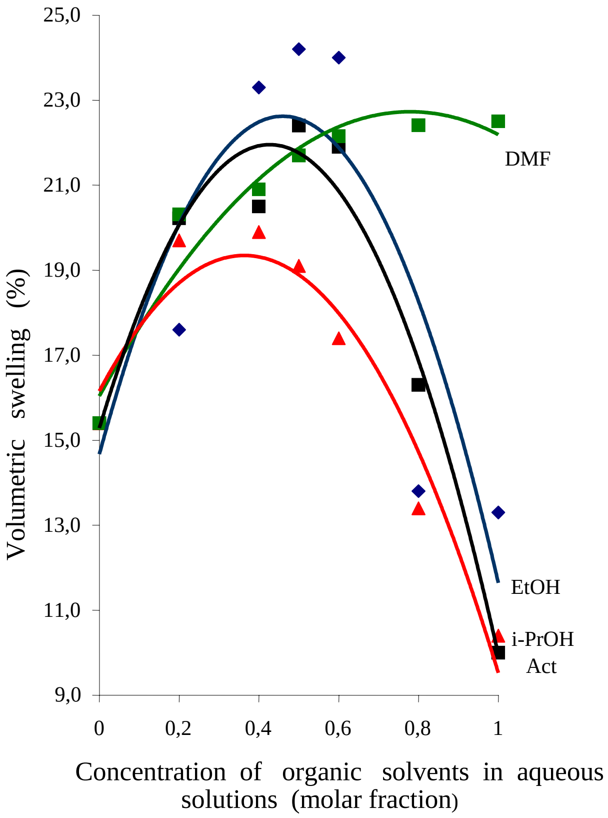

Fig. 1. Volumetric swelling of pinewood in aqueous solutions

forming hydrogen-bond complexes with the wood molecules, swell wood significantly [7].

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 solution and the wood. There preferential adsorption of one component from a solution may occur. Thus for an alcohol aqueous solutions is alcohol adsorbed preferentially [6].

On the other hand from the viewpoint of the "iceberg" theory alcohol molecules increase when molecule dissolves in water aqueous solutions of the structured nature of water. When a non-polar molecule dissolves in water it modifies the water structure in the direction of greater "crystallinity" and the water builds a microscopic iceberg around it. This effect similar to the formation of micelles in electrochromatography.

The transverse swelling anisotropy in wood was confirmed with this study. As shown in Figures 2 and 3 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 (especially lignin content) in tangential and radial cell walls and differences in the sum of cell wall thickness in the tangential and radial directions [11].

The volumetric swelling curves were similar to those, obtained for the tangential and radial swelling (Figures 1 – 3). That leads to the conclusion, that effect of synergy emerge in both transverse directions.

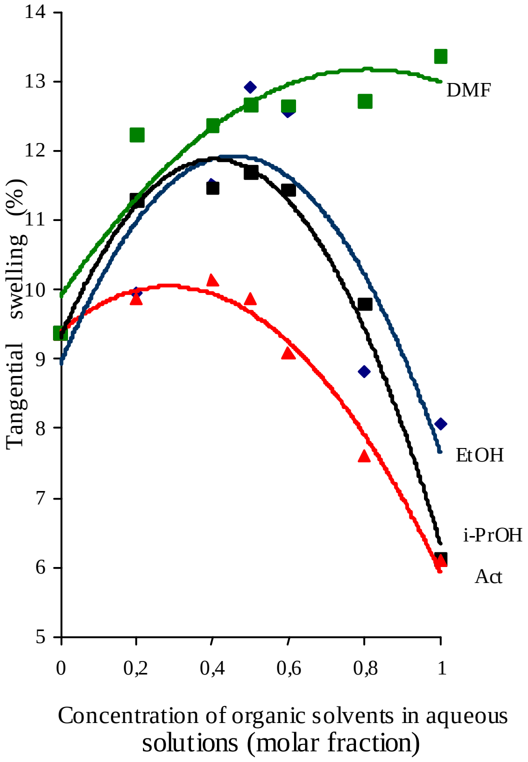

Fig. 2. Tangential swelling of pinewood in aqueous solutions

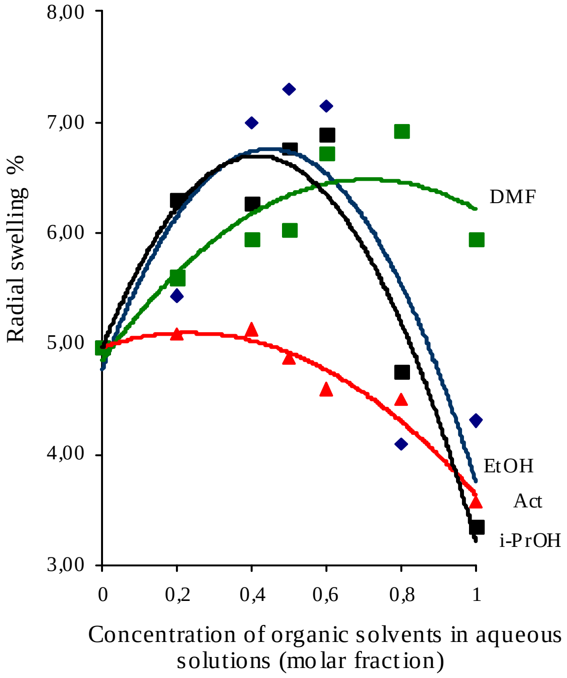

Fig. 3. Radial swelling of pinewood in aqueous solutions

Longitudinal swelling of pinewood was only around 1 % and therefore it may be neglected.

Microscopy study

The swelling of the 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. 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.

Solubility of the wood in water is more favorable at higher temperatures, and it is caused by the increase of the acidity of the solution due to the hydrolysis of the acetyl groups and formation of acetic acid. Therefore at higher temperature the extraction with mild acids could occur and the hydrolysis products of polysaccharides or lignin may appear. In according to the mass loss measurements cold water the transport of wood constituent chemicals into extract is in a minute quantity – about 1 % or less. This is well demonstrated in Figure 4 where the cells are densely packed and the compound middle lamellae (CML) has arranged in a form of continuous ribbon around the cells.

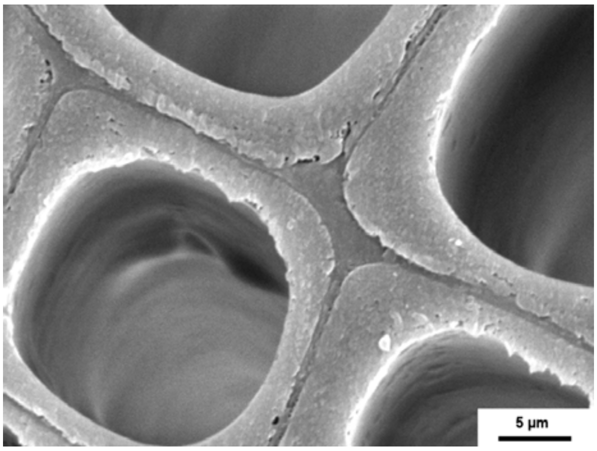

Fig. 4. The SEM micrograph of the cross section of wood swelled in water

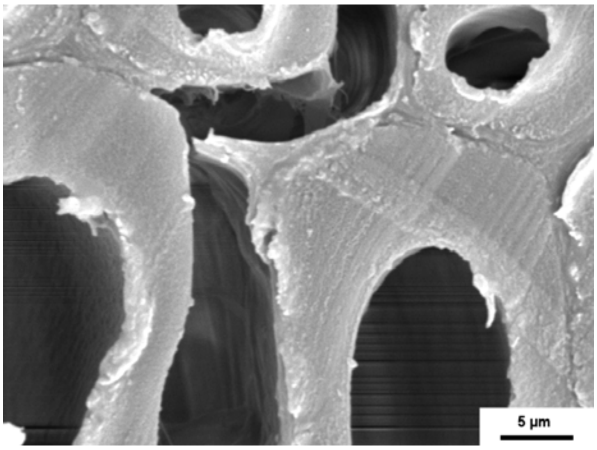

Fig. 5. The SEM micrograph of the cross section of wood swelled in ethanol

It is known neutral organic solvents do not have significant effect on wood [12] up to 100 °C. Only at temperature above 150 °C ethanol has a noticeable degradable effect on lignin and dissolves considerable part of it. The mixtures of water-alcohol have more severe effect on lignin solubility. Figure 5 shows that the swelling of wood in ethanol (96 %) at constant of temperature already caused the weakening of bonds between CML and S1 and detachment of cells due to the forces during the sectioning of samples.

The swelling of wood in ethanol-water mixtures has a great influence on the wood structure. The wood cells (Figure 6 and 7) were separated from each other and liberated CML was hanging between the detached cells. The ethanol-water mixture dissolved a main part of CML lignin and released individual cells at sectioning. The distortion of cells shape was indicates the decay in wood cell wall rigidity and the mass loss of the whole cell walls.

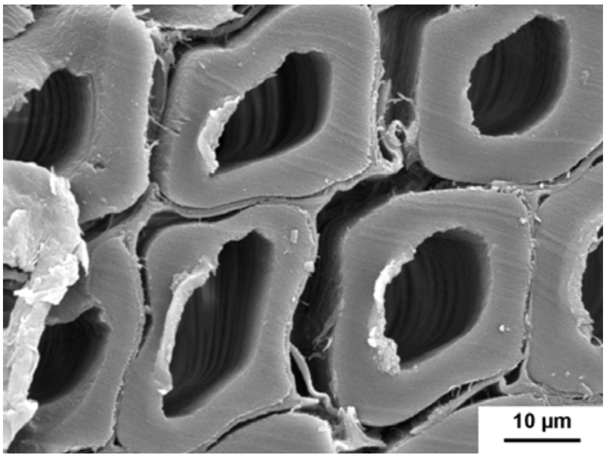

Fig. 6. The SEM micrograph of the cross section of wood swelled in ethanol-water

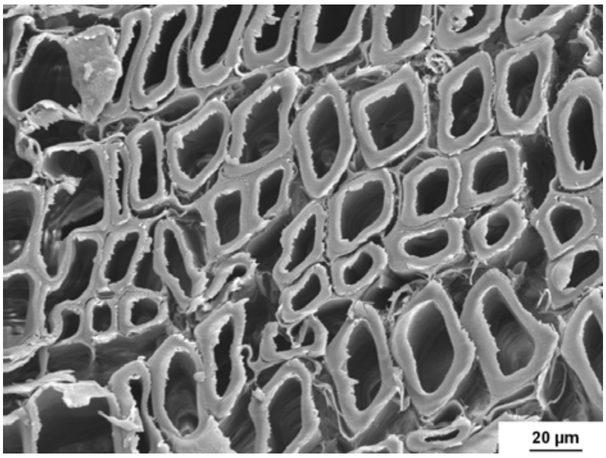

Fig. 7. The SEM micrograph of the cross section of wood swelled in ethanol-water

It is known [12] that for the high molecular fragments acetone and dioxin are better solvents for separated lignin than ethanol. One of the factors in swelling of lignin in solvents is the ability of the solvent to generate hydrogen bonds.

As it seen from the Figures 8 and 9, acetone and acetone-water mixture have a very mild effect on the cell wall structure and its bonding to the CML. Here the sensitive to the acetone lignin is not directly accessible and the water does not perform the role of preliminary swelling.

DMF has interesting and different from previous solvents influence on the cell wall layers and CML.

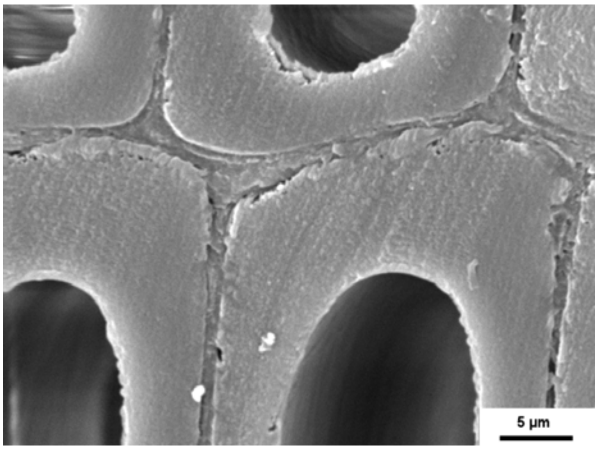

Fig. 8. The SEM micrograph of the cross section of wood swelled in acetone

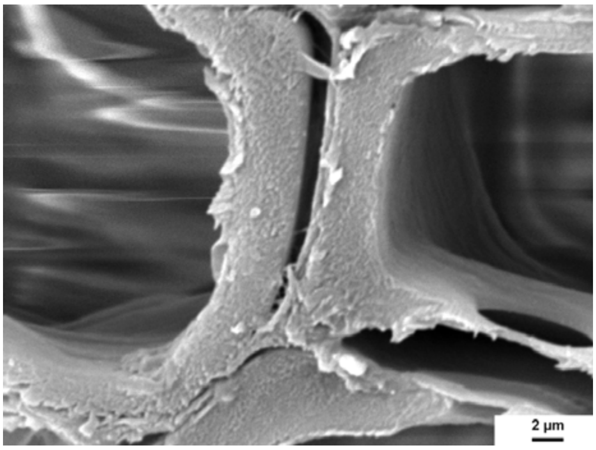

Fig. 9. The SEM micrograph of the cross section of wood swelled in acetone-water

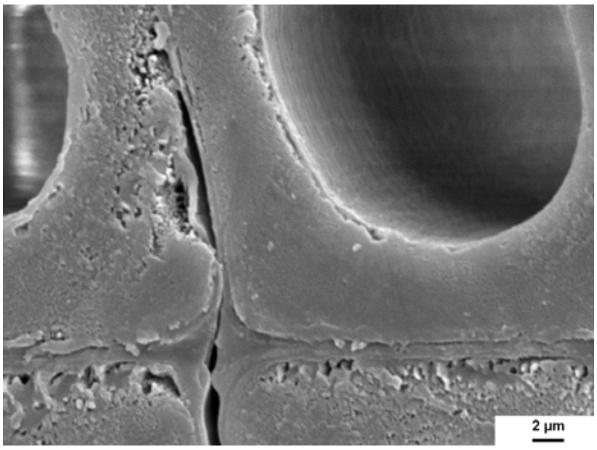

Fig. 10. The SEM micrograph of the cross section of wood swelled in DMF

As can be seen from the Fig. 10 swelling in DMF opened up the location of the primary wall layer and S3 layer.

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 (Fig. 11).

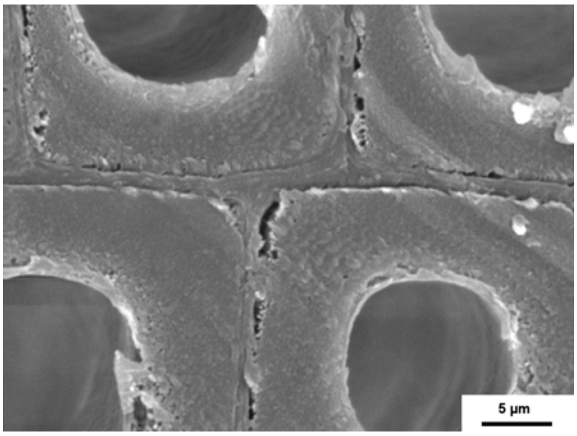

Fig. 11. The SEM micrograph of the cross section of wood swelled in DMF-water

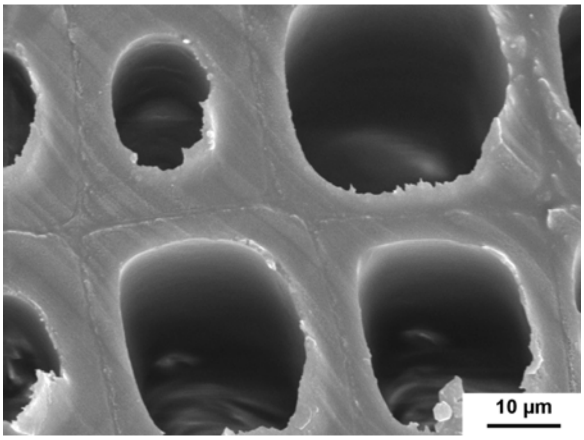

Fig. 12. The SEM micrograph of the cross section of wood swelled in isopropanol

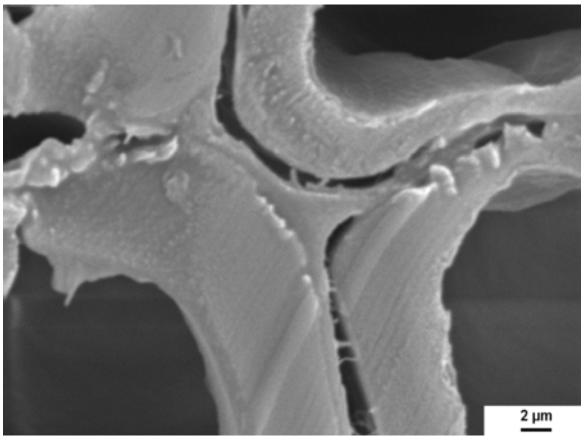

Fig. 13. The SEM micrograph of the cross section of wood swelled in isopropanol – water

The swelling of wood samples in isopropanol (Fig. 12) has a slightly different effect on the cell wall structure. It seems that the lignin has been affected and the disruption of the cell system occurred inside the CML during the swelling in the mixtures of isopropanol and water (Fig. 13).

CONCLUSIONS

Confirmation of the synergetic effects of binary solutions has been obtained. Anomalous properties of binary systems have major influence on the swelling of the wood.

In wood the complex swelling mechanism takes place. The water plays important role in the swelling and solubility of wood matrix in different solvents and water solvent mixtures.

The swelling behavior considerably depends on the pretreatment method of wood and moisture content of samples at the beginning of swelling process. In the case of swelling the wood at moisture content around 10 – 12 % the degree of swelling of wood by the binary system appears to result from the competition between alcohol and wood for water. This phenomenon suggests that wood swelling may predominantly be controlled by the free or unassociated water in the system and the hydrogen bonding affinity of the organic component. Unfortunately this theory does not agree with swelling oven-dry wood. However, the lack of interstitial and weakly bond (adsorbed) water in the wood may lead to a difference in both rate and mode of initial uptake of liquid. Such a process would also occur in commercial kiln dried timber.

Microscopy studies of wood samples show that after swelling in water the cells are densely packed and the compound middle lamellae (CML) has arranged in a form of continuous ribbon around the cells. The swelling of wood in ethanol-water mixtures has a dramatic effect on the wood structure through dissolving a main part of lignin from CML and released individual cells at sectioning. Acetone and acetone-water mixtures have an insignificant effect on the cell wall structure and it's bonding to the CML. The swelling in DMF opened up the location of the primary wall layer and S3 layer. There is no substantial difference in the influence on the cell structure between pure DMF and its mixture with water.

FUTURE PERSPECTIVES

It was determind that many similarities exist between wood and cellulose maximum swelling within various solvent chemical classes. Hence, it appears that cellulose is the primary wood polymer responsible for the major amount of wood swelling. Therefore the structural changes of wood, wood cell walls and cellulose will be investigated using alternative methods considering latest investigations of wood and cellulose swelling as well as investigation of water-organic substance mixtures at the macromolecular level.

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