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Multiple Swelling of Pinewood (*Pinus Sylvestris)* in Binary and Ternary Mixtures of Ethanol, Acetone and Water

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Samples of pinewood (*Pinus Sylvestris*) were swelled in ternary mixtures of ethanol – acetone – water. The tangential, radial and longitudinal swelling was measured and volumetric swelling of oven-dried samples was determined. Anomalous properties of binary and ternary liquid systems have cardinal influence on swelling of wood. Swelling in solutions was multiplied applying the same samples and a new solution with the same concentrations. Selected specimens were swelled in the same solution repeatedly to perform comparative tests. The values for re-swelling in new solutions were up to two times higher when the same solutions were used. Re-swelling resulted in gradual damping in swelling values. The SEM analysis showed that multiple swelling of wood in water causes decrease in the elasticity of the wood matter. The view of the latewood cells swelled in ethanol and acetone showed the disruption of compound middle lamella (CML). The enlargement of the cell apexes showed deeper impact of the water in ethanol-water mixture. When single swelling of wood in acetone – water mixtures did not reveal any substantial change in the wood structure, multiple swelling caused noticeable swelling of the S_3 layer of the cell wall.
Keywords: pinewood, ternary mixtures, multiple swelling, cell wall structure

INTRODUCTION

Scientists have studied the phenomenon of wood swelling during last 60 years attempting to determine the factors influencing that process [1 – 7]. The results of investigations 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, the relation between adsorptivity of the liquid and wood swelling on thermodynamic basis. It has been found that swelling of wood is 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 hairchecks in the wood [1 – 4].

The swelling of wood is a complex process, which is simultaneously affected by the type of wood and the solvent substrate. The influence of different factors on the swelling of wood is difficult to predict. Repeating the cycle of swelling can explain certain changes in the structure of wood, which fail to be detected after first swelling [8 – 10]. From the practical point of view it is essential to be able to predict changes in structural level if wood is in altering conditions and is subjected to recurring swelling and drying. The effect of organic substances on wood structure is recognizable and can be irreversible.

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 more thoroughly than the behaviour of wood in organic solvents.

In our previous work [7] we reported results of interaction between pine sapwood in aqueous solutions of organic substances (ethanol, isopropanol, acetone, dimethylformamide). The aim of this research has been to investigate pinewood swelling in ternary mixtures of ethanol, acetone, water and the impact of cyclical swelling on wood structure.

EXPERIMENTAL

Materials

350 sapwood samples of pine (*Pinus Sylvestris*) as typical representatives of softwood were selected for this investigation. The samples were cut from green wood in the form 20 (radial) mm × 20 (tangential) mm × × 10 (longitudinal) mm pieces and oven dried at 103 °C to constant weight. The longitudinal direction was selected as the shortest one to achieve complete penetration of the liquids in a reasonably short period of time. The density of pine varied from 0.40 g/cm^3 to 0.55 g/cm^3 and the number of annual rings was 10 to 12 per centimeter in the oven-dried condition. Radial, tangential and longitudinal swelling was measured.

Liquids used in this study were ethanol (EtOH) and acetone (Act) and distilled water. The aqueous solutions of organic solvents were prepared by different concentrations (molar fractions 0.2; 0.4; 0.5; 0.6; 0.8) and the concentrations of ternary mixtures were chosen by applying *Gibss-Roozebooms* triangle – yielding 35 test points all together.

Methods

Ten 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

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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 sealed. The swelling of wood in the liquids was determined in sealed containers after 60 days. The percentage swelling was calculated applying the equation

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

where Sw is the percentage swelling, a_{SD} is the swollen dimension, a_{ODD} is the oven-dried dimension.

In order to study the multiple swelling the samples were oven-dried again at 103 °C and placed in 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). To perform third cycle of swelling new solutions were prepared.

Investigation of cell wall structure was carried out with a scanning electron microscope JEOL JSM 840A at the 15 kV. Small sticks from the swelled wood blocks were cut out $(3 \times 3 \times 7)$ mm, frozen at the temperature of liquid nitrogen. One end of the stick was cut flat by cryoultra-microtome 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 gold by ion sputtering.

RESULTS AND DISCUSSIONS

The use of ternary mixtures leads to a four component system – liquid 1, liquid 2, liquid 3 and the cell wall, that makes harder to comprehend the interaction between the solution and wood. It is presumed that the preferential adsorption of one component from a solution might have occurred, in case of alcohol aqueous solutions it is alcohol [5].

According to previously conducted research [7] pine sapwood swelled considerably better in certain binary mixtures compared to swelling in pure solutions – so called synergetic effect of swelling occurs. Particularly strong effect occurred if one of the components was water.

The aim of this study has been to continue the investigations of interaction between wood and binary and ternary mixtures of ethanol, acetone and water and observe the impact of third component on swelling. The effect of multiple swelling on swelling values and on wood structure was also observed.

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 [4].

The volumetric swelling curves were similar to the tangential and radial swelling [7] which lead to the conclusion that the effect of synergy emerged in both transverse directions.

Swelling in ternary mixtures

The best possible way to describe swelling in ternary solutions is use of the three-dimensional phase diagram.

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 a new solution was prepared. In order to perform comparative tests selected specimens were swelled in the same solutions.

In present research the same wood was swelled in new solutions for three times (Fig. 1). Analogously to previous research [7] the synergetic effect of swelling was confirmed, especially according to the results of the first cycle. Wood appears to swell in ethanol and acetone aqueous solutions more than in pure substances. The swelling values of pinewood were higher in binary solutions of ethanol-water (molar fraction of 0.4 – 0.6) and decreased with increasing the amount of acetone in ternary solutions (Figure 1).

However it is necessary to emphasize also the lower values of swelling in ternary mixtures, with lowest possible water content (molar fraction of H_2O is 0.1). Accordingly it can be concluded, that the main contributing factor of swelling is water and the effect of organic substances must be observed depending on their structure. It is generally known that different organic substances affect different cell wall components [7, 11 – 13].

Noticeable damping in swelling values occurred during re-swelling (Fig. 1). Most significant damping appeared in ethanol and acetone aqueous solutions (MF 0.5). In spite of that, synergetic effect emerges also in case of second and third swelling – wood swells in aqueous solutions more than in pure substances.

During swelling of wood in organic mixtures the structure of wood as well as solution changes. It is known that swelling of wood in stronger solutions causes wood to discharge components into the solution. Hence, it is essential which solution is applied in the following swelling cycles. In the current research wood was swelled twice in the same aqueous solutions of ethanol and acetone. Comparative data are presented in Table 1. It is obvious, that using the same mixture in re-swelling causes the values to decreases about 50 % compared to the values, which have been achieved after swelling in new solution.

Table 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

Dimensions

As shown in Figures 2 and 3 overall dimensions of specimens after drying followed by swelling were higher than the initial and previous ones. The behaviour of wood in ethanol and acetone is quite similar. Most substantial

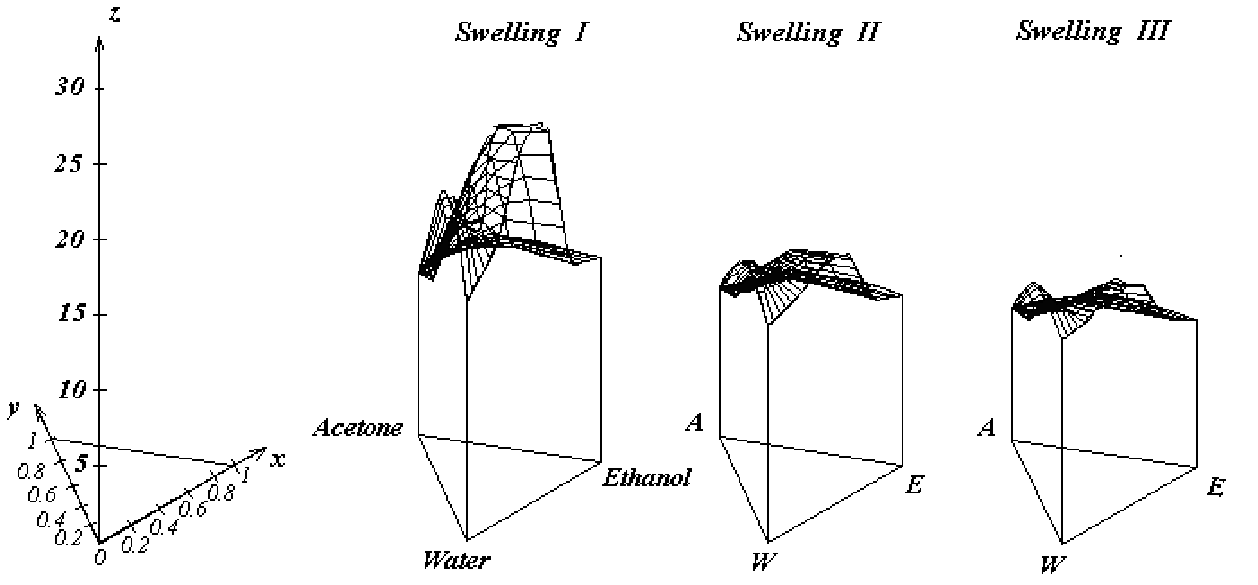

Fig. 1. Volumetric swelling of pinewood in ternary mixtures of ethanol, acetone and water with new mixtures; *x* – concentration of ethanol in aqueous solution of ethanol (molar fraction), *y* – concentration of acetone in aqueous solution of acetone (molar fraction), *z* – wood swelling (%)

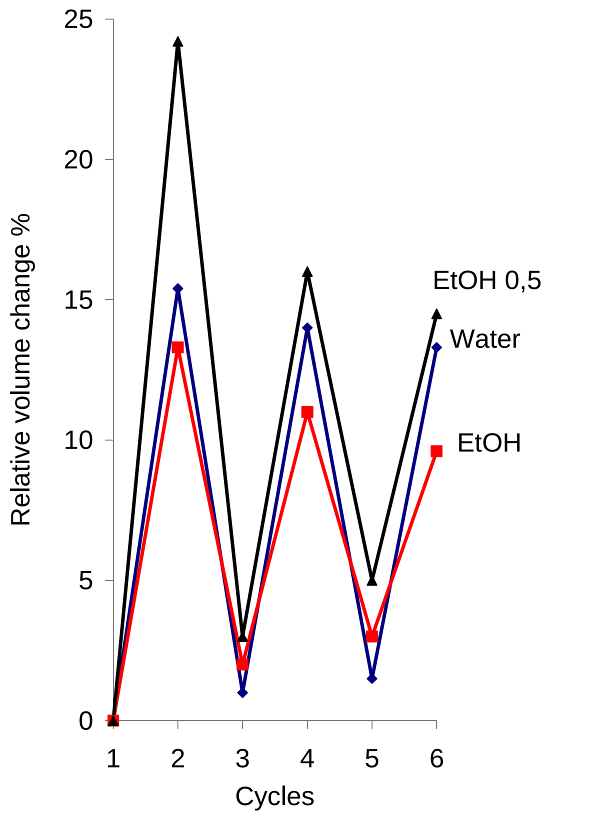

Fig. 2. Cyclic swelling of pinewood in ethanol-water mixtures (1 – initial dimensions; 2 – first swelling; 3 – oven-dried; 4 – second swelling; 5 – oven-dried; 6 – third swelling)

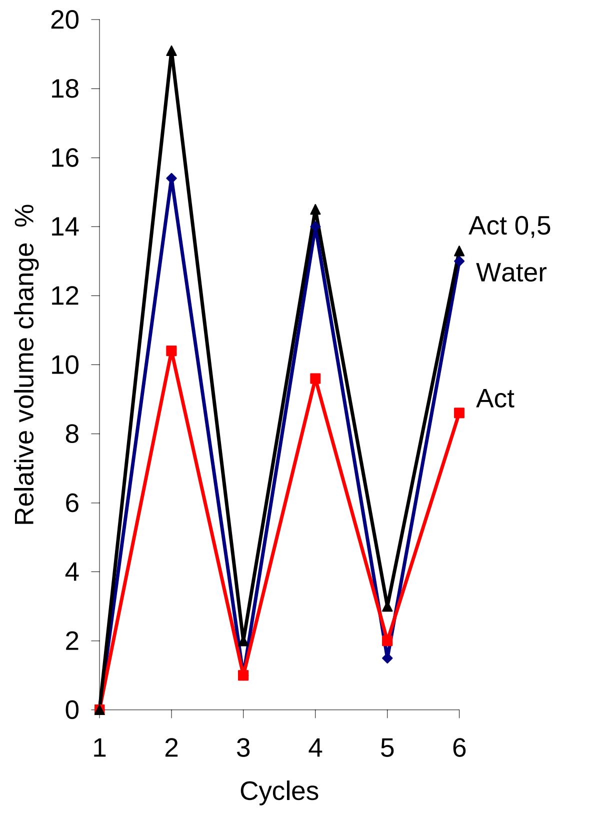

Fig. 3. Cyclic swelling of pinewood in acetone-water mixtures (1 – initial dimensions; 2 – first swelling; 3 – oven-dried; 4 – second swelling; 5 – oven-dried; 6 – third swelling)

changes occurred in aqueous solutions of both solvents (molar fraction 0.5) and least significant changes in pure solvents. After the first cycle of swelling in ethanol aqueous solution (ethanol-water, molar fraction 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 (acetone-water, molar fraction 0.5) were respectively 2 % and 3 %. Influence of binary mixtures on wood after first swelling caused the structural damages of cell wall.

Weight

If re-swelling caused the linear dimensions of samples to enlarge after every swelling-drying cycle in absolutely dry state (Fig. 2 and Fig. 3) reverse phenomenon occurred with wood mass. After swelling wood in water the mass in absolutely dry state (so called initial mass) remained like also after consecutive swelling-drying cycles. Changes in wood initial mass occurred after swelling in ethanol and acetone and in 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-ethanol aqueous solutions the change in mass was respectively 3…5 %. Decrease in mass as well as increase dimension twice was accordingly sustained in microscopic studies.

Microscopy study

A microscopy study was performed on specimens with largest swelling values after first swelling. Damping of these values was more rapid in case of multiple swelling with ethanol and acetone aqueous solutions (MF 0.5). The SEM micrographs of specimen repeatedly swelled in water and in acetone are presented on (Figs. 4 – 8) The changes developed after first cycle of swelling were discussed thoroughly in our previous work [7].

The alterations in cell wall structure did not depend on solutions used in multiple swelling – both old and new solutions caused similar changes in cell wall structure.

After multiple swelling of pine wood in water the cells were still densely packed and the compound middle lamellae (CML) formed continuous ribbon around the cells. The multiple drying between the swelling procedures and after the cry cutting had produced cracks in the cell wall clearly indicating the decrease in the elasticity of the wood matter.

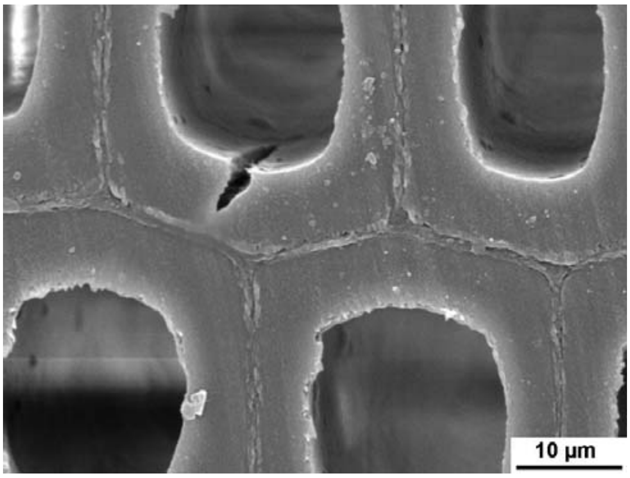

Fig. 4. The SEM micrograph of the cross section of wood swelled twice in water

Figure 5 demonstrates evidence that latewood cells have been so tremendously swelled in pure ethanol (96 %) that the normal matrix of cells has been completely distorted. The single swelling in ethanol did not generate a similar effect [7].

The enlargement of the cross-section of latewood cells swelled in pure ethanol showed the deliberation and disruption of the CML. This evidence is essentially different from the first swelling [7] of pine wood in pure ethanol. Presumably this effect was caused by the excess water (4 %) in ethanol that stimulated the remarkable swelling of wood cells.

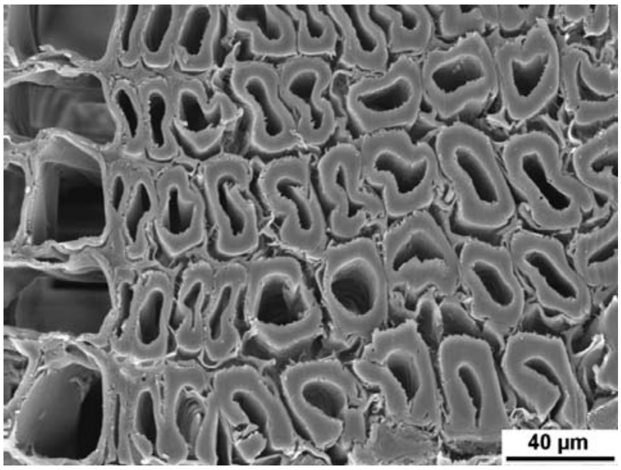

Fig. 5. The SEM micrograph of the cross section of wood swelled twice in ethanol

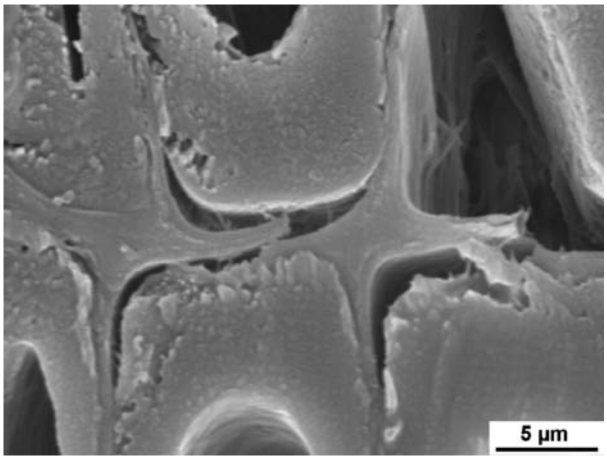

Fig. 6. The SEM micrograph of the cross section of wood swelled twice in ethanol

The last statement provided positive confirmation when observing the cross section of pine wood cells after multiple swelling in the mixture of ethanol-water.

The disruption of wood architecture due shown in Fig. 7 to the swelling in ethanol-water is very similar to Fig. 6. Only the rate of swelling is more expressive and the cell walls more distended. Therefore the influence of this small amount of water (4 %) in pure ethanol was revealed only after the multiple swelling.

Additionally the enlargement of the cell apexes showed deeper impact of the water in ethanol-water mixture. From Fig. 8 it is obvious that the CML is unbroken but mainly separated from the cell walls.

Acetone is known [11] to be a better solvent for separated lignin than ethanol, especially for the high molecular fragments. Currently lignin was not directly affected by acetone. As can be seen from Fig. 9, acetone has a mild effect on the cell wall structure and it's bonding to the CML. The fibrillar bonds between wood cell wall and CML were still present after the mechanical damage caused by the cutting knife edge.

Considerable effect, compared to the single swelling, appeared during the multiple swelling of the pine wood in the mixture of acetone-water. When single swelling did not reveal any substantial change in wood structure, multiple swelling caused noticeable swelling of the S_3 layer of the

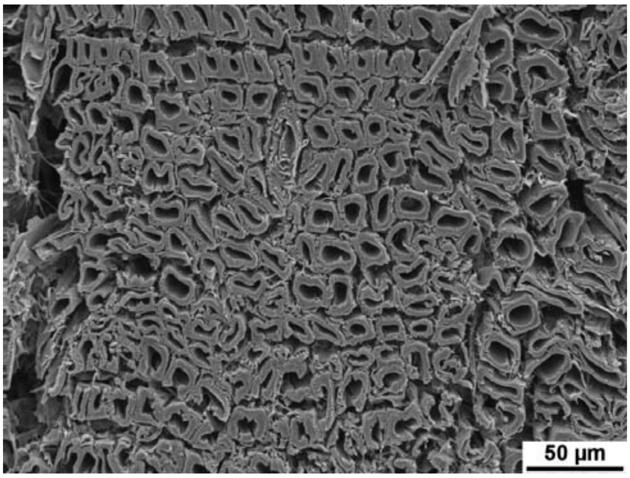

Fig. 7. The SEM micrograph of the cross section of wood swelled twice in ethanol-water (molar fraction 0.5)

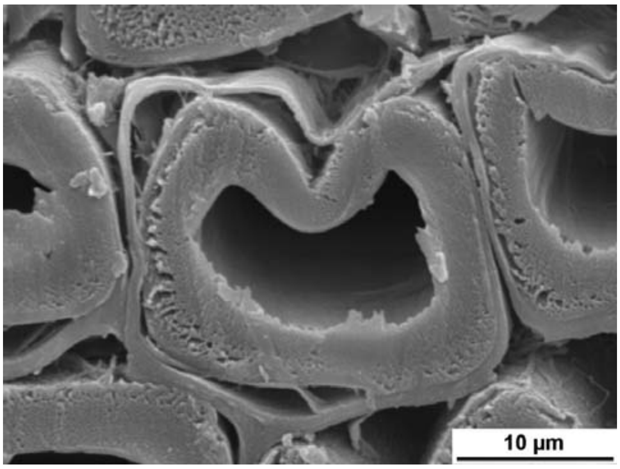

Fig. 8. The SEM micrograph of the cross section of wood swelled twice in ethanol-water (molar fraction 0.5)

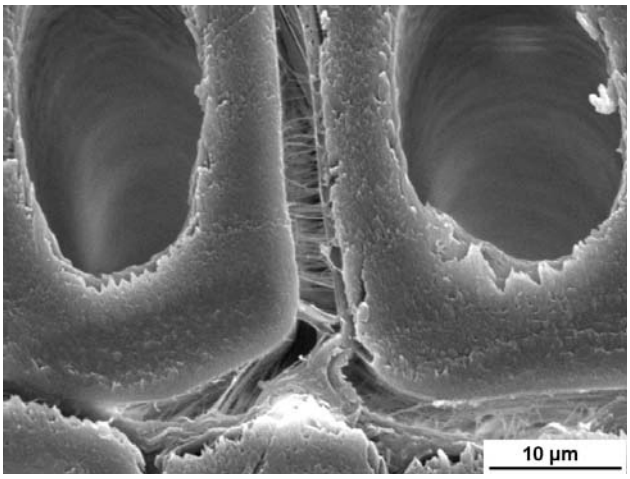

Fig. 9. The SEM micrograph of the cross section of wood swelled twice in acetone

cell wall. Consequently, during multiple swelling, water performed the role of preliminary swelling of S_3 and exposed lignin to the impact of acetone.

As shown in Fig. 11 after the third swelling in aqueous solution of ethanol (molar fraction 0.5) the middle lamellae and primary layer were separated, and due to shrinking within the structure of cell wall the continuation of further swelling process is irrelevant.

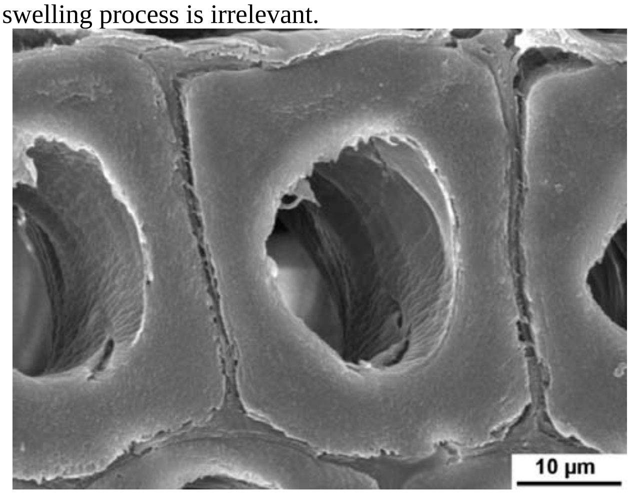

Fig. 10. The SEM micrograph of the cross section of wood swelled twice in acetone-water (molar fraction 0.5)

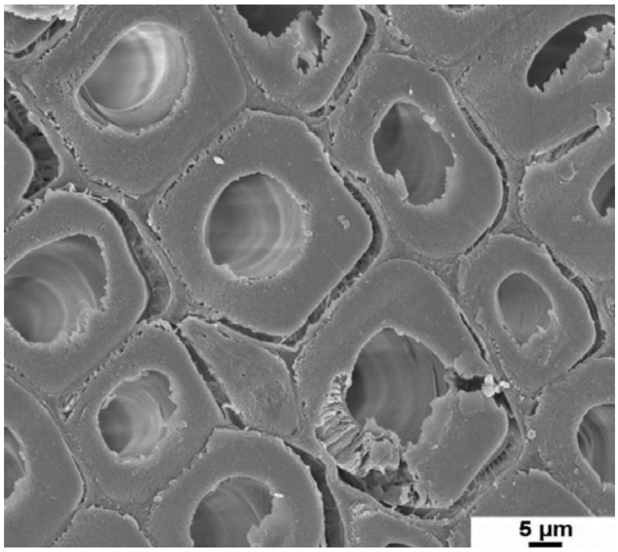

Fig. 11. The SEM micrograph of the cross section of wood swelled three times in ethanol–water (molar fraction 0.5)

CONCLUSIONS

Confirmation of the synergetic effects of binary and ternary mixtures has been obtained.

From the binary mixtures wood swelled most in ethanol aqueous solutions (molar fraction 0.4…0.6). Swelling values in acetone aqueous solutions were lower compared to the ethanol aqueous solutions. Synergetic effect occurred also with swelling in acetone aqueous solutions.

Adding third component to the solution decreased the swelling values stepwise. Lower values were in ternary mixtures with lowest possible water content (molar fraction of water 0.1).

Significant damping in swelling values occurred after first cycle of re-swelling. Damping in following cycles was more even.

The dimensions of wood increased with re-swelling however wood mass decreased compared to initial one. Remarkable changes can be detected after swelling in aqueous solutions.

After multiple swelling of pine wood in water the cells were still densely packed and the compound middle lamellae (CML) formed continuous ribbon around the cells.

In pure ethanol (96 %) the latewood cells were so tremendously swelled that the normal matrix of cells had been completely distorted. The enlargement of the cross-section of latewood cells swelled in the pure ethanol showed the deliberation and disruption of the CML. The close-up view of the cell apexes showed deeper impact of the water in ethanol-water mixture.

Acetone had a mild effect on the cell wall structure and it's bonding to the CML. The multiple swelling in acetone-water mixtures caused noticeable swelling of the S_3 layer of the cell wall.

FUTURE / PERSPECTIVES

It was detected that wood swelling in binary and ternary mixtures depends on specific organic substances and on concentration of the mixtures. Structure elements of wood cell walls were influenced by organic substances differently. Accordingly wood swells differently in various organic substances and their mixtures.

Therefore the structural changes of wood, wood cell walls and cellulose should be investigated applying alternative methods considering latest investigations of wood and cellulose swelling as well as investigation of water/organic substances mixtures at the macromolecular level.

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REFERENCES

1. **Mantanis, G. I., Young, R. A., Rowell, R. M.** Swelling of Wood. Part 1. Swelling in Water *Wood Science and Technology* 28 1994: pp. 119 – 134.
2. **Mantanis, G. I., Young, R. A., Rowell, R. M.** Swelling of Wood. Part 2. Swelling in Organic Liquids *Holzforschung* 48 1994: pp. 480 – 490.
3. **Morisato, K., Ishimaru, Y., Urakami, H.** Adsorption of Liquids and Swelling of Wood. Part VI. Saturated Amounts and Some Thermodynamic Values of Adsorptsion *Holzforschung* 56 2002: pp. 91 – 97.
4. **Ishimaru, Y., Iida, I.** Transverse Swelling Behaviour of Hinoki (*Chamaecyparis obtuse*) Revealed by Replica Method *J. Wood Sci.* 47 2001: pp. 178 – 184.
5. **Guyer, V. L., Hossfeld, R. L.** Interactions of Methanol-Water Binary Solutions with Wood *Holzforschung* 44 1990: pp. 157 – 161.
6. **O´Leary, P., Hodges, P. A.** The Relationship between Full Penetration Uptake and Swelling of Different Fluids *Wood Science and Technology* 35 2001: pp. 217 – 227.
7. **Meier, P., Kaps, T., Kallavus, U.** Swelling of Pinewood (*Pinus Sylvesteris*) in Binary Aqueous Solutions of Organic Substances *Materials Science* (*Medžiagotyra*) 11 (2) 2005: pp. 140 – 145
8. **Kollmann, F. F. P., Cote, W.,A.** Principles of Wood Science and Technology I. Springer Verlag, 1984.
9. **Naderi, N.**, **Hernandez, R. E.** Effect of Re-wetting Treatment on the Dimensional Changes of Sugar Maple Wood *Wood and Fiber Science* 29 1997: pp. 340 – 344.
10. **Rice, R. W., Peacock, E.** Acoustic Emissions Resulting from Cyclic Wetting of Southern Yellow Pine *Holz als Roh- und Werkstoff* 50 1992: pp. 304 – 307.
11. **Fengel, D., Wegener, G.** Wood: Chemistry, Ultrastructure, Reactions. Walter de Gruyter, Berlin, 1989.
12. **Klemm, D., Philipp, B., Heinze, T., Heinze, U., Wagenknecht, W.** Comprehensive Cellulose Chemistry, Volume 1, WILEY-VCH Verlag GmbH, 1998.
13. **Rowell, R. M.** Handbook of Wood Chemistry and Wood Composites. Taylor and Francis Group, 2005.