WOOD RESEARCH
57 (1): 2012
131-142

CHANGES IN STRENGTH PROPERTIES OF WOOD PULP AFTER TWO YEARS OF NATURAL DEGRADATION

Izabela Modzelewska, Magdalena Zborowska
Poznań University of Life Sciences
Poznań, Poland

Jozef Kúdela
Technical University in Zvolen
Zvolen, Slovak Republic

Leszek Babiński
Archaeological Museum in Biskupin
Biskupin, Poland

(Received October 2010)

ABSTRACT

This paper presents the results of the first phase of a research on changes in strength properties in cellulose naturally degrading (for two years) in peat soil and in water. The examined cellulose material manifested significant mass losses as well as changes in its chemical properties. Strength properties of the investigated material were found degraded considerably.

KEYWORDS: Cellulose, pulp, degradation, water environment, peat soil, strength properties, chemical properties.

INTRODUCTION

Wood in natural environment, for example, in soil or in water, undergoes degradation modifying the content and structure of the wood chemical constituents. The nature and intensity of these changes depend, to a considerable extent, on physico-chemical properties of the environment in which the wood has been stored (Hoffmann and Jones 1990, Hedges 1990). Conditions favouring the activity of microorganisms cause degradation of wood constituents and, consequently, decline in its strength properties, and total decomposition to carbon dioxide. Wood contains approximately 50 % cellulose, a constituent which exerts a decisive influence on wood strength properties. Changes in physico-chemical properties of this constituent, due to degradation processes, are the main cause of its deterioration. Therefore, it is necessary to understand the influence of the environment on changes observed in cellulose – for providing

information about the impact of the given environment on wood and, from a wider perspective – asses the chances for its preservation in specific conditions.

Among products obtained from wood are various kinds of pulps containing 80–95 % cellulose (depending on the method of its production). Cellulose degradation causes decline of dynamic properties of this material (Kačík et al. 2009), and in the case of its long storage – total decomposition (Jakucewicz 1990).

Strength properties of pulps exert a decisive influence on paper mechanical strength. These properties are evaluated in the laboratory with strength tests carried out on small paper sheets hand made from the pulp ground to a definite degree. These tests simulate the impact of forces to which paper can be exposed in performance. There are determined the following parameters: tensile strength, breaking length, stretchability, tearing resistance (resistance to tear) and bending strength. If necessary, some other parameters such as hardness, rigidity and resistance to bending or torsion strength are also determined (Przybysz 1997).

The study presented in this paper was performed within a research project studying the effect of natural degradation (after several years of storage in peat soil or water) on lignocellulosic material. The project is carried out at the Archaeological Museum in Biskupin. Apart from unbleached pulp, identical experiments are currently being performed on bleached pulp material as well as on pine and oak wood material (Babiński et al. 2006; Modzelewska et al. 2007, Zborowska et al. 2007a,b). The experimental material was stored for the period of 10 years in two different places – with the purpose to observe its multi-stage degradation. Changes taking place in the experimental material will be examined at two-year intervals from the moment of its placement in the specific environment.

This paper presents research results concerning physico-chemical and strength changes in unbleached pulp from the first stage of experiments, i.e. two years from the beginning of the study.

MATERIAL AND METHODS

Experimental material

The experimental material consisted of sheets of pine unbleached kraft pulp (origin: Mondi Packaging Świecie S.A.) 20 x 20 cm in size (200 ± 5 $g.m^{-2}$) having been stored for 2 years in the archaeological site No. 4 in Biskupin. The experiment was running in physico-chemical environmental conditions typical for the Biskupin peninsula in which the also the studied archaeological wooden materials have been buried. The examined pulp was removed from water environment (a archaeological trench filled with water in the north-western part of the peninsula) and from peat soil (from the depth of 100 cm in the central part of the peninsula). In order to prevent contamination due to the direct contact with peat, sheets of pulp were kept in bags made of agro-fabric allowing free water access.

The pulp after two years of storage has preserved its original colour and compact structure. Visible changes were observed only within 5 mm sheet borders which have turned dark-brown coloured and fragile in structure. For purpose of our research, the decomposing borders were called the external (degraded) zone; the intact internal area was called the internal zone (undegraded). Experiments considering chemical properties (solubility and content of α-cellulose) were carried out on four sheet series corresponding to the individual storage variant (water and wet peat) as well as the degree of degradation (external and internal zones).

The comparative material (original/reference cellulose) to which the obtained results were referred was cellulose stored in standard conditions in a closed, air-conditioned room with

44 ± 5 % air humidity and 20 ± 2°C temperature.

The experimental sheets were made in laboratory conditions with a Rapid-Köthen apparatus from undegraded (reference, stored in standard conditions) and degraded (stored for 2 years in peat and water) pulp milled (PFI mill) to a beating degree of 30 ± 1 °SR. During grinding as well as in the course of defibering in a separator-defibrator, considerable foaming was observed in the pulp stored in peat as well as that stored in water (Fig. 1). Usually, such phenomenon indicates improper washing of the pulp after digestion; however, during milling the original/reference pulp no foaming was observed.

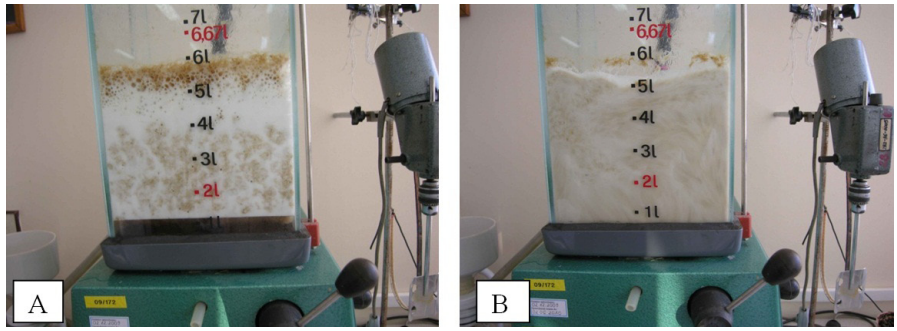

Fig. 1: Example photograph showing cellulose pulp stored in water environment for the period of two years: A) – before and B) – during defibering.

Research methodology

This experiment comprised:

- determination of the mass loss of the pulp,
- determination of selected chemical properties (solubility and proportion of α-cellulose),
- determination of selected strength properties,
- microscopic examination.

The mass loss of the pulp stored for two years in natural environment was calculated according to the following formula:

$$ML = \frac{m_0 - m_1}{m_0} \times 100$$

where: ML - mass loss (%),
m_0 – absolutely dry mass of pulp before deposition (g),
m_1 – absolutely dry mass of pulp after 2-year deposition (g).

Determination of selected chemical properties of the experimental pulp included the following assays:

- concentration of substances soluble in hot water according to TAPPI cm-08,
- concentration of substances soluble in 1 % NaOH according to TAPPI cm-07,
- concentration of substances soluble in 1 % H_2SO_4 was determined in the same way as the content of substances soluble in 1 % NaOH except that the hydroxide was replaced by appropriate acid,
- proportion of α-cellulose according to TAPPI T203 cm-09.

Assays of basic strength properties of the examined cellulose pulp as well as paper sheets manufactured from it were determined in keeping with the standards given below:

- grammage: PN ISO 536, 1996,
- breaking length, stretchability, TEA, longitudinal rigidity: PN ISO 1924-3, 2005,
- burst: PN EN ISO 2758, 2005,
- relative tear = tear resistance: PN EN21974, 2002,
- SCT (short column in-plane compression test): PN ISO 9895, 2002.

For microscopic observations was used a TESCAN VEGA 5130 electron microscope.

RESULTS AND DISCUSSION

Mass loss

Investigation aiming at determining mass losses of unbleached cellulos pulp subjected to the action of natural conditions in the archaeological site No. 4 in Biskupin showed that during the two-year exposure to conditions of wet peat and water on average 21 and 22 % of the examined material underwent total degradation and/or dissolved.

Chemical properties

The results of analysis of chemical properties of the studied bulk cellulose are presented in Tab. 1. The material left for two years in conditions of archaeological wood showed the percentage proportion of constituents soluble in water ranging from 1.8 to 4.6 %. The lowest proportions of the discussed constituents (close to 2 %) were determined in internal zones (i.e. undegraded) of the examined pulps both immersed in water and stored in wet peat. Comparing these results with those obtained for the reference cellulose pulp – 1.8 % – it can be said that in the case of internal zones, solubility did not change during the two years of experiment. Increased proportions of substances soluble in water were observed in both variants of strongly degraded external zones. In the case of the external zone stored in wet peat, 2.8 % of the discussed constituents were determined, whereas in the case of the degraded material stored in water – 4.6 %.

Tab. 1: Results of determination of selected chemical properties of cellulose pulps used in the experiment.

Cellulose pulp		Substance soluble in:			α - cellulose
		Hot water	1 % NaOH	1 % H_2SO_4	
		(%)			
Control		1.8	4.2	3.6	84.2
Removed from peat soil	External zone	2.8	10.3	11.2	77.0
	Internal zone	1.8	10.6	10.5	82.2
Removed from water	External zone	4.6	13.7	13.0	77.5
	Internal zone	2.1	10.3	11.3	81.7

The next studied property was solubility in 1 % sodium hydroxide. It was found that in this case, 10.3 to 13.7 % of the cellulos pulp exposed to natural degradation dissolved (Tab. 1). The highest solubility in alkalis was observed in the case of the external (degraded) zone of the pulp immersed in water. In the internal zone of the same material (i.e. undegraded), 10.3 % of the examined cellulose dissolved. Similar results were recorded in the case of both external

and internal zones of the pulp removed from wet peat. Comparing the above results with those obtained for the control pulp – 4.2 % – it can be concluded that processes that took place during the storage of the examined material in the natural environments (both water and wet peat) contributed to a significant increase of constituents soluble in alkaline solution.

A similar tendency was observed in the case of proportions of substances soluble in 1 % H_2SO_4. In the case of the control cellulose pulp, the applied acid was found to dissolve 3.6 % of the material, while in the case of the material left at the archaeological site, it dissolved much more of its constituents – from 10.5 to 13 %. As before, the highest proportion of the examined fraction was recorded in the degraded zone of the pulp stored in water. In the case of the material left in wet peat, substances that dissolved in the applied acid constituted 11.2 % for the external (degraded) zone and 10.5 % – for the internal (undegraded) zone.

The percentage proportion of α-cellulose in the cellulose pulp was closely connected with the strength of the examined material, since this cellulose fraction has a significant impact on strength properties of paper and paper products. The quantity of α-cellulose found in the reference pulp amounted to 84.2 % and was typical for this cellulose fraction in the discussed raw material. Similar results differing only by 2–3 % were observed in the case of internal (undegraded) pulp stored in conditions of wood deposits. Distinct changes were recorded, however, in the case of external (degraded) zones of the examined materials where, in both variants, percentage proportions of α-cellulose dropped to about 77 %.

Selected properties

Figs. 2–4 present the results of selected strength properties of paper sheets manufactured from the studied cellulose. In all three variants of the experiment, the paper sheets had similar grammage (100 ± 2 $g.m^{-2}$) and the beating degree of the material from which they were prepared in the laboratory (30 ± 1 °SR).

The obtained values of breaking length of the original cellulose as well as the material removed from the archaeological site (Fig. 2), show a very significant drop of resistance of the experimental material, both stored in water and in peat soil. Progressive cellulose degradation, irrespective of the place of storage, caused a decline of the material resistance expressed through breaking length by 52 % in the case of "peat" cellulose, and by up to 62 % – of "water" cellulose in comparison with to the original material. The breaking length of paper sheets made from the original pulp was assessed at 8.53 km, in the case of degraded cellulose stored in peat soil – 4.06 km, and of cellulose kept in water – only 3.24 km.

The products made from degraded cellulose manifested markedly lower strength compared to the reference. For instance, in the case of the assessment of SCT resistance, the obtained values were as follows: control cellulose: 3.737 $kN.m^{-1}$, peat degraded cellulose: 2.735 $kN.m^{-1}$ and water degraded cellulose: 2.732 $kN.m^{-1}$ (practically there was no difference between the two degraded types).

The best stretchability was obtained in paper manufactured from the original cellulose: 2.87 % (Fig. 2), followed by the paper from "peat" cellulose – 1.81 % and "water" cellulose with its resistance of 1.19 %.

A similar tendency was observed for the tear resistance and longitudinal rigidity. The "peat" cellulose achieved the value of 571.5 mN, while in the case of the cellulose degraded in water environment; this resistance fell to only 416.2 mN (Fig. 2).

The highest values of longitudinal rigidity were determined for paper sheets made from the reference cellulose – 782.75 $kN.m^{-1}$ and the lowest – for paper sheets made from degraded cellulose stored in water environment – 523.09 $kN.m^{-1}$ and the difference amounted to about 34 %.

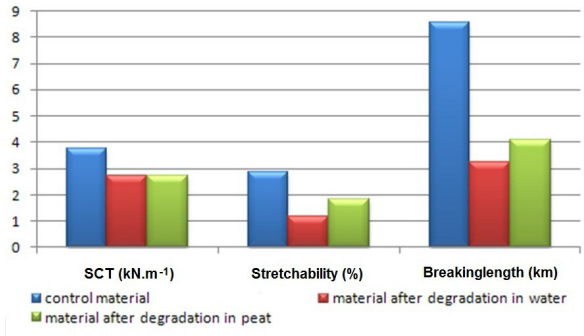

Fig. 2: Diagram presenting results of SCT, stretchability and breaking length in the control material and in the material after degradation in water and in peat.

Also the comparison of the resistance to burst of the paper articles manufactured from cellulose degraded in water and wet peat revealed that in comparison to the reference cellulose, the values of these parameters were lower by 68–79 %, respectively (Fig. 3).

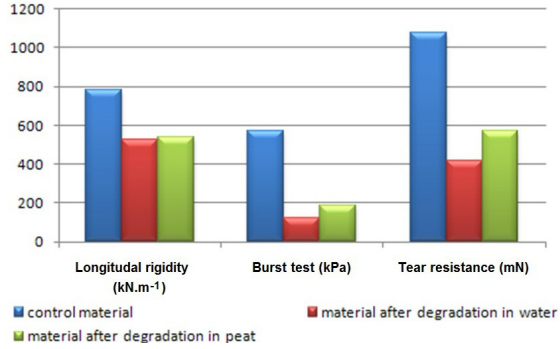

Fig. 3: Diagram presenting results of evaluation of: longitudinal rigidity, burst and tear resistance in the control material and in the material after degradation in water and in peat.

The lowest results for TEA – 26.15 J.m^{-2} were recorded for cellulose stored in water – although they could be expected for cellulose degraded in peat – 51.41 J.m^{-2} (Fig. 4). Changes in the chemical composition of the degraded cellulose were probably responsible for the reduced absorption capacity of the entire system.

The values of air permeability of the examined paper sheets manufactured from the reference material and the material degraded in water were similar (control material – 46.24 sec., material after degradation in water – 37.59 sec.), whereas the material subjected to degradation in wet peat environment was characterised by a much lower value (14.5 sec.).

The comparison of measurement results of strength parameters of paper sheets made from the studied cellulose types reveals a distinct declining tendency from the control cellulose, through cellulose degraded in wet peat and, finally, degraded in water environment (Figs. 2, 3, 4).

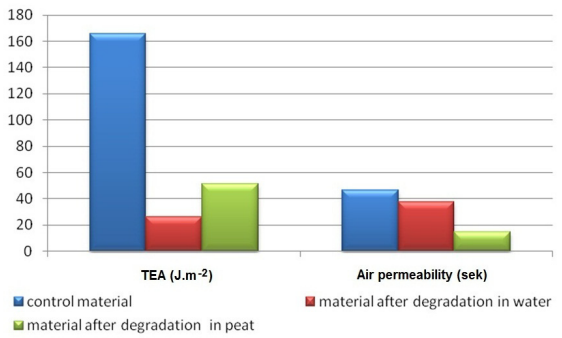

Fig. 4: Diagram presenting results of evaluation of: TEA and air permeability in the control material and in the material after degradation in water and in peat.

Microscopic examination

Significantly worsened mechanical properties of the pulp buried in anaerobic conditions for two years indicate changes to the pulp structure. These changes are of two types – impaired hydrogen bonds between the fibres due to pulp swelling, and cell wall degradation associated with enzymatic decomposition of the cell wall itself. There cannot be excluded cellulose degradation by abiotic factors, including alkaline water, in which the test material was left (Babiński et al. 2007)

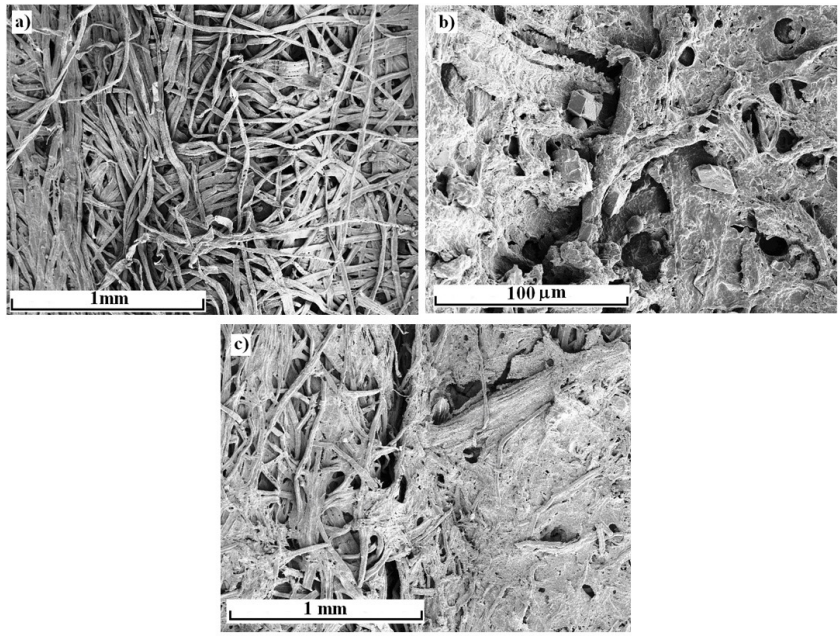

Fig. 5: Pulp surface. a) control sample, b) sample buried for 2 years in water, c) sample buried for 2 years in peat soil.

Pulp is a complex mixture of pressed cellulose fibres (Fig. 5a) interconnected by means of hydrogen bonds. Water penetrating among cellulose fibres impairs the bonds that hold them together (Bučko 2001). There are also impaired hydrogen bonds connecting the fibrils. Sediments observed on surface of many pulp samples buried in water as well as in peat soil (Fig. 5b, c) hindered restoring of these bonds in case of reverse drying. The sediments were observed on the sample surface only. They did not penetrate inside the samples.

The second type of disturbance was caused by destructive impacts of anaerobic conditions and bacteria. This type was observable mostly on pits in tracheids and parenchyma cells (Fig. 6). Mainly on the sample surface but also inside the samples (Fig. 7) thick about 2 mm was also observed a similar phenomenon in the case of pine archaeological wood (Babiński et al. 2002).

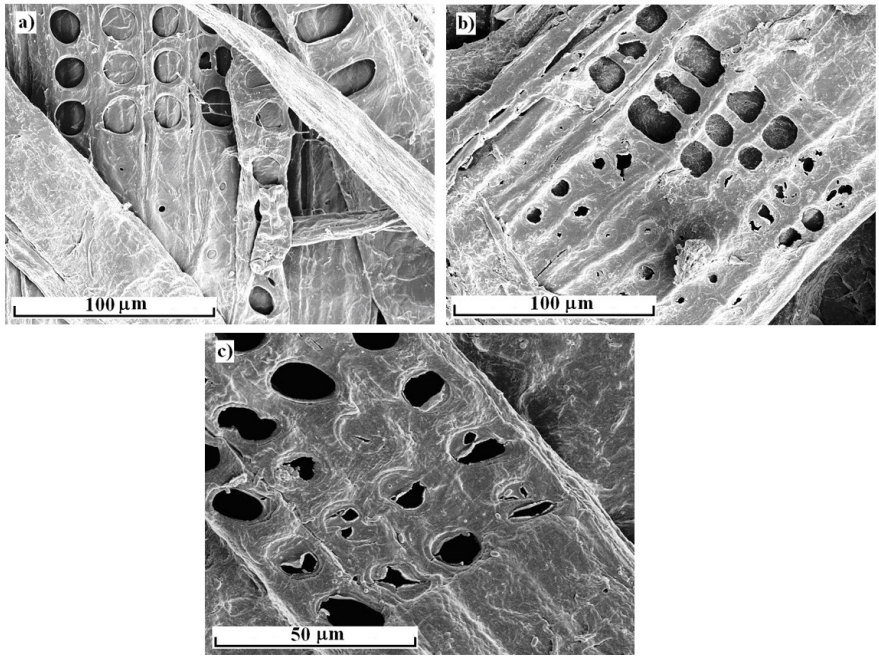

Fig. 6: Cross fields. Pits of the samples buried in anaerobic conditions show decomposition symptoms a) control sample, b) sample buried for 2 years in water, c) sample buried for 2 years in peat soil.

The surface of pulp buried in peat soil also manifested presence of fungal hyphae (Fig. 8a) and enzymatic decomposition of cell walls and bordered pits in their neighbourhood (Fig. 8b, c). Cellulose fibres near the hyphae were very fragile – see the cracks across micro-fibrils (Fig. 9a, b).

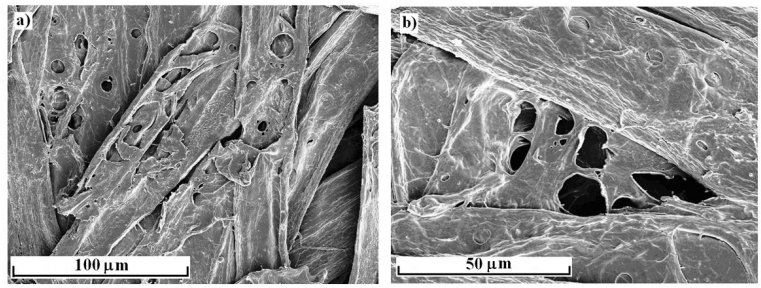

Fig. 7: Impaired pits inside a sample. a) sample buried for 2 years in water, b) sample buried for 2 years in peat soil.

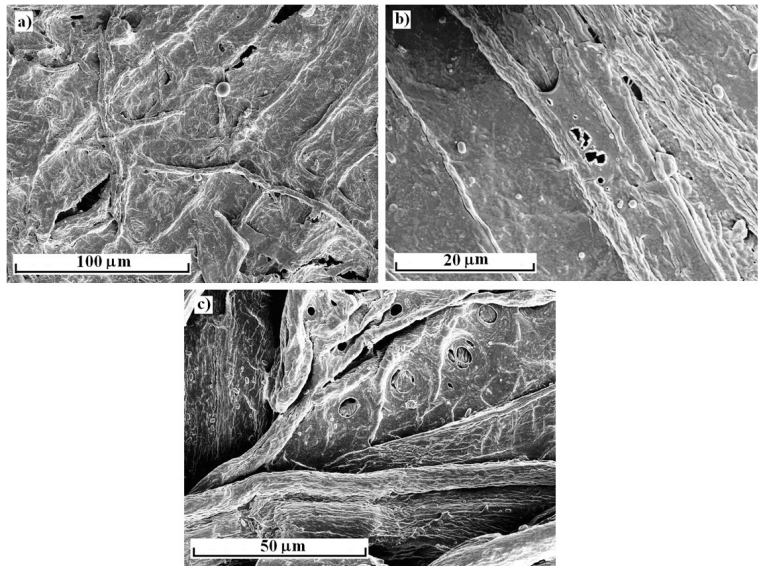

Fig. 8: Fungal hyphae on pulp surface and enzymatic decomposition of cell wall and pits.

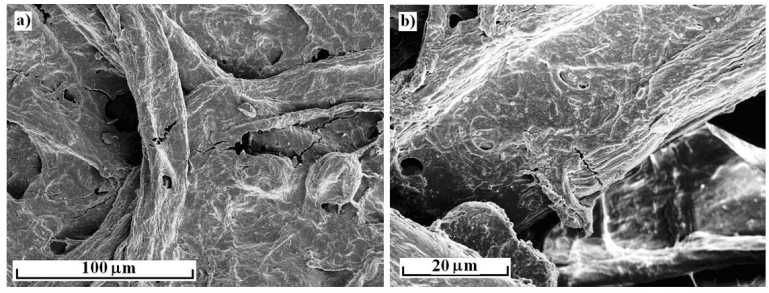

Fig. 9: Cracks across cellulose fibres confirm their degradation by fungi.

The impaired hydrogen bonds between cellulose fibres and the cell wall degradation can be supposed to be the primary cause of worsened mechanical properties of the studied pulp.

CONCLUSIONS

In all experimental treatments, strength properties of paper sheets manufactured from cellulose after degradation, irrespective of whether the process occurred in water or in wet peat environment, impaired significantly in comparison with the samples obtained from the reference cellulose. The lowest values were obtained for the cellulose stored for the period of 2 years in water.

It is not possible to attribute the observed decline in strength properties of the experimental material to changes that occurred in the chemical composition of the cellulose system during the two-year period of deposition in peat soil. The main chemical changes that did take place occurred in the external zone. Smaller changes appeared in the internal part, which constituted about 95 % of the sheet area. The degradation of the above mentioned properties can partly be blamed on microorganisms, among others, bacteria in water and peat soil, and fungi in peat soil which we observed under a microscope. However, it seems that the main cause of such considerable degradation of strength properties was the disruption of bonds between cellulose fibres during swelling of cellulose pulp in water environment. Fibrous materials exhibit considerable capability for gas, liquid and solid sorption, and for very rapid swelling. In the case of plant fibrous semi-finished products, water which penetrates deep into the fibres weakens or breaks cross linkages between fibrils of the cell wall. Bonds between cellulose fibres and micro- and macrofibrils are weakened. The swelling process of fibrous semi-products is of intercrystalline nature. Plasticised, flexible and swollen cellulose fibres are more resistant to fibre shortening during grinding.

In the paper manufacturing process, water is a very important chemical agent. A special attention is to devote to the interaction of water polar molecules with cellulose and hemicellulose hydrocarbon groups in breaking up and creating hydrogen bonds. Split hydrogen bonds occurring inside the fibres during the milling process – provide, in such a way, preconditions for internal and external fibrillation. Indispensible elements of this process include water polar molecules which, by breaking hydrogen bonds between structural fibre elements, reduce the stiffness of ground fibres, and allow them to achieve appropriate structural and strength properties required for the manufactured paper.

The advancing external and internal fibrillation during grinding as well as long period of storage of the experimental material in water or in wet peat caused additional disruption of the fibre structure in the degraded material.

REFERENCES

1. Babiński, L., Kúdela, J., Kokociński, W., 2002.: Archaeological softwood. Part I. Structur and properties. In.: Wood structure and properties´02. (Eds. Kúdela and Kurjatko), Zvolen, Arbora Publishers 2002, Pp. 73–80.
2. Babiński, L., Zborowska, M., Gajewska, J., Waliszewska, B., Prądzyński, W., 2006: Decomposition of the contemporary oak (*Quercus* sp) in conditions of the wet archaeological site in Biskupin. Folia Forestalia Polonica, Seria B – Drzewnictwo 37: 9-23.

3. Babiński, L., Fejfer, M., Prądzyński, W., 2007: Environmental monitoring at the Lusatia culture settlement in Biskupin. Poland, Journal of Wetland Archaeology 7: 51-72.
4. Bučko, J., 2001: Chemical processing of wood. (Chemické spracovanie dreva). Zvolen, Technická univerzita vo Zvolene, 427 pp. (In Slovak).
5. Hedges, J.I., 1990: The chemistry of archeological wood. In: Archeological Wood – Properties, Chemistry and Preservation (Eds. R.M. Rowell and R.J. Barbour), Pp. 112-140, American Chemical Society, Washington.
6. Hoffmann, P., Jones, M.A., 1990: Structure and degradation process for waterlogged archeological wood. In.: Archeological Wood – Properties, Chemistry and Preservation (Eds. R.M. Rowell and R.J. Barbour), Pp. 35-65, American Chemical Society, Washington.
7. Jakucewicz, S., 1990: Raw materials used in the paper manufacture and their resistance to aging. (Surowce stosowane do produkcji papieru i ich odporność na starzenie). Archiwa, Biblioteki i Muzea Kościelne 59: 179-187. (in Polisch).
8. Kačík, F., Kačíková, D., Jablonský, M., Katuščák, S., 2009: Cellulose degradation in newsprint paper ageing. Polym. Degrad. Stab. 94(9): 1509–1514.
9. Modzelewska, I., Zborowska, M., Prądzyński, W., Kasprzak, K., 2007: Changes of selected mechanical properties of cellulose after two years of natural degradation. (Zmiany wybranych właściwości wytrzymałościowych celulozy podwuletnim okresie naturalnej degradacji). Rocznik AR 42: 11-19. (in Polisch).
10. Przybysz, K., 1997: Pulp and paper technology. Vol.2. Technology of paper. (Technologia celulozy i papieru. cz. 2. Technologia papieru). Wyd. Szkolne i Pedagogiczne, Warszawa, 278 pp. (in Polisch).
11. Zborowska, M., Modzelewska, I., Prądzyński, W., Waliszewska, B., 2007a: Evaluation of changes in the cellulose system following a two-year period of deposition in an archaeological site in Biskupin. W: Selected Processes at the Wood Processing, Zvolen, 2007, poster.
12. Zborowska, M., Babiński, L., Gajewska, J., Waliszewska, B., Prądzyński, W., 2007b: Physical and chemical properties of contemporary pine wood (*Pinus sylvestris* L.) in conditions of a wet archaeological site in Biskupin. Folia Forestalia Polonica, Seria B – Drzewnictwo 37: 9-23.

Izabela Modzelewska, Magdalena Zborowska
Poznań University of Life Sciences
Wojska Polskiego 28
60-637 Poznań
Poland
Corresponding author: izabelajanicka@poczta.fm

Jozef Kúdela
Technical University In Zvolen
T. G. Masaryka 24
960 53 Zvolen
Slovak Republic

Leszek Babiński
Archaeological Museum In Biskupin
Biskupin
Poland