University of Sopron

Simonyi Károly Faculty of Engineering, Wood Sciences and Applied Arts

Cziráki József Doctoral School of Wood Science and Technologies

Theses of the doctoral (PhD) dissertation and bibliography

Modification of the properties of natural wood by thermo-hydro-mechanical and chemical processes

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INTRODUCTION AND OBJECTIVES

A process was developed to replace and improve the technology of Thonet steam bending, to provide wood that can be bent even at room temperature. It was the compression of wood parallel to the grain, patented in 1917. The first patent for this process was followed by several other patents, and today the industrial technology is available as an electronically controlled hydraulic system. Since 2015, a laboratory compression tool connected to an Instron 4208 universal material testing machine has been operating at the University of Sopron. With the custom-designed tool, many tests can be performed during compression, which was not possible in previous researches. Wood samples measuring $20 \times 20 \times 200$ or $20 \times 30 \times 200$ mm (tangential direction × radial direction × fiber direction) can be compressed in the longitudinal direction with up to 33% of their original length. The side walls of the semi-closed tool are heated; their position is adjustable and can move with the sample as necessary. At the macroscopic level, the properly performed longitudinal wood compression does not cause visible changes. Therefore, its product can be used for any purpose, while microscopically the waviness/pleating of the originally smooth cell walls can be observed.

The environmentally friendly, free of chemicals longitudinally compressed (aka pleated) wood is suitable for furniture parts (legs, armrests, backrests, and edge bandings), interior design elements (handrails, wall coverings), sports equipment, vehicle parts and instrument elements, and for use in restoration and other work.

There have been a lot of questions about pleated wood. The dissertation seeks to expand the available knowledge with a wide range of new knowledge, to present several of the most recent research types in addition to the basic research topics:

- revising and validating certain results in the literature
- conducting basic researches that have been missing so far (e.g. spring-back, equilibrium moisture content, and shrinkage-swelling)
- studying the effects of pleating, using new research possibilities (cell structure in 3-dimension and chemical functional groups)
- the large deterioration of dimensional stability is a serious problem; its elimination was also a research goal (impregnation with lactic acid).

MATERIALS AND METHODS

The first phase of pleating is the plasticisation of wood in saturated steam. Softened wood must be kept hot and moist until compression is complete. The most commonly used longitudinal compression treatment induces a 20% deformation compared to the original length of the sample. This compression ratio also found to be suitable for beech (*Fagus sylvatica* L.) and sessile oak (*Quercus petraea* (Matt.) Liebl.) wood species used in our studies. Low-density wood species cannot be compressed because their cell structure fails even at low compression level. Two main procedures are used: first, when the compression is complete, the modification process ends, and the samples are immediately ready for use. In the other method, wood is held in a compressed state for some time after compression, to form fixed samples.

As a result of the pleating of hardwoods, the bending modulus of elasticity is significantly reduced, which indicates a high degree of pliability (bending, twisting). The properties of pleated wood are most affected by the following factors:

- compression ratio
- fixation time
- moisture content at use.

In addition, the wood species, its tissue properties, the rate of compression, the initial moisture content before compression, and countless other factors influence the final result of pleating.

During tests, we always strived for objectivity, repeatability and if possible, the application of standard methods. Further information on the materials and methods used will be provided when presenting the results of the specific research.

RESULTS AND THE THESES OF THE DISSERTATION

Thesis 1: Fixation and its physical-mechanical effects
Fixation is keeping the sample at a constant size after compression. Fixation amplifies the physical-mechanical effects of compression. The shortest recommended fixation period is 1 minute, which increases the maximum deformation during 4-point bending tests to 353%, the modulus of elasticity to 37%, and the bending stress to 44% compared to untreated samples. With several hours of fixation, the bendability of wood increases above 600% (Báder and Németh 2018a). The results of the samples fixed for 3 hours, 5 hours and 18 hours are almost the same.
Furthermore, the change of the compressive stress during fixation and the remaining shortening indicate the extent of the changes in the properties of the sample with a good correlation (Báder and Németh 2018a).

In general, during fixation the compressive force initially decreases rapidly and then the decrease gradually slows down, but continues even after hours when the sample has cooled down. After 20% longitudinal compression, the remaining shortening increases with the fixation time (Figure 1). The wood undergoes structural changes, especially in the first minute of fixation. Pliability improves and mechanical properties typically deteriorate. Based on the observations, the beech samples always have a higher spring-back − i.e. a smaller remaining shortening − compared to the oak samples. The generally recommended minimum fixation time is 1 minute, which is an ideal combination of economical production and increased pliability. Depending on the special requirements of the product, both the compression ratio and the fixation time can be increased.

Using the determined correlations, if we know the properties of some samples, we can specify the pliability of the whole population with high certainty. Based on the change in the compressive stress, this is already possible during the fixation process, or later, based on the remaining shortening. Both can be used to make predictions to determine the maximum pliability of samples made from the same raw material in a similar way.
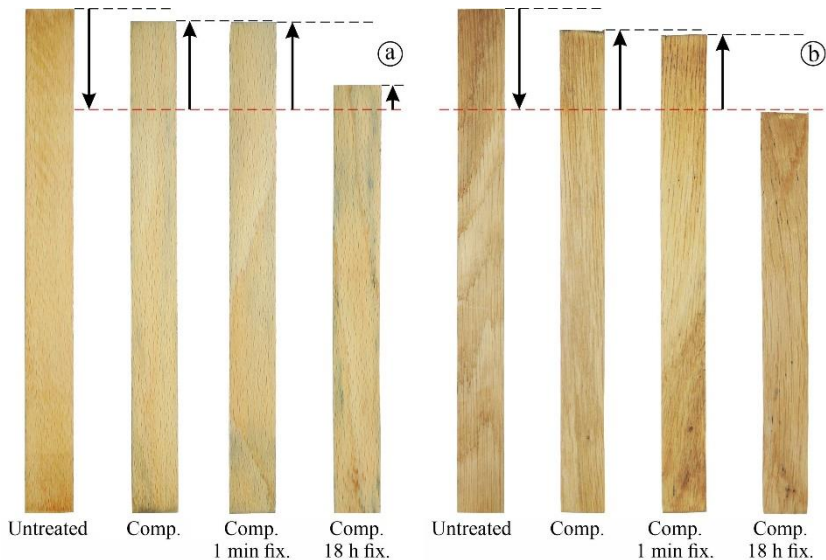
Figure 1 Remaining shortening of beech (a) and oak (b) samples as a result of longitudinal compression by 20% (red line) and different fixation times. From left to right, respectively: untreated; compressed; compressed and fixed for 1 minute; compressed and fixed for 18-hour samples

Thesis 2: Micromechanical changes

As a result of longitudinal compression and fixation for a long-time, mechanical properties at the cell-level change significantly. The measurements demonstrated that the indentation modulus of the S2 cell wall layer decreases by 48%, which is explained by the misalignment of the microfibrils. In the S2 cell wall layer, the total deformation work increases by 14% and change towards higher elasticity (Báder et al. 2019).

After 20% longitudinal compression and fixation for a long-time, the indentation modulus of the secondary cell wall S2 was examined parallel to the grain. The treatments resulted in greater flexibility and less ductility at the cell wall level compared to untreated wood. Macromechanical changes, which are the result of buckling of cell walls, outweigh the micromechanical changes that cause opposite behaviour. Analysing the nanoindentation results, oak and beech samples show similar micromechanical changes and trends as a result of the treatment.

The S2 cell wall layer of fibers is composed of a tissue of microfibrils. At the ultrastructural level, AFM images showed 3 dimensional microfibril disorientation as a result of pleating (Figure 2). This results in the weakening of the cell walls.
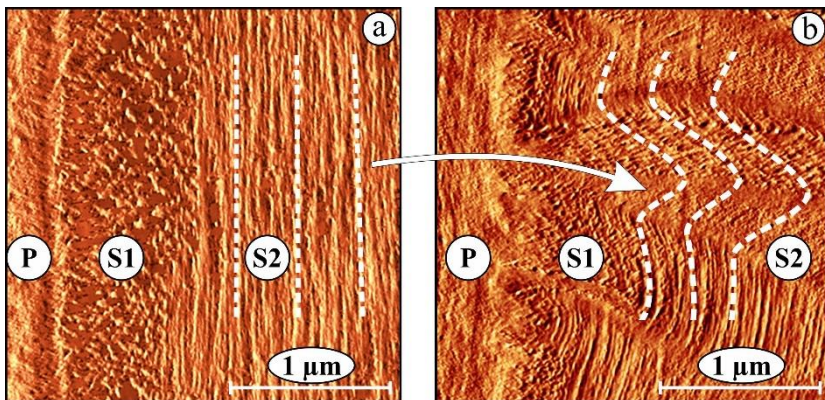
Figure 2 Images of a fiber cell wall of an untreated (a) and a longitudinally compressed oak specimen exposed to long fixation time (b) made by atomic force microscope. The dashed lines indicate the microfibril direction in the S2 layer cell wall (based on Báder et al. 2019). Abbreviations: P – primary cell wall; S1 and S2 – layers of the secondary cell wall

Thesis 3: Properties of the wood tissue
The spring-back of wood takes place within 3 minutes after pleating (Báder and Németh 2020). After compression, the vessels appeared intact, while the walls of the fibers were slightly wavy. For samples fixed for a long-time, strong distortions appeared both on the walls of vessels and fibers. Smaller fiber lumina and pits often completely disappeared (Báder and Németh 2018a). Upon fixation for a long-time, the waves of the cell walls intrude into the cell lumina. But unlike vessels, fibers are deformed significantly near the thin-walled parenchyma cells. The height of the ray cells is reduced by 25% and the fibers can be shortened by up to 20%.

After 20% compression of oak samples, they were fixed for 1 minute. The weight and length of the samples were monitored continuously after the end of the treatment. The effect of spring-back is stress reduction, which may be the reason for the longitudinal increase of the samples. After the compression forces ceased, the samples regained most of their original length in the first few seconds, and then their length remained constant in the period between 3 and 120 minutes.
Images made by scanning electron microscope show the typical effects of pleating on vessels and fibers (Figure 3). Images of buckled fibers by pleating have not been appeared so far in scientific publications. We used X-ray micro-computed tomography (XµCT) for non-destructive, three-dimensional analysis of the tissue of oak samples compressed and fixed for a long-time. Quantitative analysis of the cells was performed using different sieve thresholds.
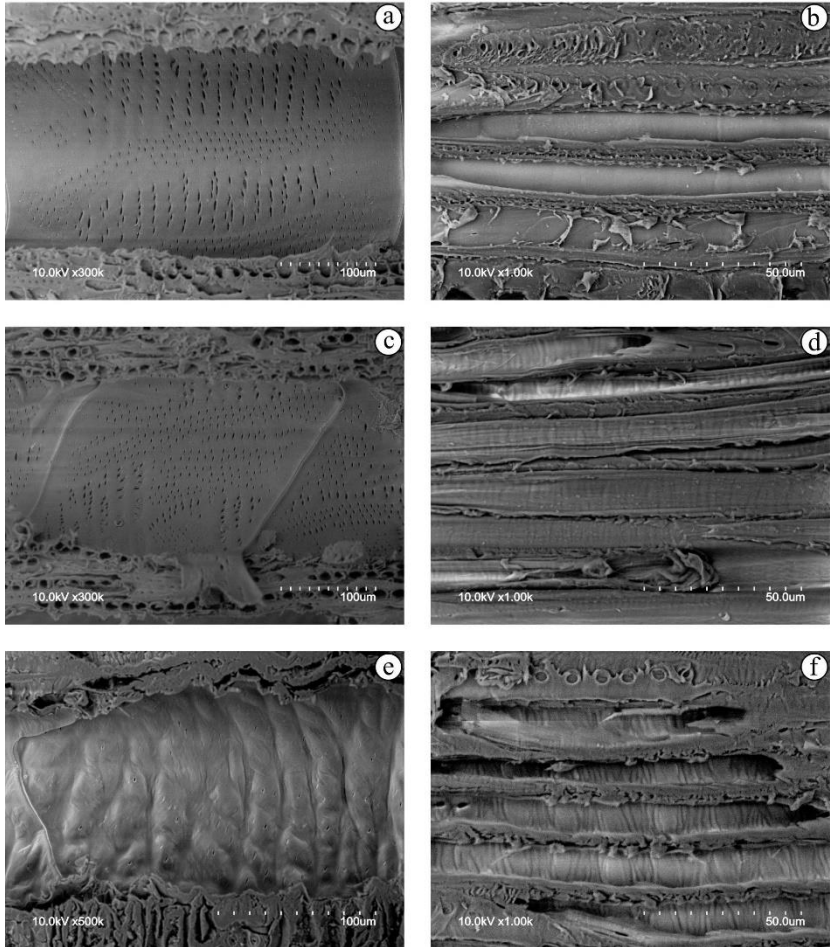
Figure 3 Images of oak wood made by scanning electron microscope: untreated vessel (10 kV ×300; a), untreated fibers (10 kV ×1000; b), vessel compressed and not fixed (10 kV ×300; c), fibers compressed and not fixed (10 kV ×1000; d), vessel compressed and fixed for a long-time (10 kV ×500; e), fibers compressed and fixed for a long-time (10 kV ×1000; f)

Thesis 4: Changes in the wood-water relations
Pleated samples shrink by 0.4% in the direction parallel to the grain with the decrease of moisture content in the range above the fiber saturation point due to the new chemical bonding points formed on the increased cell wall surface (Báder and Németh 2020). The memory effect occurs with a value above 10% during the first swelling of longitudinally compressed samples fixed for a long-time. From the shrinkage-swelling results of the samples, we concluded that if the saturated size in the direction parallel to the grain of the sample is compared with the next absolute dry size instead of the previous absolute dry size in the calculation of the first swelling value, an approximate real swelling result is obtained free of memory effect.
The cross-sectional and volumetric changes of shrinkage and swelling after pleating were not significant. However, shrinkage and swelling in the direction parallel to the grain was 0.8% for compressed beech, 1.3% for compressed oak, and 1.8-2.1% and 2.4-2.7% for compressed-fixed samples, respectively.
The mechanical properties of wood change with the moisture content and the degree of changes for pleated wood sometimes differs significantly from that of untreated wood. For the best possible pliability, the moisture content of pleated wood should be close to the fiber saturation point (Báder and Németh 2019a).

Based on observations of beech and oak wood species, the memory effect is extremely high in the first swelling parallel to the grain of compressed samples fixed for a long-time. Wood tries to restore its original pre-compressed state and dimensions, as it tries to re-establish the original position and structure of its cells. The size of the shrinkage-swelling specimens was 12x12x20 mm (tangential direction × radial direction × longitudinal direction), the accuracy of measurements was 0.001.

During the first desorption of beech samples, pleated wood adapts more quickly to the changed temperature and humidity, therefore its drying can be performed in a shorter time compared to the untreated wood. The water adsorption of pleated wood is slightly slower than that of untreated wood, so it swells and shrinks less when used indoors due to limited but rapidly changing temperature and humidity.

Comparative bending- and compression tests were performed on longitudinally compressed beech wood fixed for 1 minute, with different moisture contents. The compressive strength parallel to the grain exhibits the smallest sensitivity to changes in moisture content by an α value of 3.2%, followed by 4.2% for its modulus of rupture, 5.0% for its modulus of elasticity and 5.4% for stress at a 4 mm crosshead displacement. With increasing moisture content, the α value of both the bendability coefficient and the highest deflection during a 4-point bending test causes increases of 4.2% and 7.6%, respectively.

Thesis 5: Effect of different compression rates and applicability of wood with redheart
To compare the compression rate of samples with different lengths, a relative rate of compression [%/min] was introduced. It uses basic units to express how much the wood shortens per unit length and unit time. Compressing too slowly as well as the presence of redheart decreases the yield. For faults observable at the macroscopic level, the part with redheart is always damaged first and in most cases cracks along the wood rays can be observed (Báder and Németh 2017e).

A 20-25%/min relative rate of compression was used for the laboratory equipment, as the number of failures in beech and oak samples was high at lower speeds (1.5%/min). When 75 samples softened in saturated water vapor at atmospheric pressure were pleated at a rate of 20-50%/min, the yield became 98.6%.
Typical wood defects (knots, grain slope, etc.) are unacceptable for pleating, however, healthy redheart is permissible, although it decreases the yield. If a failure occurs due to redheart, cracks along the wood rays will occur in most cases. The redheart is always damaged first, after which the failure can spread to the redheart-free area. The method of plasticisation has no effect on the failure of wood with redheart.

Thesis 6: Chemical study, changes in functional groups
Based on the infrared spectroscopic examination of samples steamed, compressed, compressed and fixed for a long-time, the hydroxyl groups as well as the C-O and C-H functional groups of the polysaccharides and lignin changed, compared to the untreated samples. Based on the spectra, all beech sample groups can be separated, but for oak only the long-time fixed group is separable. Beech wood is more sensitive to these modifications (Báder et al. 2020).

The aim of this research was to explore the chemical changes of beech and oak wood species caused by thermo-hydro-mechanical treatment. Samples were examined at different stages of the modification with a Fourier transform infrared spectroscope equipped with a diffuse reflectance accessory (DRIFT). Detailed interpretation of the infrared spectra made it possible to identify the changes in the hygroscopicity of the wood and to explore the changes in the relationship between the structural elements in the polymer matrix of the wood by the applied treatments.

Thesis 7: Improving the dimensional stability of longitudinally compressed wood

Pleating multiplies the size change of pleated wood parallel to the grain due to varying moisture content. By impregnating beech wood with lactic acid and then *in situ* polymerizing it, the dimensional stability was significantly improved, while all constituents remained biodegradable. After the lactic acid treatment of pleated beech wood, its swelling and shrinkage parallel to the grain approach that of the untreated wood, while the cross-sectional and volumetric dimensional stability values more than doubled (Báder and Németh 2019b).

If the shaped and dried pleated wood is rewetted, it will partially regain its original shape due to the memory effect. For pleated wood, the dimensional change parallel to the grain is 4-6 times greater compared to untreated wood, which is a serious dimensional stability problem. Pleated wood, as an organic product, should also be further modified with naturally degradable materials and environmentally friendly solutions. Oak and beech wood as well as an aqueous solution of L(+)-lactic acid monomer (concentration ≥ 90%) were used for the experiments. Water was removed from the monomer solution by cooking and then the monomer was oligomerised. After impregnating the samples using vacuum, the lactic acid introduced into the wood was polymerized at 120 °C. For oak, impregnation could not be solved. The total increase of weight due to impregnation was 73% for uncompressed beech and 64% for pleated beech. As a result of high lactic acid uptake, the absolutely dry sizes of uncompressed beech samples increased by 13.5%, 4.6% and 0.2%, while the sizes of pleated wood increased by 13.6%, 4.9% and 1.1% (tangential direction × radial direction × fiber direction). The lactic acid treatment of natural beech wood has been successful and lactic acid treatment can be used in the future to improve the dimensional stability of untreated or otherwise modified wood species suitable for impregnation.

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