

High-pressure Treatment of DMAc/LiCl Swollen Softwood Pulp

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Swollen softwood cellulose pulp in a DMAc/LiCl solvent system was compressed under elevated pressure (up to 900 MPa) in a Bridgman anvil press. The influence of high pressure on two cellulose systems was studied by measuring X-ray diffraction, mechanical and optical properties and observing scanning electron micrographs of the morphology. Compressed swollen cellulose, washed with distilled water, had lower elastic modulus and hardness compared to swollen cellulose washed with a combination of 2-propanol and deionized water. This work showed that material with lower mechanical properties will be affected more by compression and will result in higher mechanical properties after pressure treatment. Transmitted light in the visible range for both systems was increased after elevated pressure was applied. The XRD measurements revealed the decrease of the cellulose crystallinity after high pressure treatment for all swollen cellulose samples. The morphology of the compacted samples showed noticeable differences between the compact smooth surface and the layered core.

Keywords: Cellulose; Compression moulding; High-pressure; N,N-dimethylacetamide; Swelling; Mechanical properties; Optical properties

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INTRODUCTION

Throughout history, biomass has been a popular starting material for the production of a large variety of products. Cellulose is a natural polymer found in nearly all plants and is considered the most valuable fraction of biomass. Paper, cardboard, and textiles are major commodities produced from cellulose fibres. Cellulose can be transformed into many different products through the dissolving and regenerating or derivatising processes.

Mechanical, or combined mechano-chemical, actions on polysaccharides play an essential role in modern processing and modification technologies. High-pressure technology is a well-known technique that has been applied in food processing for shelf-life extension, better quality, and nutrient preservation (Farkas and Hoover 2011). Applying high pressure is one of the techniques that have been explored for enhancing thermal properties of polysaccharides submitted to pressures in a range of 0.5 to 2 GPa (Zhorin *et al.* 2010), increasing chemical reaction kinetics during the production of

cellulose derivatives (Rogovina *et al.* 1995), or increasing xylan accessibility in cellulose fibres (Oliveira *et al.* 2012).

Lignocellulosic material is complex and composed of cellulose, hemicelluloses, lignin, extractives, and several inorganic compounds. Numerous pre-treatment methods have been developed to lower the crystallinity and increase the accessibility of cellulose. These include methods based on enzymes, physical or chemical methods of swelling, and dissolution and fractionation mechanisms (Ehrhardt *et al.* 2007). Swelling happens when a fluid does not fully disrupt the inter-polymer interactions, leaving fibre and fluid molecules to change position up to a limited value. Upon swelling, the diameters of the cellulose fibres increase, sometimes by a large amount, whereas longitudinal changes are minimal (Le Moigne *et al.* 2010). The swelling of cellulose fibres in a DMAc/LiCl solvent system is heterogeneous. When fibres are placed in DMAc/LiCl, solvent molecules only penetrate the semi-permeable and elastic parts of a fibre. Diffusing molecules radially expand the secondary wall, which causes the expansion and bursting of the primary wall, as seen in many other solvents (Le Moigne and Navard 2010). Unswollen parts of the fibre still contain the helical arrangement of the fibrils, as is the case for most swelling agents. When fibres swell, intermolecular bonds are broken as a result of the stresses produced by the swelling process. With a very strong solvent, it is possible to disrupt the entire crystalline structure (Mantanis *et al.* 1995).

The modification of cellulose fibres, swollen with water under high pressure, was studied by Figueiredo *et al.* (2010). The results demonstrated that high pressure processing promotes the hydration of pulps and affects the structural organization of cellulose. In particular, the crystallites of elementary fibrils recrystallize, leading to increases in the average crystallite width and the degree of crystallinity. The high-pressure treatment allows the penetration of water molecules into otherwise inaccessible cellulose surfaces. These authors showed that high-pressure treatment decreases the hornification of dried pulp and improves fibre flexibility and elasticity. High-pressure processing is thus an interesting method for modifying chemical pulps and must be further studied to expand its application scope.

High-pressure has never been applied on cellulose fibres swollen with DMAc/LiCl. This solvent system is known to disrupt the hydrogen bonding network of cellulose and change its supramolecular structure. The objective of this paper is to determine if a combination of DMAc/LiCl swelling and high-pressure can have an effect on the structure, understand the origin of the effects, and see how this can be used to create new materials. To this end, the mechanical and optical properties of compressed samples were measured and the results were correlated with the cellulose sample morphologies.

EXPERIMENTAL

Materials

Softwood dissolving pulp was purchased from Domsjö Fabriker, Sweden. Dissolving pulp was produced from a controlled mixture of spruce and pine (60:40), by a two-stage sodium-based cook, to achieve a sulphite pulp with very low lignin content (0.6%) and high α -cellulose content (93%). The viscosity of the pulp was 530 ± 30 mL/g, according to the standard ISO 5351 (2010), and the degree of polymerization was 780

(Domsjö 2011). Cellulose was swollen with *N,N*-dimethylacetamide (Sigma-Aldrich, Finland) and lithium chloride (Merck, Finland). All chemicals were used as received, without further purification.

Swelling of Softwood Pulp with DMAc/LiCl Solvent System

Swelling chopped softwood dissolving pulp pieces in DMAc/LiCl involves a solvent exchange procedure, described elsewhere (Obradovic *et al.* 2014). When the solvent exchange procedure was finished, a transparent gel was formed. The gel, at this stage of mixture, was composed of 3.7 wt% cellulose and 96.3 wt% DMAc/LiCl and was coagulated by two different methods using two different non-solvents: distilled water and a 40:60 mixture of isopropyl alcohol and deionized water. For the first method, the transparent gel was washed with distilled water. Distilled water was exchanged with fresh distilled water after 1, 4, and 24 h. This treatment solidified the gel. After solidification, the sample was dried at ambient temperature and is referred to hereafter as Cell_DW. For the second method, the transparent gel was washed with a mixture composed of isopropyl alcohol and deionized water (40:60). Samples were washed twice with 100 mL of this mixture. After this washing step, samples were soaked in 300 mL of deionized water to remove residual isopropyl alcohol. The samples were then cleaned by running tap water overnight to remove the lithium (Nayak *et al.* 2008). The resultant dry product will be referred to hereafter as Cell_2PDW.

High-pressure Treatment

High-pressure treatments were performed on the two types of dry solid cellulose samples described above, Cell_DW and Cell_2PDW. Pressure was applied in two steps. The first medium pressure step was a precursor to a high-pressure step, and it was used to prepare the sample to perform the second step (Privas *et al.* 2013). The two sets of dry cellulose samples (Cell_DW and Cell_2PDW) were cut to produce 300 mg pieces and placed in a 10-mm diameter cylindrical mould. The mould filled with dry cellulose was placed in a hydraulic Carver press, shown in Fig. 1. The pressure applied in the first step was 156 MPa at room temperature, for 5 min. After this medium pressure step, 10-mm cellulose cylinders were produced with a thickness of approximately 3 mm. These cellulose cylinders were then placed in a cylindrical copper gasket ring (Fig. 1). The copper rings had an inside diameter of 10 mm, outside diameter of 15 mm, and thickness of 5 mm. The copper rings deform under pressure.

The first function of the copper rings is to confine the sample, preventing cellulose from escaping from the pressure chamber. The second function of the copper rings is to provide an additional pressure as a result of its radial deformation during compression. To increase the deformability of the copper rings, a low dislocation density state was obtained by annealing the copper rings at 600 °C for 1 h. The oxidation of the annealed copper ring surface was removed by a sulphuric acid solution treatment. The Vickers hardness of the copper rings was measured as $HV_{10}=37$.

Cellulose cylinders placed in the cylindrical copper gasket rings were put between the two anvils of a Bridgman device, shown in Fig. 1 (Privas *et al.* 2013), where a compressive force is applied with a foot hydraulic pump, while measuring pressure. Cellulose samples were submitted to pressures between 0.5 and 0.9 GPa for 5 min at room temperature. After compression, the cellulose samples became flat disks.

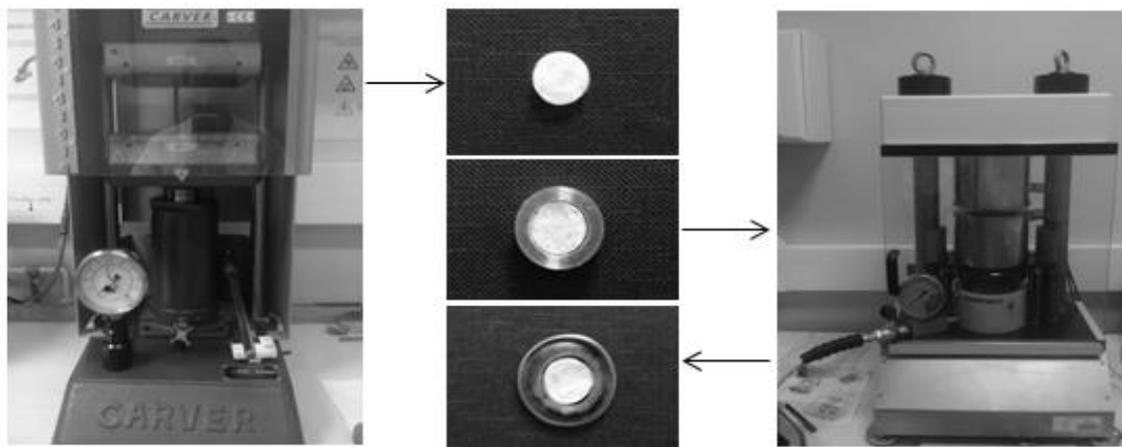


Fig. 1. Carver press (left), cellulose sample in copper ring before and after compression (middle), and Bridgman press (right)

Optical Characterization of Pressed Cellulose

The optical transmittance of the cellulose specimens after high pressure treatment was measured from 200 to 1000 nm, using a Shimadzu UV-Vis 2600 spectrometer equipped with an ICR-2600 Plus two-detector integrated sphere coated with BaSO₄. The UVProbe software program was used for analysing the results. Cellulose films with thicknesses ranging from 0.2 mm to 2 mm were placed in a film holder and put inside the integrated sphere.

X-ray Diffraction of Pressed Cellulose

The XRD patterns of the reference pulp and pressed samples were recorded at ambient conditions on an X-ray diffractometer (Bruker Discover D8, Germany), the samples were mounted on glass discs with double-sided tape and measured. The intensity of radial scans for each sample was recorded using a Cu K α radiation that was generated at an operating voltage of 40 kV and a filament current of 40 mA. The range of scattering angle (2θ) was from 10 to 45° (scanning rate = 3 s/step, step size = 0.02°).

Field Emission Scanning Electron Microscopy of Pressed Cellulose

The morphology of the samples was examined using a Leo Gemini 1530 field emission scanning electron microscope with an In-Lens detector. After high-pressure treatment, the samples were air-dried, sectioned, using a doctor blade, and coated with carbon in a Temcarb TB500 sputter ceter (Emscope Laboratories, Ashford, UK). The optimum accelerating voltage was 2.70 kV and magnifications were 1,500, 10,000, 25,000, and 50,000X.

Mechanical Characterization of Pressed Cellulose

Mechanical properties of the cellulose samples were measured with a UBI1 Nanomechanical Test Instrument (HYSITRON, Inc.), using a continuous stiffness measurement in a force controlled mode with a Berkovich-type triangular diamond pyramid. The continuous stiffness measurement technique gives access to contact stiffness, hardness, elastic modulus, and creep resistance. Nanoindentation elastic modulus (E) and hardness (H) are defined from the following equations:

$$E = \frac{dP}{dh} \frac{1}{2} \sqrt{\frac{\pi}{A}} \quad (1)$$

$$H = \frac{P_{max}}{A} \quad (2)$$

where P_{max} is the applied load at the maximum depth of penetration, A is the contact area, and dP/dH is the slope of the initial portion of the unload curve in the load-displacement plot. At least five tests were performed on each sample, with a peak load force of 500 μN , and the average values were calculated. The nanoindentator was calibrated against standards with a maximum standard deviation of 10%.

RESULTS AND DISCUSSION

Optical Characterization of Compressed Cellulose Samples

The swelling process plays an important role in the chemical processing of cellulose. The purpose of a swelling step is usually to lower crystallinity and increase the accessibility of cellulose molecules. A solvent composed of N,N-methylacetamide and lithium chloride is suitable for processing, characterization, or homogeneous derivatization of cellulose. This solvent system can also be utilized as a swelling agent. When fibres are placed in DMAc/LiCl, solvent molecules penetrate the fibre surface, ends of the fibre, and places where the wall structure has been damaged (Pionteck *et al.* 1996). Once regenerated from the DMAc/LiCl solvent system, the X-ray diffraction pattern of cellulose exhibited peaks similar to untreated cellulose (Cell I), or amorphous cellulose depending on the used anti-solvent (Obradovic *et al.* 2014). Cellulose samples were structured with crystallites of cellulose I in a matrix of paracrystalline and amorphous cellulose, indicating that solvent during the swelling process does not penetrate crystalline regions. Decrystallization of the crystalline domains results in thin layers peeling from the cellulose structure. Peeled layers retained some of the molecular orientation of the original structure (Duchemin *et al.* 2007).

It has previously been reported that cellulose molecules in DMAc/LiCl overlap when the cellulose (softwood dissolving pulp, $M_w=3.8 \times 10^5$) concentration is above 0.3 wt% (Ishii *et al.* 2006). When the overlap of polymers occurs, cellulose chains can associate with each other and form a gel, if the thermodynamical conditions are favourable. Such conditions can be reached when adding a non-solvent such as water to the swollen state. In this case, the addition of water to the cellulose/DMAc/LiCl solution generated a turbid gel as a result of a phase separation mechanism. During phase separation, some regions have different mean refractive indices than others because of the presence of crystalline entities in a non-crystalline region, or the presence of holes. The optical properties depend on the refractive index ratio and the size of the scattering entities (Meeten and Navard 1989).

The choice of anti-solvents in the solidification process had a great influence on the cellulose structure. As reported in the authors' previous paper (Obradovic *et al.* 2014), adding distilled water to the swollen cellulose mixture induces the formation of a purely amorphous sample, while adding a mixture of 2-propanol and deionized water

gave cellulose samples with X-ray patterns typical of cellulose I crystals. Cellulose crystallinity has an impact on the overall transparency of the materials formed either after the addition of water or 2-propanol and deionised water. Cellulose samples with crystalline regions had more opaque domains than those that were non-crystalline, showing that the crystallites can strongly scatter light. Thus, crystallites must either be large or be aggregated in such a way that their dimensions are similar to or larger than the wavelength of visible light. The difference in structure and its consequences on turbidity is kept when applying a pressure. Figure 3 shows a clear difference between the optical transmission spectra of the various cellulose samples. Submitted to such high pressures, the samples were strongly compacted and no large holes were present anymore, so the scattering from them was very low. The high transmittance difference between the two treatments is thus linked to the presence of crystalline scattering objects. The non-crystalline samples had a transmittance of about 70%. Their turbidity is due to the presence of tiny amounts of chromophores (Rosenau *et al.* 2000), which absorb and scatter light, linked to inhomogeneity in the organization and orientations. Samples containing crystals had an average transmittance of around 30% in the visible range. Figure 3 shows that the magnitude of applied pressure had an effect on the transmittance, with an increase in transmittance with increasing pressure. This effect, seen on both sets of samples, is easily explained by two factors: one being the further reduction of tiny holes, and the second being the smaller thickness when pressure is increased.

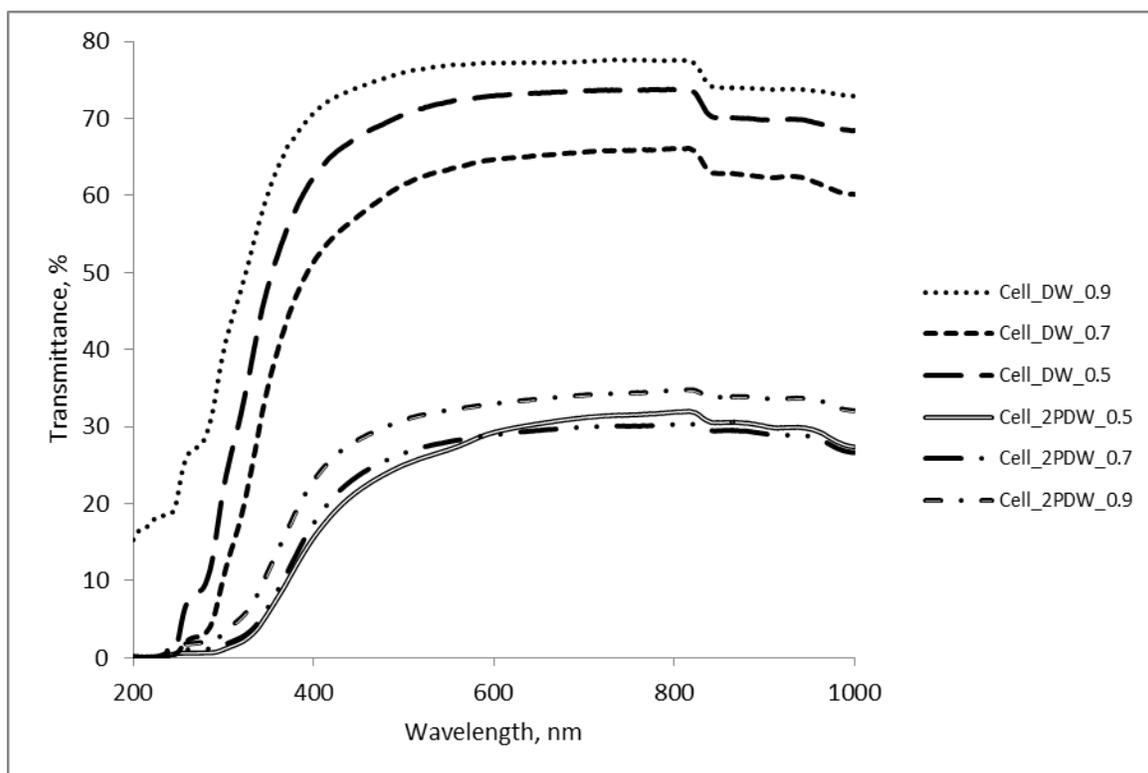


Fig. 3. Optical transmission spectra measured with UV-Vis spectrometer for two types of swollen cellulose fibres pressed with high pressure. Cell_DW- samples washed with distilled water; Cell_2PDW- samples washed with a mixture of 2-propanol and deionized water; numbers associated with each curve represent the applied pressure in GPa

X-ray Diffraction of Compressed Cellulose Samples

The X-ray patterns of the reference softwood dissolving pulp and compressed cellulose samples are presented in Fig. 4. The untreated reference pulp showed typical cellulose I_β diffraction angles 14.9°, 16.7°, and 23.0° corresponding to diffraction planes (1-10), (110), and (200), respectively. The diffraction peaks of the (1-10) and (110) were merged into a broad band (Marcovich *et al.* 2001). The peak at 34.6° angle is assigned to (004) plane.

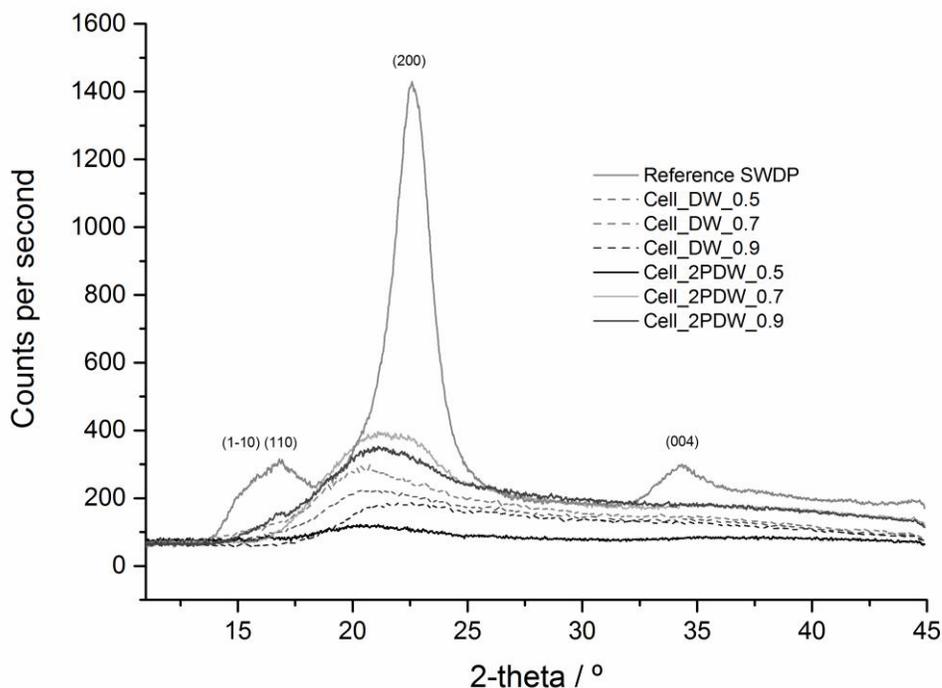


Fig. 4. X-ray diffractogram of the reference pulp and two types of swollen cellulose fibres pressed with high pressure. Cell_DW- samples washed with distilled water; Cell_2PDW- samples washed with a mixture of 2-propanol and deionized water; numbers associated with each curve represent the applied pressure in GPa

The crystalline structure of reference pulp was lost after swelling and high-pressure treatment. The prominent peak at $2\theta = 21.15^\circ$ was 10° wide at half maximum height, and it is generally agreed that the peak can be assigned to amorphous cellulose (Duchemin *et al.* 2007). Work of Privas *et al.* (2013) revealed no changes in the crystalline allomorph after high-pressure treatment of cotton. Pure untreated cotton samples preserved cellulose I crystallinity with small increase in the thickness of the crystallites. In a present work, cellulose structure was already altered due to breakage of hydrogen bonds by solvent system prior to compression step. As shown by the authors' previous work (Obradovic *et al.* 2014), cellulose samples Cell_DW had amorphous structure, and cellulose samples Cell_2PDW had cellulose I crystallinity with decrease in degree of crystallinity, after swelling treatment. After high compression the crystallinity decreases severely for both set of samples. Most affected decrease in the crystallinity is noticed for cellulose sample Cell_2PDW.

Mechanical Characterization of Compressed Cellulose Samples

Nano-indentation tests were used to investigate the mechanical properties of the highly pressed samples. The elastic modulus and hardness, measured by nano-indentation (using Eqs. 1 and 2), are shown in Table 1, as well as the values of the mechanical properties for unpressed samples (Obradovic *et al.* 2014). For both types of regenerating treatments, the elastic modulus and hardness were relatively constant. The very weak trend of lower values observed at 0.9 GPa seems to be due to inhomogeneous deformations of the copper ring.

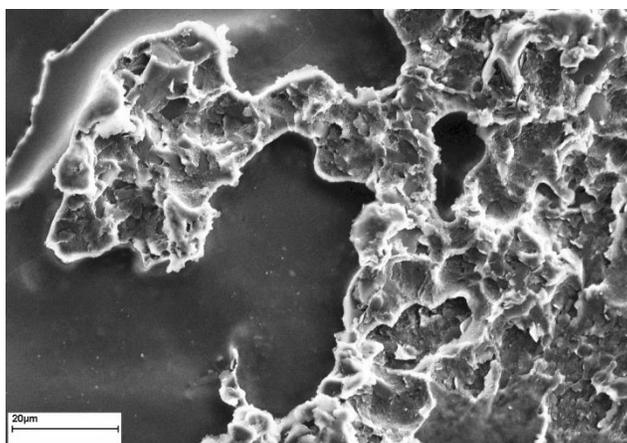
As far as the elastic modulus is concerned, there was a noticeable, small effect of applied pressure. The average value of the elastic modulus for the system of cellulose/distilled water was 2.9 GPa, and it was 7.1 GPa for the system of cellulose/2-propanol/deionized water. These values are in the range of the transverse modulus of cellulose fibres. Reported values for the transverse modulus for regenerated cellulose fibres are between 4.9 and 6.7 GPa (Gindl *et al.* 2008), with flax fibre at 8 GPa (Baley 2002), and jute fibre around 5.5 GPa (Cichocki and Thomason 2002). The mean value of the hardness for cellulose regenerated with distilled water was 170 MPa, and it was 360 MPa for cellulose regenerated with 2-propanol/deionized water. An increase in mechanical properties for both materials can be explained by higher compaction of material, leading to less nano-free volume areas between cellulose microfibrils. The mean values of the mechanical properties are larger in the case of the Cell_2PDW sample. The strength of the starting material is the parameter controlling the mechanical properties of the compressed sample. In the case of compressed cotton, low strength fibres were easier to convert into many microfibers of nanometre size, which recombined into a compact material with better mechanical properties (Privas *et al.* 2013).

Compared to the unpressed sample, a very significant increase of two orders of magnitude for both elastic modulus and hardness was observed in cellulose regenerated with distilled water system. This can be a result of several effects. The first is that the starting material had a disordered structure with many tiny holes between the cellulose fibrils oriented in different directions. Such a structure does not provide a good resistance to mechanical forces. When applying high pressure, fibrils are forced to move and fill holes, leading to a much more compact structure, which in turn will show a higher mechanical resistance. High-pressure treatment decreases defects, primarily voids, caused by trapped air bubbles in a formed gel. During the drying stage, evaporating water leaves pores in the material. This can be seen in the scanning electron micrographs shown in Fig. 5.

The second issue was the difficulty maintaining the sample in the ring. Applying such a high pressure led to matter escaping, which probably changed the overall organization. During medium- and high-pressure treatments, there was a small noticeable loss of material. Pintiaux *et al.* (2013) reported a 63% increase in the Young's modulus, dividing the initial mass by two. Another effect of higher mechanical properties for the mentioned system can be in the chosen characterization method, as nanoindentation probes a very thin layer located on the surface of the material. The sample surface, which was directly in contact with anvils, was more compacted than the inner part of the material.

Table 1. Mechanical Properties Measured with Nanoindentation for Two Types of Swollen Cellulose Fibres Pressed with High Pressure

Sample	Er (GPa)	Hardness (MPa)	Force (μN)	Depth (nm)
Cell_DW	0.05	6.5	200	3932
Cell_DW_0.5 GPa	2.8	140	500	974
Cell_DW_0.7 GPa	3.4	180	500	806
Cell_DW_0.9GPa	2.4	190	500	302
Cell_2PDW	7.0	380	5000	2839
Cell_2PDW_0.5 GPa	7.4	380	500	1100
Cell_2PDW_0.7 GPa	8.1	420	500	716
Cell_2PDW_0.9 GPa	5.7	300	500	607

**Fig. 5.** Scanning electron micrograph of the cellulose (DMAc/LiCl/distilled water system) surface pressed with 0.9 GPa; magnification 1.00 kX

Morphology of Compressed Cellulose Samples

SEM observations of compressed samples revealed a structure under the outer layer (Fig. 6). It was not present every time, but is reminiscent of a spinodal decomposition. Spinodal decomposition is a phase separation mechanism by which a solution of two or more components can separate into distinct regions with distinctly different chemical compositions and physical properties. The structure formed by spinodal decomposition showed the formation of an outer layer with different characteristics than the inner part of the sample. The outer layer was highly compressed and had a different organization than the rest of the sample, and there was a clear boundary between this layer and the sample. These thin surface layers were detached by making a very linear propagation as soon as the fracture was initiated. There was no simple correlation between the fracture propagation angles, which suggests that this layer was not monocrystalline.

The outer layer had a very good chain orientation, which gave linear propagation when detaching, with long, straight borders. This suggests that cellulose chains were oriented in the direction of the propagation. Thus, one can imagine a mechanism similar to what led to the rolling of the primary cell wall of swollen natural fibres (Le Moigne *et*

al. 2010). The thin peeled layer had a higher contraction at the outer surface than at the surface touching the sample, suggesting that the chains were oriented with an orientation factor decreasing from the surface to the inside of the sample. A similar observation was made by Privas (2013) on cotton fibres compressed in a similar manner.

The higher orientation of the outer layer caused the rolling of many detached layers on the surface. The diameters of the rolls were between 5 and 12 μm , with an estimated layer thickness of 50 to 80 nm (Fig. 7). A similar mechanism, albeit of different origin, has been observed for rolling of the primary cell wall during the swelling of a native cellulose fibre. In this case, the diameters of each of cylinders ranged from 2.2 to 2.7 μm for cotton hairs and wood fibres, for a primary wall thickness of approximately 100 to 400 nm. Thus, it can be deduced that the orientation gradient was much less pronounced than the one of the primary layer because the radius of gyration was much larger.

The inner part of the material had a different structure than the compacted surface. In most cases, the cross-section images (Fig. 8) of compressed samples showed a layered structure, with layers perpendicular to the compression plane.

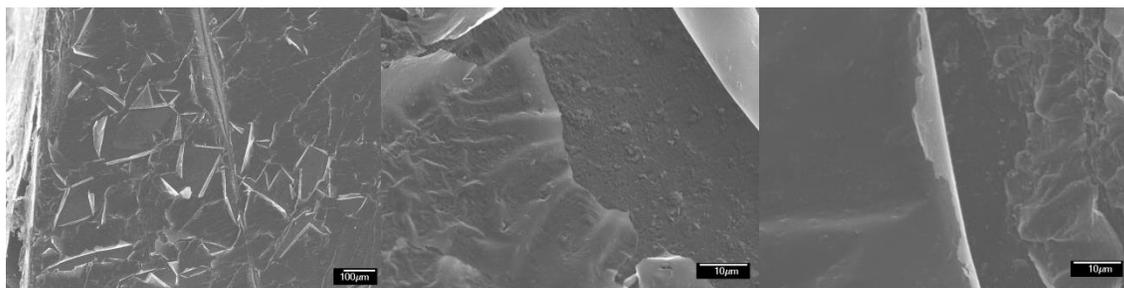


Fig. 6. Scanning electron micrographs of the rolled outer layers

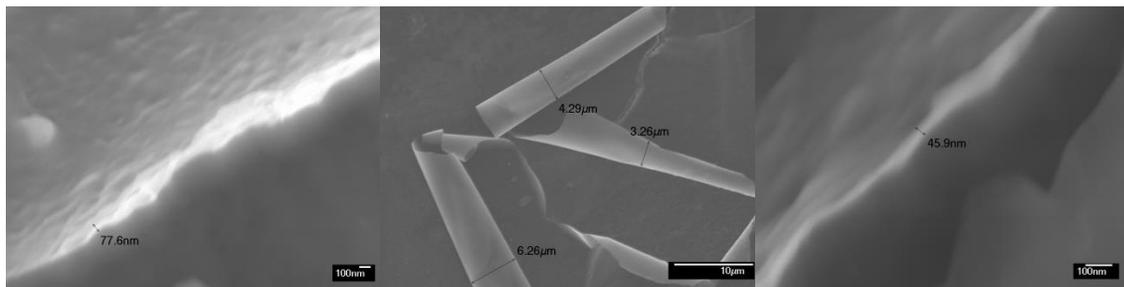


Fig. 7. Scanning electron micrographs of the diameter and thickness of the rolled outer layers

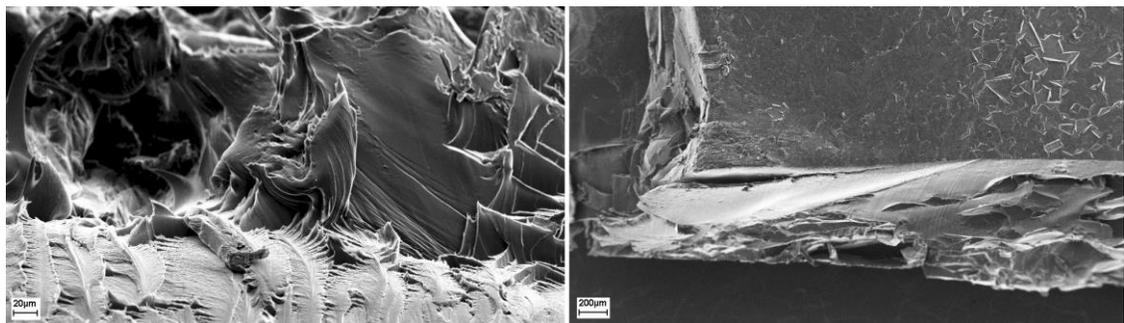


Fig. 8. Scanning electron micrographs of the cross-section of Cell_DW_0.5 (left image) and Cell_2PDW_0.5 (right image)

High-pressure compaction of cellulose samples produced an inhomogeneous material composed of a compact rough surface and core with layered structure. High-pressure treatment decreased surface defects, which are primarily voids, caused by trapped air bubbles in the formed gel. During the drying stage, evaporating water leaves pores in the material.

CONCLUSIONS

1. Softwood pulp swollen with a DMAc/LiCl solvent system was compressed in a Bridgman anvil press with pressures up to 0.9 GPa. The mechanical properties, optical properties, and structure of the compressed cellulose were analysed. Results of the analysis allowed for further studying the influence of high pressure on swollen cellulose fibres.
2. The main conclusion is that the strength of prepressed swollen cellulose is a parameter controlling the mechanical properties of the final material. The mechanical properties of the compressed cellulose increase with decreasing strength of the initial material. These results are best shown for the cellulose/DMAc/LiCl/distilled water system, where the elastic modulus and hardness increased significantly after high pressure. The system of cellulose/DMAc/LiCl/2-propanol/deionized water had much higher starting mechanical properties, which were not affected by compression.
3. The optical properties of pressed swollen cellulose fibres were affected by compression in a Bridgman anvil system. The changes in transmitted light of the compressed samples were small but increased progressively with increasing pressure for both cellulose systems.
4. The XRD measurements revealed a decrease of the cellulose crystallinity after high pressure treatment. All six samples had amorphous diffractogram with slightly changes in intensity at $2\theta = 21^\circ$.
5. An SEM analysis revealed inhomogeneous material composed of a compact rough surface and a core with a layered structure. High pressure caused a reduction of surface pores originating from the drying stage.

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