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Preparation of three-dimensional cellulose objects previously swollen in DMAc/LiCl solvent system

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Abstract

Three-dimensional shaped cellulosic objects were produced via a two-step procedure: swelling of softwood pulp (93% cellulose; 4.5% hemicellulose; 54% crystallinity) in DMAc/LiCl followed by moulding. Swollen cellulose pulp in the form of gel was solidified with two different anti-solvents: distilled water and, combination of 2-propanol and deionized water. The solid cellulose material was further moulded in a custom-built prototype mould. Role of anti-solvent was to solidify the swollen cellulose fibres and prepare mouldable solid specimens. The anti-solvent was chosen based on the following criteria viz., recoverability, stable chemical reactivity, availability, cost and previous research in the anti-solvent area. The choice of solidification solvent had a great influence on the structure and mechanical properties of the final cellulose material. Results of different characterization techniques showed that when the cellulose gel was washed with distilled water, it had a significantly higher amount of Lithium cations (ICP-MS and Raman), amorphous structure (X-ray) and lower mechanical properties (Nanoindentation), compared to samples washed with a combination of 2-propanol and deionized water. Increase in viscosity as previously reported and changes in the NMR and IR spectra of DMAc upon LiCl suggested the formation of an ion-dipol complex, where Lithium cation resides adjacent to the oxygen of the carbonyl group of DMAc. Formed macrocation $[DMAc_n+Li]^+$ was preserved between cellulose chains in cellulose specimens washed with distilled water and had essential role in the disruption of initial bonds and thus enhancing mouldability. Electron microscopy (FE-SEM) studies showed that the surface of cellulose after mechanochemical treatment was rough with no presence of fibres.

Abbreviations: DMAc: N,N-dimethylacetamide; FE-SEM: field emission scanning electron microscope; ICP-MS: inductively coupled plasma mass spectroscopy; RSD: relative standard deviation; SD: standard deviation; SWDP: softwood dissolving pulp; WAXD: wide angle X-ray diffraction

Introduction

Cellulose is an abundant natural polymer suitable for making a large variety of materials and chemicals. Several cellulosic derivatives can be compounded, pelletized and processed, depending on the cellulose derivative and compounding conditions. Some of the classical tools for thermoplastic processing are extrusion, injection or blow moulding, spinning and filming forming (Quintana et al. 1995).

However, the use of these techniques for processing pure cellulose is impossible since the polymorphs of cellulose I and II does not melt. Recently, several attempts were made to shape pure cellulose, mainly wood pulp, without any chemical treatment. One such study is the compression moulding of wood fibre materials. Researchers used only water as a processing aid and at the end they obtained all-cellulose composite plaques from pulp of high cellulose purity (Nilsson et al. 2010). In another study, cellulose was plasticized, without chemical modification, by the use of the combination of mechanical shear, uniaxial pressure and laser radiation (Schroeter and Felix 2005).

Since cellulose does not melt, processing of cellulose materials is usually based on dissolution in solvents and regeneration to two-dimensional objects such as fibres and films. However, cellulose among other features has a complex system of hydrogen bonds that prohibits dissolution of cellulose in common organic and inorganic media. Disruption of hydrogen bond network can be done mechanically or chemically. Cellulose with complete amorphous structure is usually prepared by ball milling (Zhang et al. 2007). Another alternative to interrupt this hydrogen bonding network is by using high pressure treatments. When polymers are subjected to high pressure, a rearrangement at all levels of their structural organization occurs (Ioelovich 2008). Structural rearrangements in polymers subjected to high pressure may be related to possible changes in the intensity of intermolecular interactions. In the case of cellulose, X-ray diffraction analysis suggests that the crystalline phase may be destroyed, leaving an amorphous state (Zhorin et al. 2010). Beside the mechanical methods, there are several chemical treatments for producing amorphous cellulose. Reported methods are deacetylation of cellulose acetate under non-aqueous alkaline conditions (Wadehra and Manley 1965) and regeneration of cellulose dissolved in different solvent systems (Ciolacu et al. 2011; Volkert and Wagenknecht 2008). The disadvantage with conventional amorphous cellulose is its tendency to recrystallize into cellulose II in the presence of water.

Physical and chemical properties of cellulose are strongly influenced by the arrangement of the cellulose molecules. There are two types of hydrogen bonds present in cellulose fibres viz., intramolecular interactions occurring between the C-3 OH group and oxygen of the pyranose ring, and intermolecular hydrogen bonds occurring between the C-6 OH group and oxygen of the glucosidic bond of another molecule. Hydrogen bonds form cellulose crystallites that are very difficult to penetrate by solvent molecules. Furthermore, if the starting material is amorphous cellulose, reactivity of chains will be much higher, for example, the enzymatic hydrolysis of cellulose to glucose (Haan et al. 2007). Besides its high reactivity, amorphous cellulose is necessary for drawing and shaping process. Togawa and Kondo (1999) investigated the drawing process of cellulose films. In order to achieve high draw ratio, hydrogen bonds needed to be dissociated during the drawing process. The drawability is hindered by intermolecular hydrogen bonds, since these bonds restrict the mobility of polymer chains. For successful drawing of cellulose films, hydrogen bonds were suppressed prior to the drawing process, with DMAc/LiCl solvent system. Processing of natural materials such as wood or cellulose is not as convenient as processing synthetic polymers. Conventional processing of synthetic polymers involves thermal processing. Higher temperatures in thermal process of natural materials lead to the decomposition of materials before melting. Zhang (2012) presented a process for producing plastic cellulose material without chemical modification or addition of additives. Cellulose powder was ball milled before it was subjected to the back pressure equal channel angular pressure. The purpose of this mechanical pretreatment was to disrupt the cellulose particles and enhance the chain entanglement. The storage modulus was higher for the ball-milled samples compared to the un-milled ones. The

XRD results showed the decrease in crystallinity and crystal size. Crystallinity of cellulose powder was reduced, which allowed production of cellulose plastics under the strong shear-deformation conditions.

Swelling process of cellulose fibres prior to dissolution is an important step of cellulose chemistry and technology. Main part in the interactions of cellulose with external agent is the change in morphology. The swelling of cellulose in various solvent systems has been the subject of numerous investigations. The heterogeneous swelling of the fibres was observed long time ago in chemical mixtures like sodium hydroxide or N-methylmorpholine N-oxide (NMMO) in water. The same mechanisms were also observed when using solvents like ionic liquids (Cuissinat et al. 2008a) and other chemicals (Cuissinat 2006). From all these studies, it was shown that the key parameter in the dissolution mechanism is the morphology of the fibre. If the original wall structure of the native fibre is preserved, the dissolution mechanisms are mostly similar to wood, cotton, and other.

The present research work aims to take advantage of the modifications in the intermolecular interactions, wherein a swelling treatment enables cellulose moulding. Cellulose pulp was thus swollen with DMAc/LiCl solvent system, washed and dried before further processing. Formability of these treated cellulose samples were evaluated. The objective of this study was to explore the possibilities of moulding pre-swollen cellulose materials and to understand the role of disrupting the intermolecular bonds of cellulose without derivatization.

Materials and Methods

Materials

Softwood dissolving pulp was acquired from Domsjö Fabriker, Sweden. Dissolving pulp is produced from a controlled mixture of spruce and pine (60%:40%) by a two-stage sodium based cooking to give a sulphite pulp with very low lignin content (0.6%) and high alpha- cellulose content (93%). The viscosity of pulp was 530 ± 30 ml/g according to ISO 5351 standard and the degree of polymerization was 780 (Domsjö 2011). Cellulose was swollen with *N*,*N*-dimethylacetamide (Sigma-Aldrich, Finland) and lithium chloride (Merck, Finland). Acetone was purchased from J.T. Barker. All chemicals were used as received without further purification.

Swelling of pulp in DMAc/LiCl solvent system

The pulp was first chopped into small pieces of 2.0 g each. Swelling of softwood dissolving pulp in DMAc/LiCl involves the following solvent exchange procedure. Initially, each cellulose sample was suspended in 300 cm^3 distilled water for 1h at room temperature. After filtration, it was immersed into 200 cm^3 acetone for 1h and subsequently, into 100 cm^3 *N*,*N*-dimethylacetamide for 1h at room temperature. 50 cm^3 DMAc was heated to 40 °C followed by the addition of 3.0 g Lithium chloride to the solution. When the swelling procedure was finished, a transparent gel was formed. The gel was solidified by distilled water and exchanged for fresh distilled water after 1h, 4h and 12hAfter solidification, the cellulose referred hereafter as Cell_DL was dried at room temperature for further processing. Second solidification procedure involves the washing of transparent gel with solvent composed of isopropyl alcohol and deionized water (40:60). Samples were washed twice with 100 ml of this solvent. After washing, the samples were soaked in 300 ml deionized water to remove residual isopropyl alcohol. Further to remove Lithium from cellulose, samples were exposed to running tap water overnight (Nayak et al. 2008) and the resultant product will be referred herafter as Cell_RS. The whole experimental part is depicted in Figure 1.

((Figure 1))

Moulding of swollen cellulose specimens

A cylindrical mould (Fig. 2) with a piston was built in stainless steel. Dried sample was put in the mould, closed with the piston and placed on a regular hydraulic press (Enerpac bench press). Sample was pressed at about 70 MPa vertical pressure for a couple of seconds at room temperature (Fig. 3)

((Figure 2))
((Figure 3))

Optical microscopy

Swelling mechanism of cellulose in DMAc/LiCl solvent system was studied with a Nikon Eclipse E200 optic microscope attached to a Nikon DS-Fi2 digital camera. Swelling treatment was recorded after 10 minutes, 20 minutes and 30 minutes.

Determination of crystallinity using X-ray diffraction (XRD)

X-ray diffraction measurements were performed on a goniometer (PW3020) using CuKα radiation generated at 30 mA and 40 kV. The CuKα radiation consists of Kα1 (1.54060 nm) and Kα2 (1.54443 nm) components. Dried cellulose samples were cut and put on plastic substrate. Scans were obtained from 15 to 70°, 2θ degrees in 0.02 degree steps for 1.5 seconds per step. Degree of crystallinity (I_c) was calculated from the ratio of the height of 002 peak (I_{max}) and the height of the minimum between the 002 and 101 peaks, shown in equation (1):

$$Ic = 1 - \frac{Imin}{Imax} \qquad (1)$$

Determination of cellulose structure using Raman spectroscopy (FT-Raman)

Cellulose samples were analysed with The Thermo Scientific Nicolet iS50 spectrometer. The Raman system is equipped with 1064 nm diode laser. The laser power used for chemically treated sample excitation was 500 mW, and 1024 scans were accumulated. Reference pulp was excited with 0.35 W power, and 32 scans were collected. Omnic software program was used to find peak positions and process the spectral data.

Determination of Lithium ion concentration analysed by ICP-MS

The samples are first digested with a microwave digestion system from Anton Paar, Multiwave 3000. Sample amount have been balanced in a range of 0.1 g to which have been added 5 cm^3 65% HNO_3 suprapur from Merck and 1 cm^3 30% H_2O_2 suprapur. The temperature in the microwave oven was up to 200 °C. The analysis was performed with a ICP-MS from PerkinElmer Sciex Elan 6100 DRC+. The standardization has been done with a multi standard from ULTRA SCIENTIFIC, item: IMS-102. The analyzing method has been the standard performance with the following parameters: Sweeps: 11; Replicates: 7; Dwell time: 100; 10 ppb Rh was used as an internal standard solution.

Field Emission Scanning Electron Microscope (FE-SEM)

The morphology of samples was examined by a Leo Gemini 1530 field emission scanning electron microscope with In-Lens detector. After moulding, samples were dried in air and sectioned using a doctor blade prior to be coated with carbon in Temcarb TB500 sputter cater (Emscope Laboratories, Ashford, UK). Optimum accelerating voltage was 2.70 kV and magnifications were 1,500; 10,000; 25,000 and 50,000X.

Mechanical characterization

Mechanical properties of cellulose samples were measured with UBI1 Nanomechanical Test Instrument (HYSITRON, Inc.) using a continuous stiffness measurement in a force controlled mode with Berkovich type triangular diamond pyramid. Continuous stiffness measurement technique offers measurements of contact stiffness, hardness, elastic modulus, creep resistance, and fatigue properties of materials. Nanoindentation elastic modulus (E) and hardness (H) are defined with following equations (2) and (3):

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

$$H = \frac{Pmax}{A} \qquad (3)$$

Where P_{max} is the applied load at the maximum depth of penetration, A is the contact area and $\frac{dP}{dh}$ is the slope of the initial portion of the unload curve in the load-displacement plot. Prior to Nanoindentation tests, cellulose samples were pressed with Pellet Press of FTIR. At least 6 indentations were performed on each sample, with the peak load force of 5000 µN for sample where solvent was removed with 2-propanol and deionized water and 200 µN for swollen sample washed with just distilled water.

Results

Swelling of cellulose in DMAc/LiCl solvent system

Swelling of cellulose fibers in DMAc/LiCl solvent system is also a heterogeneous process. When fibers are placed in DMAc/LiCl, solvent molecules penetrate only to the semi-permeable and elastic parts of the fiber wall. The diffused molecules cause radial expansion of the secondary wall. These localized swollen parts along the fiber gives the impression of balloons (Navard and Cussinat 2006). The balloons were formed in the first couple of minutes. In the course of swelling, balloons were bursting and fragments arise. After 30 minutes of treatment, a two phase system was visible. It can be observed from Figure 4, that there were some intact fibers still exist. In the swelling process Cl^- ions formed hydrogen-type interactions with hydroxyl group hydrogens of cellulose, breaking the existing bonds in the interior of the structure. Meanwhile Li^+ ions interacted with carbonyl group oxygen of DMAc molecule forming $[DMAc_n+Li]^+$ macrocations. Macrocations acted as a spacer between cellulose chains prohibiting the formation of intermolecular hydrogen bonds. When fibers swell, intermolecular bonds are broken as a result of the stress produced by swelling process. With a very strong solvent it is possible to disrupt the entire crystalline structure (Mantanis et al. 1995). In this particular case swelling of 30 minutes was sufficient to reduce crystallinity of fibers to the necessary amount with which molding process is possible. Shorter swelling time would not decrease the crystallinity sufficiently, and this results in a brittle non-mouldable material. Longer swelling time would go to dissolution stage, where cellulose II would arise.

((Figure 4))

Effect of swelling treatment on crystallinity analysed by XRD

Native and most regenerated cellulose consists of crystalline and non-crystalline domains. The physical properties and reactivity of cellulose is strongly influenced by the arrangement of cellulose molecules. Interactions between cellulose and reactive substances occur first in non-crystalline domains. The X-ray patterns of reference pulp, sample washed with distilled water

(Cell_DL) and sample washed with organic solvent (Cell_RS) are presented in Figure 5. X-ray diffractogram for the reference softwood dissolving pulp had two peaks, characteristic of the cellulose I crystal structure. The crystalline structure of softwood pulp was lost after swelling in DMAc/LiCl and solidifying with distilled water. Duchemin (2007) studied the transformation of microcrystalline cellulose due to partial dissolution in 8% DMAc/LiCl. His work helped in understanding the phase transformation that occurs during dissolution in this particular solvent system. Dissolution occurs through the continuous peeling of layers of crystal domains. The peeled layers may retain some cellulose I structure from which they were removed, but generally they were too thin to contain crystallite chains. This is the reason that precipitated peeled layers seemed as amorphous cellulose. Significant crystalline diffraction was not observed in Cell_DL specimens, indicating that the slow solidification of samples in distilled water produced crystallites of a small size or with imperfections in the crystalline structure. Cell_RS specimen has diffraction peaks at 15.0° and 22.3°, indicating cellulose I structure. Although the sample had same crystallinity patter as native cellulose, swelling treatment resulted in a decrease in the degree of crystallinity from 0.54 to 0.43.

((Figure 5))

Effect of swelling treatment on cellulose structure analysed by FT-Raman

Raman spectra in the frequency region 300-3700 cm^{-1} for the reference pulp, Cell_DL and Cell_RS are shown in Fig. 6, which infers the spectral changes occurred upon the loss of crystallinity. Between 1000 and 1200 cm^{-1}, there are ring bond stretches and C–O stretches. The angle bends (CCC, OCC, COC, OCO), C–O stretches, and methylene bending appear between 700 and 800 cm^{-1}. Between 400 and 600 cm^{-1} are the heavy atom bending, C–O and ring bending, and some ring stretching. And between 200 and 400 cm^{-1} are ring torsions. Spectrum of a crystalline substance contains sharp discrete bands whereas the amorphous materials contain broad diffuse bands (Socrates 2001). The broad band in the 3100-3600 cm^{-1} region that was due to the OH-stretching vibrations gave information concerning the hydrogen bonds. The peak characteristic of hydrogen bonds from the Cell_DL sample became wider in comparison to the peak from reference pulp, which can be correlated with the interruption of the intra- and intermolecular hydrogen bond by swelling treatment. The Cell_DL spectrum exhibits a strong band at 605 cm^{-1} which is due to the bending motion of the O=C–N group of DMAc molecule. Amide I band characteristic for C=O stretching vibration can be seen at 1650 cm^{-1}. This band is a typical carbonyl adsorption band of tertiary amides. The Raman spectrum from sample Cell_RS was similar to reference pulp, except for the missing 605 cm^{-1} and 1650 cm^{-1} peaks. In general, all amides have one or more bands of medium-to-strong intensity, which may be broad, in the region 695-550cm^{-1} which are probably due to the bending motion of the O=C–N group. The carbonyl absorption band of tertiary amides occurs in the region 1670-1630 cm^{-1}. The lack of these two peaks indicates the absence of DMAc in Cell_RS samples.

((Figure 6))

Residual of Lithium analysed by ICP-MS

Concentration of Li ions in cellulose samples was measured with inductively coupled plasma mass spectroscopy as a function of treatment time in the solvent. As shown in the Table 1, Li^+ ion concentration revealed that, cellulose samples after swelling with DMAc/LiClcontained more lithium ion than compared with the reference soft dissolving pulp. The small size of Li^+ ions allows them to interact with glucan chains, including more restricted regions near the oxygen linkers. The concentration of Li^+ ions decreased from 672.04 to 526.98 ppm with decrease in the swelling time from 30 to 20 minutes. It can be concluded that Li^+ ions stayed between cellulose chains, and the amount of Li^+ ions is affected by the swelling time. Specimens solidified with 2-propanol and deionized water had significantly lower amount of Lithium ions, indicating that solvent removed most of the cations. Taking into account the result from Raman spectroscopy of specimen Cell_RS, it can be concluded that most of the DMAc/LiCl is expelled. This is in agreement with findings of Nayak and co-workers (2008). Their study showed insignificant amount of DMAc and Li^+ ions (10.61 ppm) present in the films even after washing with a 2-propanol and deionized water mixture, and subjecting it to running water. Observed difference between Cell_DL and Cell_RS samples regarding the content of retained Lithium cation might be

due to the final exposure to water. Time Cell_DL samples spent in a beaker with distilled water was in total 29 hours, while Cell_RS samples were exposed to running water over night. Even before the exposure to water, Cell_RS sample had a lower amount of macrocation. Majority of macrocation was already washed with anti-solvent composed of 2-propanol and deionized water. This solvent has a lot more power in dissociating cellulose with solvent complex.

Effects of swelling treatment on the morphology of fibres analysed by FE-SEM

The morphological structure of cellulose samples treated with DMAc/LiCl and moulded was observed using scanning electron microscopy. The scanning electron micrographs (Fig. 7) showed the heterogeneous and rough surface of cellulose moulded samples. This is consistent with the findings of Yun and co-workers (2008). In their study, curing of cellulose previously dissolved in DMAc/LiCl with deionised water led to objects with wrinkled rough surface and non-homogeneously generated layered structure. FE-SEM images (Fig. 8) demonstrate the microfibril bundles structure. Similar discovery was reported by Wei and Cheng (2007) when they studied the effect of solvent exchange on the structure of cellulose. They concluded that solvent activation prior to dissolution of cellulose led to the fibrillation of treated fibre surface. These findings indicated that chemical and mechanical treatment of cellulose caused destruction of cell wall organisation and led to re-organisation of microfibrils into layers. Fibrils are destroyed by swelling treatment, and reassembled in a whole new structure. SEM images of Cell_RS samples were not taken, since moulding step wasn't possible to perform.

((Figure 7))
((Figure 8))

Mechanical Properties

The nanoindentation tests were used to investigate mechanical properties of cellulose sample. The elastic modulus and hardness of specimens measured by nanoindentation are shown in Table 2. The surface roughness had impact on the measurement especially for the shallow penetrations, so average values were calculated from 18^{th} till 33^{rd} cycle. Both hardness and elastic modulus were significantly higher in Cell_RS compared to that of Cell_DL. Results of mechanical testing for Cell_DL samples were expected since speciments had amorphous structure, which made them less rigid, weaker and easily deformed. Solvent trapped in samples affects the surface morphology and mechanical properties of the material. Trapped $[DMAc_n+Li]^+$ macrocations hinder cellulose to form ordered structure by weakening the inter-molecular hydrogen bonds between cellulose chains which results in low mechanical properties (Yun et al. 2008). Cellulose samples with crystalline structure have higher hardness and elastic modulus. Increased crystallinity is associated with increase in rigidity and hardness. Our results suggest that disruption of hydrogen bonding network via intermolecular non-covalent bonding allows the preparation of mouldable cellulose.

Conclusions

The objective of this study was to prepare moldable cellulose materials without chemical modification. Cellulose swelling is essential for producing cellulose products. DMAc/LiCl solvent system was used to swell cellulose with the aim to broaden its application in producing functional materials. Swelling process was necessary in breaking the existing bonds in the interior of the structure, thus lowering crystallinity of cellulose fibers. Reduced crystallinity can be even more diminished by preserving solvent between cellulose chains. It can be accomplished using distilled water as an anti-solvent. Retained swelling solvent acted as a spacer between cellulose chains prohibiting formation of intermolecular hydrogen bonds. Separated cellulose chains had disordered structure, which made them ductile and easily deformed. If solvent is washed away from specimens with mixture of isopropyl alcohol and deionized water, intermolecular hydrogen bonds are reformed. In that case material became brittle and lost its feasibility for molding. Three dimensional cellulose objects can be produced only if the DMAc/LiCl solvent system is present in

cellulose specimens. Our future research will focus on alternatives to mimic this behavior using solvents/agents which are easier to recycle and upscale to industrial applications.

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436 **Table 1** Determination of lithium ion concentration with ICP-MS for reference pulp, cellulose
437 containing DMAc/LiCl (Cell_DL) and cellulose where DMAc/LiCl was removed (Cell_RS).
438

Sample	Content mg/kg	SD mg/kg	RSD %
Reference	0.02	0.01	64.90
Cell_DL, 30 min	672.04	17.80	2.60
Cell_DL, 20 min	526.98	8.73	1.20
Cell_RS, 30 min	1.79	0.02	1.30

439

Table 2 Mechanical properties measured with nanoindentation for cellulose containing DMAc/LiCl (Cell_DL) and cellulose where DMAc/LiCl was removed (Cell_RS).

Sample	Elastic modulus, MPa	Hardness, MPa	Force, μN	Depth, nm	Cycle
Cell_DL	54	6.5	200	3932	33
Cell_RS	6993	381.4	5000	2839	33

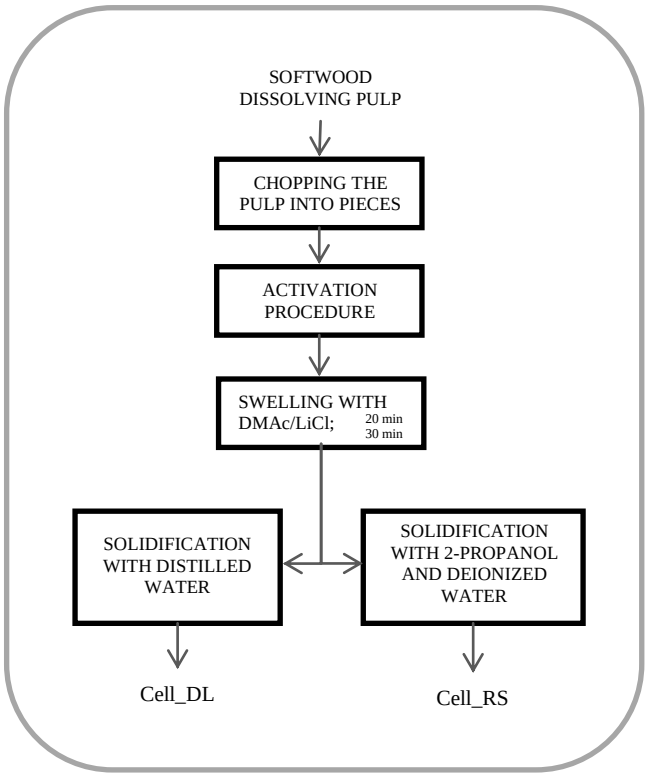


Fig. 1 Schematic representation of the experimental work.

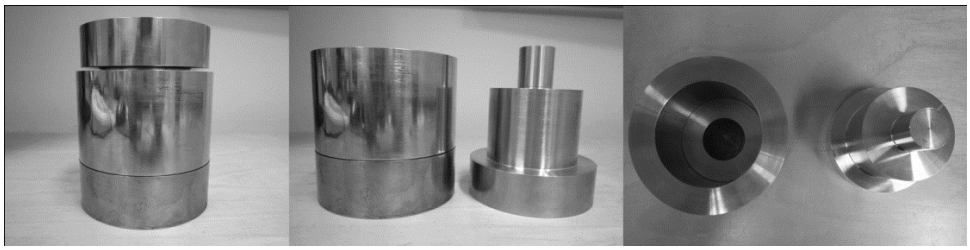


Fig. 2 Pictures of prototype mould from stainless steel

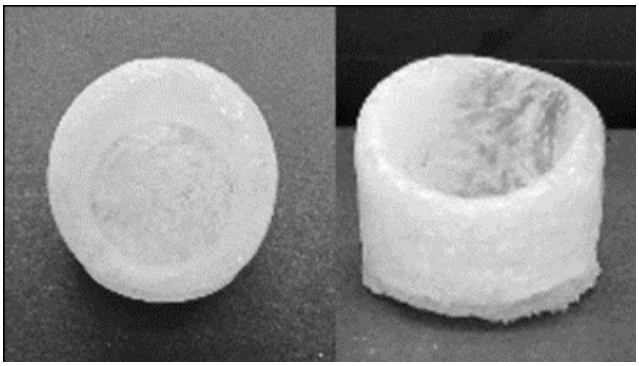


Fig. 3 Images of the moulded sample (Cell_DL)

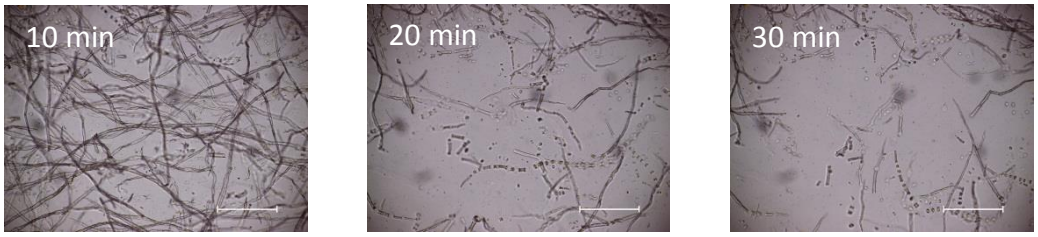


Fig. 4 Optical micrographs during the swelling process of cellulose in DMAc/LiCl solvent sytem. Bar represents 500 µm.

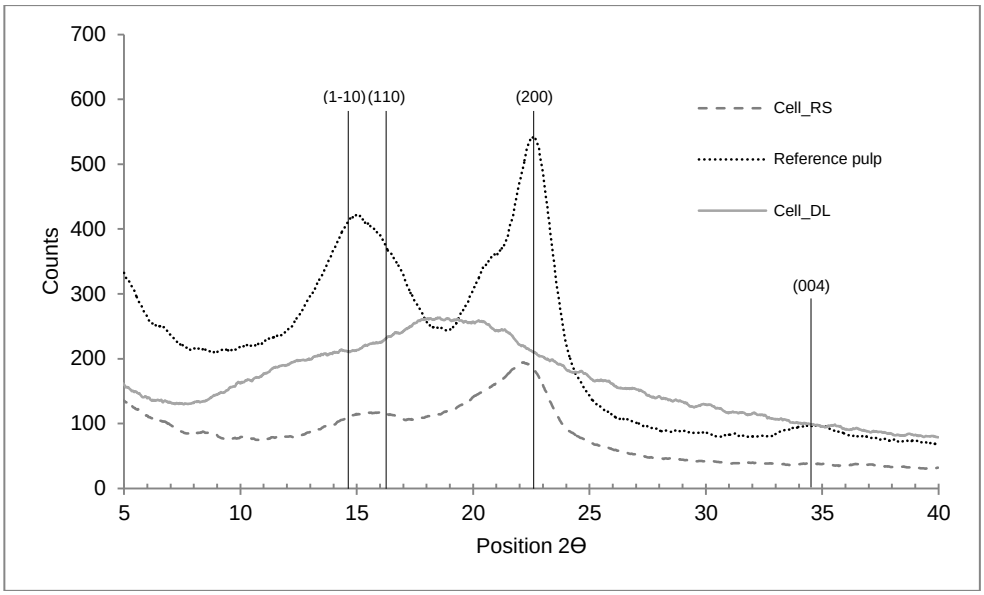


Fig. 5 X-ray diffractogram of reference pulp, swollen cellulose washed with distilled water (Cell_DL) and swollen cellulose washed with mixture of 2-propanol and deionized water (Cell_RS)

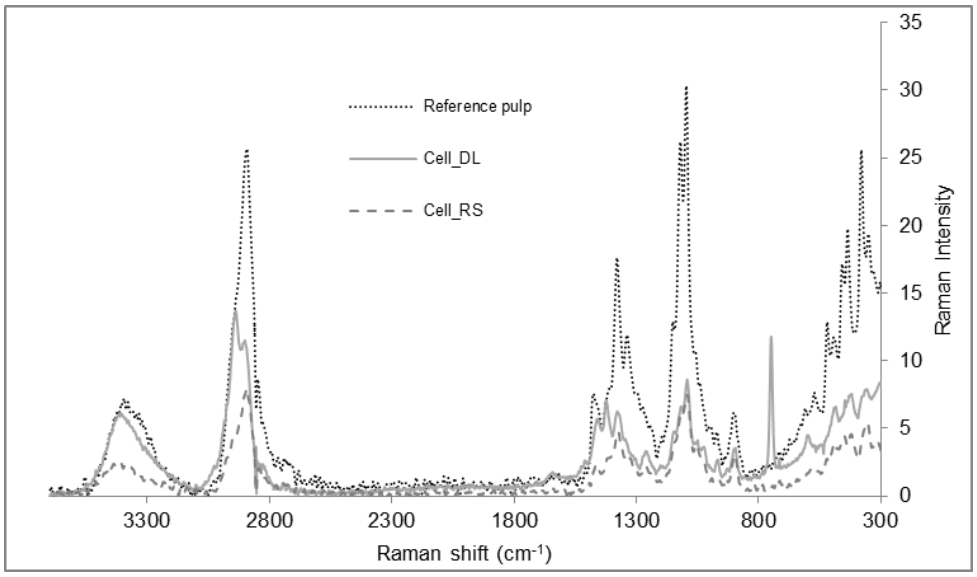
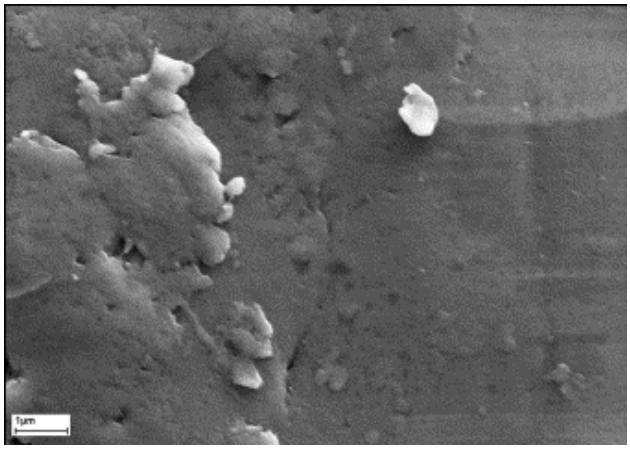
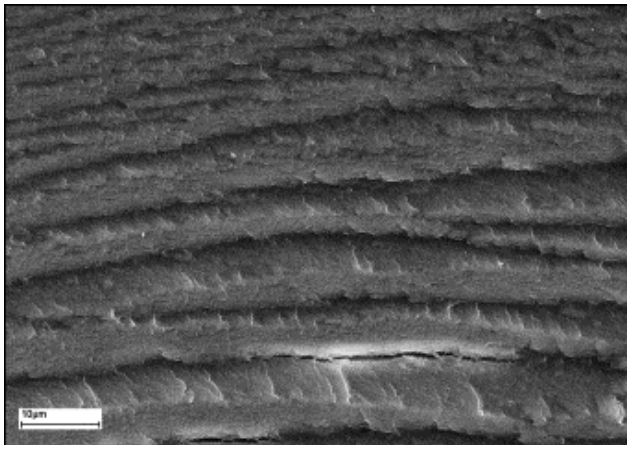


Fig. 6 Raman spectra for reference pulp, swollen cellulose washed with distilled water (Cell_DL) and swollen cellulose washed with mixture of 2-propanol and deionized water (Cell_RS)

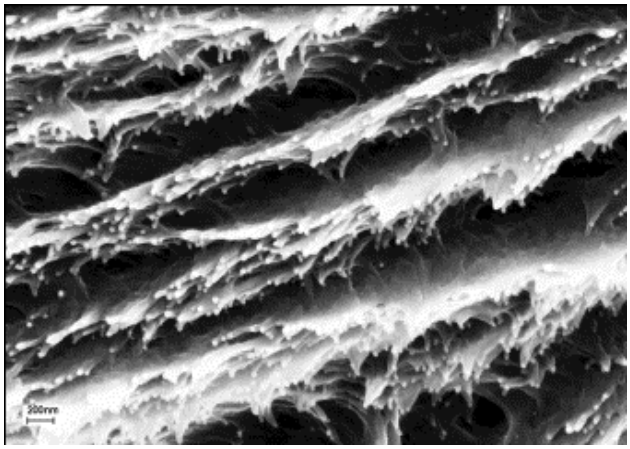


(a)

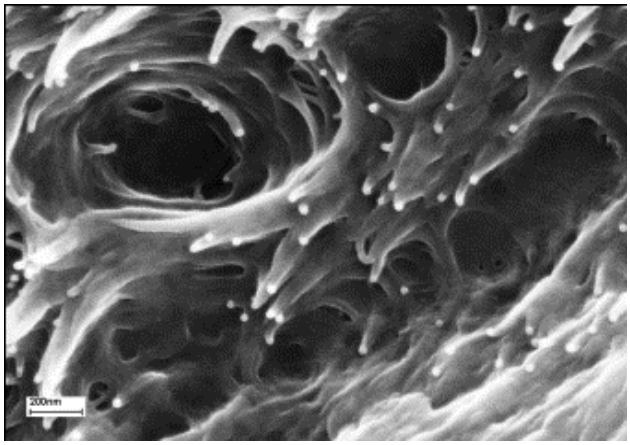


(b)

Fig. 7 SEM images of the swollen cellulose surface Cell_DL (magnification (a) 10,000 x and (b) 1,500 x)



(a)



(b)

Fig. 8 SEM cross-sectional images of the swollen cellulose Cell_DL (magnification (a) 25,000 x and (b) 50,000 x)