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ABSTRACT

The present study concerns a practical approach to survey water sorption properties of ionic liquid ([EMIM]OAc) treated papers with and without chemical crosslinking. Ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) can be used to transform sulfate pulp paper to regenerated cellulose film-like material. The fusion process increases both the dry and wet strength of the paper, improves oxygen and grease barrier properties, and increases paper transparency. The transformation is brought about by dissolution of the surfaces of the cellulosic fibers followed by precipitation and fusion of the fiber surfaces. Treatment conditions can be adjusted to produce partial dissolution of the fibers resulting in paper-like materials with improved wet-strength, or to achieve substantial or full dissolution resulting in transparent, regenerated cellulose film-like materials. From the industrial feasibility point of view, understanding the water sorption properties of IL-treated paper and the process parameters to control it are crucial. Results show that the treatment makes the paper more sensitive to both liquid water and water vapor, the magnitude depending on the degree of fiber dissolution and restraint of sheet shrinking during the treatment. Decreased water absorption and improved sheet dimensional stability were achieved by use of chemical crosslinking.

Introduction

Packaging materials are crucial to daily life, enabling the transportation and storage of innumerable materials and food products. However, global awareness of the microplastics problem associated with plastic-based packaging[1] and fossil-derived carbon dioxide emissions[2] has brought to the fore the need to develop sustainable alternative packaging materials. One potential solution is all-cellulose materials, which have novel properties that may be used to compensate for the use of conventional package materials.[3] A recent study by Tanaka et al.[4] showed that it is possible to transform paper into transparent plastic-like 'all-cellulose' material using the ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) as a solvent for cellulose. The process comprises four steps: impregnation of IL from a co-solvent, dissolution *via* heat activation, purification from IL, and drying. Fiber surface fusion takes place in the final step. The fusioned paper sheet behaved as a regenerated

cellulose film, having both elevated dry and wet strengths. According to the study, the treatment condition could be adjusted to produce paper-like sheets, fully regenerated film-like sheets, or other in-between materials. The strongest treatment conditions produced a film that was fully transparent and had excellent oxygen and grease barrier properties. In a later study by Khakalo et al.[5] it was shown that by application of the method to partially delignified wood plies it is possible to achieve superior tensile properties compared to native wood. Furthermore, the used approach resulted in almost eightfold tensile strength improvement in the direction perpendicular to fiber orientation, resulting from the fusion of adjacent wood fibers. The findings reported by Tanaka et al.[4] and Khakalo et al.[5] suggest that paper and wood treated with ionic liquids could find applications in the manufacture of cellulose-based packaging materials and various wood-based items. The water sorption properties of IL-treated paper examined in the present

study is a key area of interest which, to our knowledge, has not been reported previously.

Good dimensional stability in varying humidity and when wetted and dried is a desired material property. Due to the great importance of the dimensional stability of various paper and wood products, the factors affecting the water sorption properties have been thoroughly studied.[6–12] Typically, insufficient or non-uniform dimensional stability of printing papers cause deterioration of print quality and curling and cockling of printed products. In packaging, poor dimensional stability causes buckling and creep of packages. Often, unequal sidedness of moisture content and dimensional stability emphasize the problem. Dimensional changes in paper are caused by varying moisture-induced swelling and shrinking of fibers. In the relative humidity (RH) range 0–100% cellulosic fibers expand approximately 1% in the longitudinal direction and approximately 20% in the lateral direction.[6,7,9] Due to this, fiber orientation has a large effect on the dimensional stability of paper. The degree of pulp beating and paper shrinkage during the drying process also have a significant effect on the dimensional stability of paper.[6–10] The wetting of paper by liquid water can be effectively decreased by surface sizing and coating. However, those methods do not significantly affect the dimensional changes caused by long-term humidity changes or wetting. According to Fahey and Chilson,[10] the in-plane dimensional increase in representative pure softwood chemical pulp handsheets over the range RH 30–90% is 1.25–1.37%, and 3.25–3.92% from RH 30% to water soak. In a study by Botkova et al.,[13] liquid water induced maximal volumetric swelling of handsheets made from unrefined soft wood sulfate pulp fibers was in the range 56.02–62.76%. The high degree of swelling is due to lateral swelling of the fibers and disruption of the inter-fiber hydrogen bonds.

Regenerated cellulose based cellophane has a chemistry alike to sulfate pulp paper.[14] Compared to paper, which is formed principally from wood fibers held together by inter-fiber hydrogen bonds, cellophane is a more continuous material built from cellulose chains *via* intermolecular bonding. In the manufacturing process, viscose solution is piped to a casting machine, where it is extruded through a slit into an acid bath in which it coagulates into a regenerated cellulose film. Driven rolls carry the film through a further series of baths, where it is washed and bleached. Extrusion, viscose drag and tentering of the film my machine rolls result in molecular orientation in the film, and further, unisothropic properties

of the film. Depending on the application, the film is treated with softening materials such as glycerol, with colorants, and coated for moisture-proofing and heat-sealing. An optional method for manufacture of regenerated cellulose film using NMMO-based lyocell technologies was presented by Fink et al.[15] Cellophane is transparent, grease-proof, and impermeable to gases and odors, and is used primarily as a packaging material. As with paper, a disadvantage of cellophane film is its sensitivity to water.[16,17] In a study by Stamm,[18] thickness swelling and water absorption of uncoated, glycerine-plasticized cellophane films in liquid were in the range of around 120–130% and 85–90%, respectively. Swelling of sheets in the machine and cross-direction was around 2.2–2.5% and 3.7–4.0%, respectively. Takahara et al.[19] stated that the much better dimensional stability of cellophane film in planar directions is due to the planar orientation of cellulose crystal planes in the film and the orientation of the noncrystalline cellulose chain segments parallel to the film surface. A fundamental difference in the examined materials is that in IL-treated paper the orientation of crystals and amorphous regions may to some extent resemble their orientation in the original paper[4,5] whereas in cellophane film the orientation is dictated by the extrusion and drag of the viscose solution and elongation of the film the during regeneration stage.[20,21]

In the present study, the dimensional stability of IL-treated paper in liquid water and in varying humidity was examined and compared to untreated reference paper and uncoated additive-free cellophane film. A challenge for accurate measurements arose from substantial in-plane shrinking of the sheets in the final stage of the IL-treatment, that is, drying of the IL-treated sheets in the laboratory. The dried sheets were distorted from their original dimensions, indicating that the amount of shrinkage was not uniform throughout the sheet. Similar shrinking in the final drying stage was observed by Haverhals et al.[22] in a study concerning IL ([EMIM]OAc) treated cotton fabric. Le Moigne et al.[23] state that contraction of cotton fibers, sulfite pulp fibers, and regenerated cellulose fibers taking place in partial dissolution of the fibers originates from extended conformational state of cellulose chains. In the case of natural fibers the extended conformational state arise from bio-deposition, and in the case of regenerated cellulose fibers from forces caused by extrusion of viscose solution and drag of the fibers. The contraction of the fibers results from relaxation of the extended conformation of the cellulose chains to a more condensed state.[23]
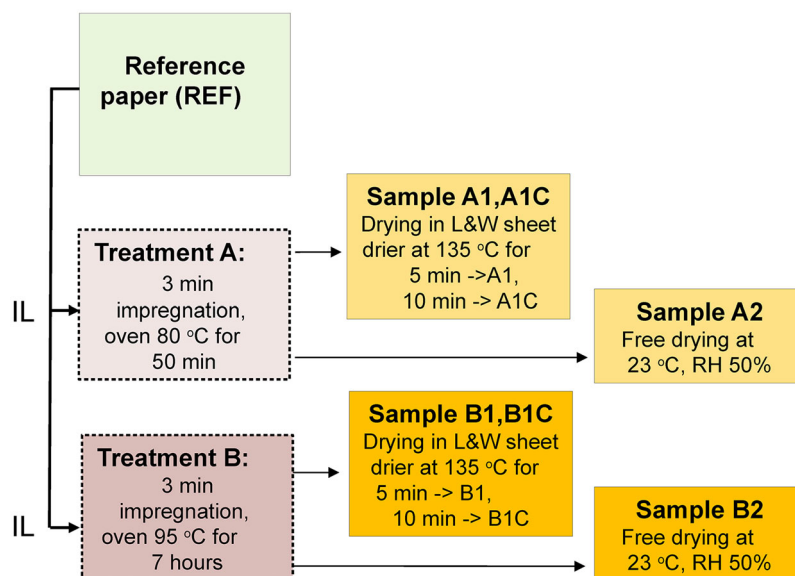
Figure 1. Partial dissolution process of paper with [EMIM]OAc–water and subsequent drying of the treated paper sheets. Impregnation and heat activation and drying conditions are shown in the boxes. Marker 'C' refers to addition of crosslinking agents to the final washing water of the IL-treated sheets.

Due to non-uniformity in sheet shrinking and in sheet swelling, a water image analysis based method was used to measure surface area changes (%) of entire sheets. Free dried samples that were both strongly curled and too stiff for image analysis based measurements were measured manually using a flexible measuring tape. Another aim of the study was to clarify whether the dimensional stability of IL-treated papers could be improved by chemical crosslinking of the sheets. The chemical crosslinking was performed following method presented earlier by Korpela and Orelma.[24]

Experimental

Materials

Bleached pine sulfate pulp was obtained from a Finnish pulp mill. Laboratory handsheets (size $140 \times 140 \, mm^2$) of $100 \, g/m^2$ (relative humidity (RH) 50%) grammage were prepared according to ISO standard 5269-1:05. Cellophane film Cellophane^{TM} 350 PØØ was purchased from Futamura Chemical Co. Ltd. The film is uncoated and contains no softeners. 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAc, purity 95%) was purchased from IoLiTec GmbH, Heilbronn, Germany. [EMIM]OAc was not purified before its use in the treatment of paper. Chemical crosslinking of IL-treated paper handsheets was carried out using glyoxal with an aluminum sulfate catalyst. The used glyoxal was obtained as 40% solution in water from Merck KGaA (USA).

Rectapur grade aluminum sulfate-14-hydrate ($Al_2(SO_4)_3 \cdot 14H_2O$) was obtained from VWR International. All water used in the study was purified with a Milli-Q device.

Methods

Partial dissolution of paper sheets by ionic liquid

Partial dissolution of handsheets was carried out with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) following the method presented earlier by Tanaka et al.[1] with a few exceptions. [EMIM]OAc was diluted with water to 75 wt% concentration before the treatment. Paper sheets ($140 \times 140 \, mm^2$, weight ~1.96 g) stored at RH 50% were dipped into the [EMIM]OAc solution for 3 min. The absorbed amount of IL solution was around $10 \pm 0.5 \, g$ per sheet. Impregnated paper sheets were placed on a plate covered by aluminum foil and heated in an oven, causing the water to quickly evaporate and the fibers to partially dissolve. The samples (Figure 1) were prepared using the following oven temperatures and treatment times: (Ref) reference without any treatment; (A) 3 min impregnation, 80 °C, 50 min; (B) 3 min impregnation, 95 °C, 7 h. The heat-treated paper sheets carrying [EMIM]OAc on aluminum foil were then placed into water for minimum 24 h. The water was changed four times to completely wash out all remaining ionic liquid. The aluminum foil was carefully peeled from the treated sheet after the first rinsing. The rinsed sheets were then wet-pressed at 3.5 bar for 5 min (ISO 5269-1:05). The wet-pressed sheets were dried using

two different methods: Samples A1 and B1 were dried using an L&W Rapid Dryer (ABB Ab/Lorentzen & Wettre) at 135 °C for 5 min. Samples A2 and B2 were allowed to dry freely on aluminum foil at 23 °C and 50% RH. The dried sheets were stored at 23 °C and 50% RH.

Chemical crosslinking

Chemically crosslinked samples A1C and B1C were prepared otherwise in the same way as A1 and B1, except the final washing of sheets A1C and B1C was performed with water containing 4.0 wt% glyoxal and 1 wt% aluminum sulfate-14-hydrate. Soaking was carried out for 120 min immediately before wet-pressing. Determination of the amount of crosslinking chemicals in the sheets was based on the measured amount of elemental sulfur in the sheets. For full curing of the crosslinking chemicals, the sheets were dried and heated in an L&W Rapid dryer at 135 °C for 10 min. The sheets were then stored at 23 °C and 50% RH.

Chemical analyses of IL-treated papers by solid state 13 C CP/MAS NMR spectrometry

Changes in the crystallinity of the sulfate pulp fibers after [EMIM]OAc treatment were characterized by using a 13 C cross polarization magic angle spinning (CPMAS) NMR spectrometer (Bruker AVANCE-III 400 MHz, Bruker BioSpin, Germany). For all samples, 20,000 scans were collected using an 8 kHz spinning frequency, 2-ms contact time, and a 5-s delay between pulses.

Elemental analysis

Nitrogen, carbon, hydrogen, and sulfur contents were determined using a FLASH 2000 series analyzer.[25] Three replicates of each sample type were measured and the average values are reported.

Liquid water absorption and dimensional changes

Each sample was soaked in Milli-Q water to monitor water sorption up to 24 h. For measurement of water absorption, the sheets were removed from the water, placed between paper towels, gently pressed to remove excess water, and weighed. For the measurement of area change, the sheet image was scanned by a copying machine (CANON Image RUNNER C5550i) at a resolution of 300 dpi in jpeg format. Then, the sheets were returned to the water. The above measurement process took 5 min, which was subtracted from the soaking time. Three parallel trials were made for each sample. Sheet area was calculated from scanned images using FIJI software (ImageJ with plug-ins). In

the case of freely dried samples A2 and B2, which were curly and stiff, the surface area was determined manually using a flexible measuring tape. The dimensions were measured in the x and y directions at three positions (top, middle, bottom) and the average values were used to calculate the sheet area (Figure S1, Supplemental Information). Deviation in measured sheet dimensions was less than ±1 mm. In each case, three parallel sheets were measured and the calculated average sheet areas are reported. To determine the thickness of single wet sheets, eight wet sheet pieces were stacked on top of each other and the pile thickness was measured with a micrometer.

Water vapor absorption and desorption

Water vapor absorption and desorption was measured using a humidity control cabinet (RH 10–90%, 23 °C). In the case of cyclic water sorption measurement, the samples were kept in RH 10%, 30%, 70%, and 90% for 120 min before weighing, and in RH 50% for 16 h, respectively. In the cyclic humidity measurement, two parallel samples were tested and the average values are reported.

Mechanical properties of IL-treated papers

The mechanical properties of the prepared samples were measured at 10%/min strain rate and 30 mm span using a Lloyd LS5 tensile tester (AMETEK Measurement & Calibration Technologies, Florida, USA) equipped with a 1 kN load cell. All samples were conditioned for at least 24 h at 23 °C, RH 50%. Each sample was cut into a strip (15 mm × 50 mm) for testing. At least eight replicates of each sample type were measured, except for B1C (with three replicates), which was too fragile to handle. For measurement of wet strength, the samples were soaked overnight in Milli-Q water.

Results and discussion

Ionic liquid treatments

The effect of IL-treatments ([EMIM]OAc) on visual appearance, dimensions, and shape can be seen in Figure 2. Just as in the earlier study by Tanaka et al.,[4] increased severity of IL-treatment resulted in increased sheet transparency and density, and in more substantial in-plane shrinking. Samples A1, A1C, and A2 still had a somewhat paper-like feel and appearance, whereas more severely treated samples B1, B1C, and B2 resembled stiff plastic film. More severely treated papers also shrank more substantially. In both cases, free dried sheets were notably curled. As a
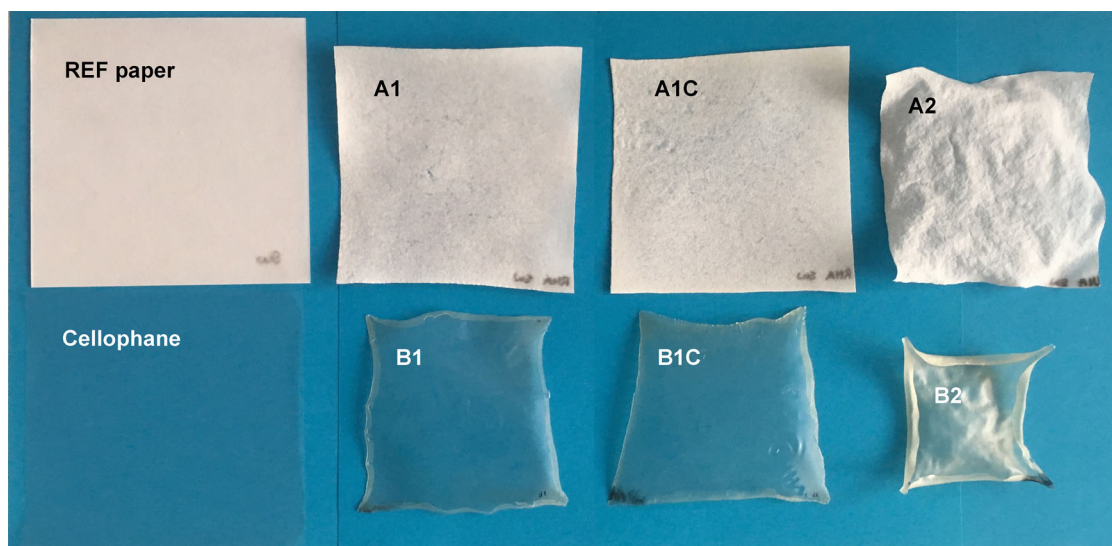
Figure 2. Reference paper sheet, cellophane film, and [EMIM]OAc-treated paper samples. Samples A1, A1C, B1, and B1C are dried in L&W laboratory sheet drier. Samples A1C and B1C are chemically crosslinked by glyoxal and aluminum sulfate. Samples A2 and B2 are dried freely at room temperature on aluminum foil.

result of crosslinking, the sheets became stiffer and more fragile.

As a result of the IL treatments the crystallinity index (CI) of the paper decreased and the cellulose I polymorph was transformed to cellulose II (Figure S2, Supplemental Information). Measurement was done using 13 C CP/MAS NMR spectroscopy, which is an established tool used to distinguish between cellulose I and II polymorphs and for determination of CI.[26,27] After the milder treatment A, a change from cellulose I to cellulose II crystalline form was clearly evident, but the transformation was not complete, as some residual cellulose I was left over. With the more severe treatment B, the cellulose I signal vanished and was entirely replaced by the cellulose II signal. As expected, the cellophane film consisted of pure cellulose II and non-crystalline cellulose.

Based on elemental nitrogen content, the milder treated sheets (A) contained no measureable residual [EMIM]OAc. In the more severe treated sheets, the amount of [EMIM]OAc was approximately 0.12% (wt%). Based on the elemental sulfur content of the sheets, the amount of retained glyoxal and aluminum sulfate in sample A1C was approximately 1.0% and 0.25%, and in B1C 1.2% and 0.31%, respectively.

IL treatments resulted in substantial increase in sheet density (Figure S3, Supplemental Information). In the case of more severe treatment (B), the sheet density increased from the original 0.54 g/cm^3 close to cellophane film density of 1.50 g/cm^3, evidently due to partial dissolution and fusion of the cellulosic fibers. In addition, the IL treatments produced substantial changes in sheet dimensions (Figure 2, Table T1,

Supplemental Information). Compared to sheet drying in the L&W sheet drier, free drying resulted in smaller sheet area, higher sheet thickness, and in the case of free drying substantial curling of the sheets.

The effects of IL treatment on the properties of samples A1 and B1 (Table T2, Supplemental Information) are in accordance with earlier published results.[4] Compared to drying the IL-treated sheets with an L&W Rapid Dryer, free drying resulted in somewhat lower dry and wet strength but higher stretch at break. Chemical crosslinking made the sheets substantially more fragile and decreased both the tensile strength and stretch at break of dry and wet sheets. The low tensile strength of the crosslinked sample B1C is likely a consequence of the fragility of the sheets. The higher tensile strength and lower stretch at break of cellophane film in the machine direction (MD) compared to the cross direction (CD) are evidently due to drawing the cellophane film in the machine direction during film manufacture and also due to the orientation of the cellulose chains and crystals in the MD direction.[20,28]

Reduction in sheet area due to IL treatment occurred both in the dissolution stage and in the subsequent washing stage (Figure 3). Sheet area reduction in the dissolution stage possibly resulted from longitudinal contraction of the fibers, which, according to Le Moigne,[23] is related to relaxation of extended and oriented cellulose chains to a more random condensed state. Interestingly, substantial additional decreases in sheet area occurred when the IL-containing sheets were dipped in water for removal of the IL. This was possibly a consequence of precipitation of
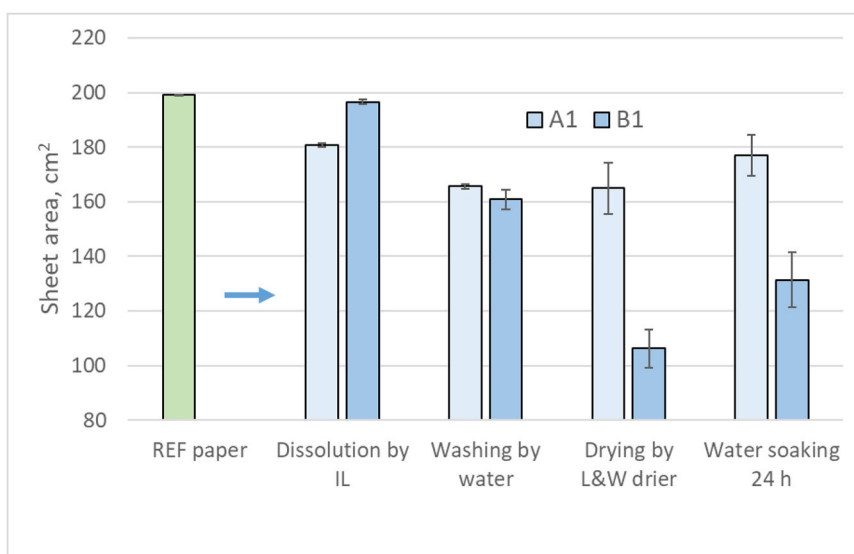
Figure 3. In-plane shrinking of paper sheet at different stages of IL treatment A and B and subsequent soaking in water (see sample codes in Figure 1).
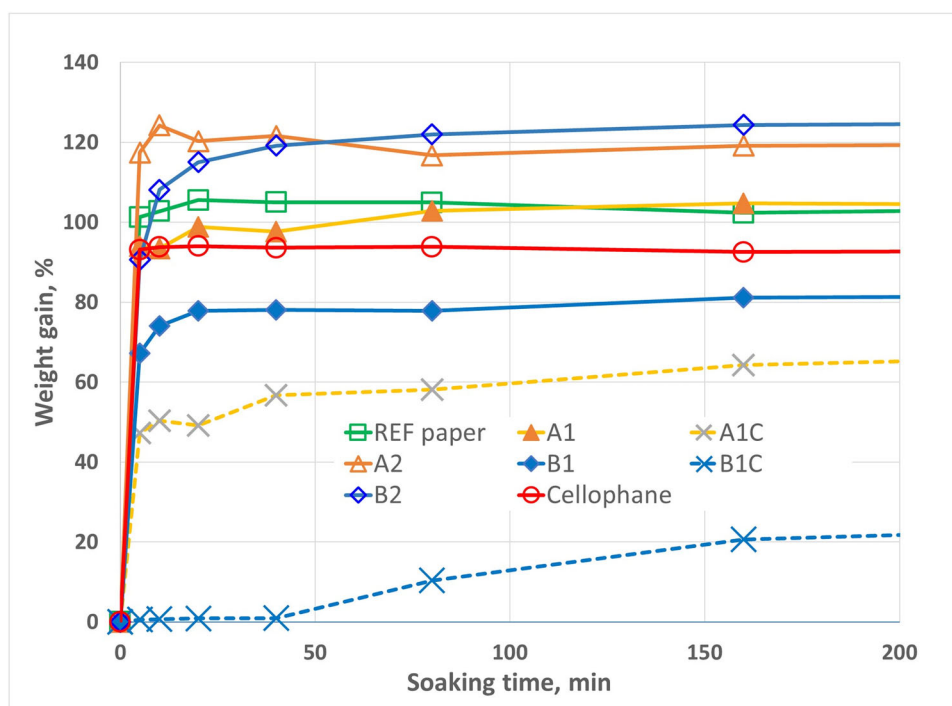

Figure 4. Weight (%) of reference paper, cellophane film, and IL-treated paper sheets in water soaking (23 °C) as a function of soaking time (min.).

the partially dissolved cellulose chains, resulting in compaction of the fibers and the whole sheet. After the washing stage, the wet shrunk sheets resembled flexible jelly plastic. In order to maintain the original area and shape of the paper throughout IL treatment, shrinking must therefore be restrained in both the dissolution and washing stages. In the case of sheet A1, no significant shrinking took place in the subsequent drying stage, whereas in the case of more severely treated sample B1, reduction in sheet area was

substantial. This may be related to loss of fiber internal structure. As Figure 3 shows, the decrease in sheet area was partly recovered as the sheets were soaked in water.

Liquid water absorption

The reference paper, IL-treated papers and cellophane film all absorbed liquid water readily (Figure 4). Equilibrium moisture content was achieved within
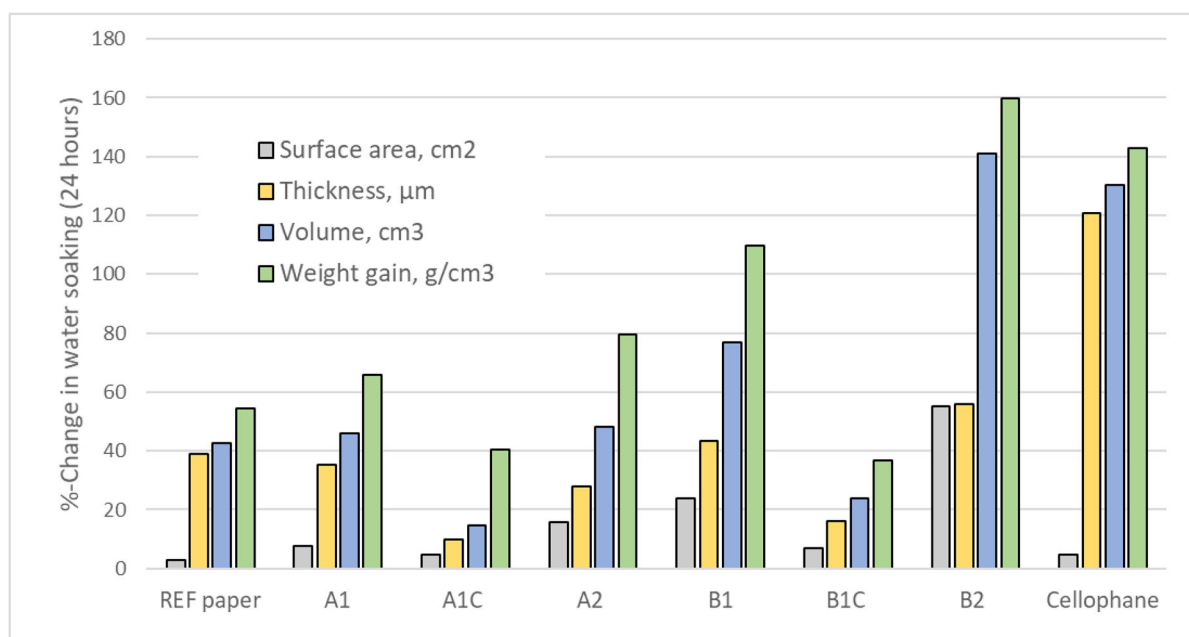
Figure 5. Increase in sheet dimensions (%) of reference paper, cellophane film, and IL-treated paper sheets (see sample codes in Figure 1) in water soaking experiment (24 h, 23 °C).

approximately one hour with all samples except the crosslinked sample B1C. Highest weight gain was shown by the freely dried samples A2 and B2, and the lowest by the crosslinked samples A1C and B1C.

Table T3 (Supplemental Information) and Figure 5 show how the dimensions of the reference paper, cellophane film and IL-treated paper sheets change during 24-h (23 °C) water soaking. Low in-plane swelling and high thickness swelling is characteristic of both paper and cellophane film as in-plain shrinkage is restrained during the manufacture of both materials.[6–8,18,19] In accord with this, freely dried IL-treated paper sheets (A2, B2) showed higher relative in-plane swelling in water than restraint-dried sheets (A1, B1). It is notable that due to the strong shrinking tendency, drying the sheets in the L&W Rapid Drier did not prevent shrinking of the IL-treated sheets, but in-plane shrinking of the sheets was somewhat reduced compared to free drying. However, higher IL-treatment severity and free drying both clearly increased the swelling tendency of sheets during water soaking (Figure 6). Chemical crosslinking decreased sheet swelling substantially in both the thickness and in-plane direction. Glyoxal is supposed to form acetal- and hemiacetal linkages between adjacent cellulose molecules, thus preventing water-induced swelling of the fibers and the whole sheet. In a study by Peterson and Livingston,[29] chemical crosslinking of cellophane film with dialdehyde starch (dosage 6.0%) decreased weight gain of the film in water soaking by 69%. In

the present study, crosslinking reduced sheet weight gain by about 63% (B1 vs. B1C).

Adsorption and desorption of water vapor

Figure 7 shows the rate of water vapor absorption and desorption of the reference paper, cellophane film, and the IL-treated paper sheets as RH is raised from 50% to 90% and lowered from 50% to 10%. With all samples, the majority of water absorption and desorption took place within the first two hours. Cellophane film absorbed somewhat more water than the reference paper as the RH was increased from 50% to 90%. The results for cellophane film are concordant with the literature data.[18,30] Also, the IL-treated paper sheets absorbed somewhat more water vapor than the reference paper. The slower water vapor absorption and desorption rates of the more severe IL-treated samples B1 and B2 compared to cellophane film may be at least partly a consequence of the substantially higher thickness of the IL-treated sheets (137 and 188 μm vs. 24 μm, respectively).

Figures 8 and S4 (Supplemental Document) show the weight change of the sheets in cyclic humidity. In the test, the moisture content of cellophane film and the non-crosslinked IL-treated paper sheets showed clear hysteresis. Although extensively studied, the mechanisms behind sorption hysteresis is still somewhat unsolved.[7,31,32] According to an early study by Urquhart and Williams,[33] upon
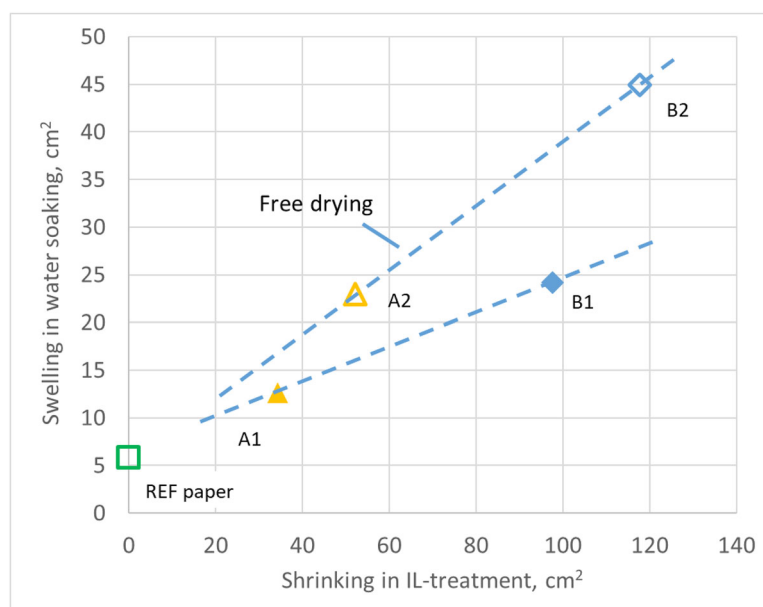
Figure 6. In-plane area shrinking of sheets in IL-treatment vs. in-plane area swelling of the sheets in water soaking (24 h, 23 °C). REF = reference paper, A1, A2, B1, and B2 = IL-treated papers (see Figure 1).
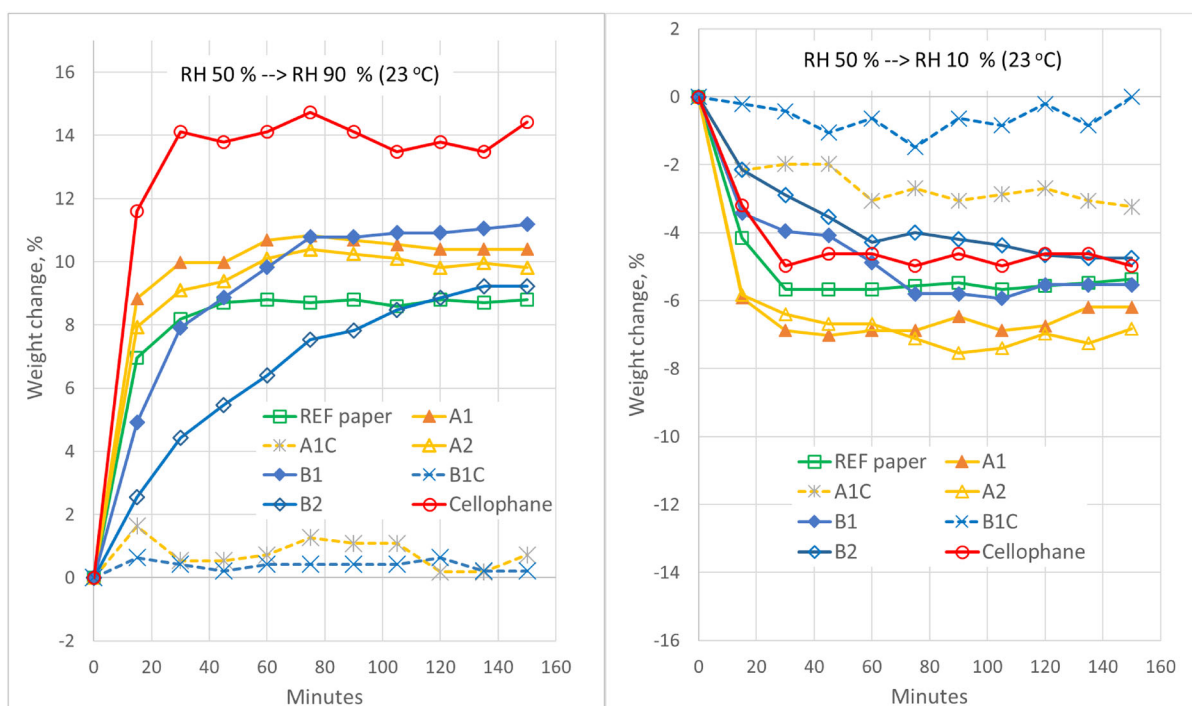

Figure 7. Rate of water vapor absorption and desorption of reference paper, cellophane film, and IL-treated paper sheets at increased and decreased relative humidity (RH 50% → 90%, and RH 50% → 10%).

absorption of water some bonding hydroxyl groups become free to associate more water. Barkas[34] explained the phenomenon through swelling stresses resulting in irreversible plastic deformations in the fiber wall. In the case of paper products, the release of internal stresses at high moisture contents causes irreversible shrinkage in MD but little change in CD.[7] Release of internal stresses in the film may

also explain the higher hysteresis of cellophane and samples A1 and B1 compared to the freely dried samples A2 and B2 (Figure 7).

Based on our results, crosslinking treatment seems to have significantly reduced both water vapor adsorption and desorption of the IL-treated paper sheets (Figure 7). The effect of crosslinking was apparent also in the cyclic humidity test (Figures 8 and S4
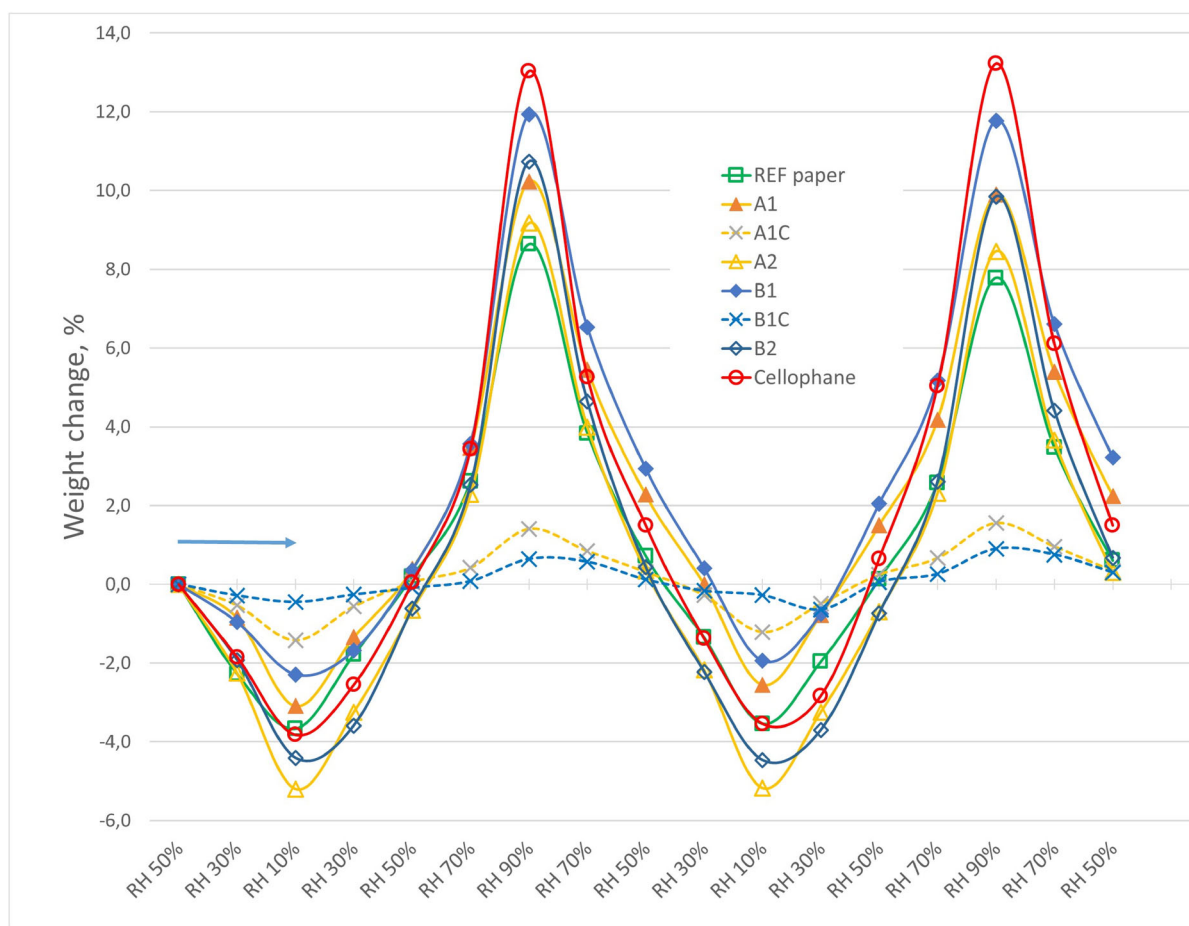
Figure 8. Moisture content vs. relative humidity of reference paper, cellophane film, and IL-treated paper sheets in cyclic relative humidity exposure (23 °C). Arrow shows direction of exposure.

(Supplemental Information)). The formed crosslinks clearly substantially decreased the number of cellulosic hydroxyl groups capable of associating with water. By using a lower crosslinking agent dosage or crosslinking agents that form longer linkages between adjacent cellulose molecules it may be possible to produce films that are both flexible and dimensionally stable. This remains an area for further development.

Concluding remarks

The results of the present study show that the mechanical and water sorption properties of IL-treated paper sheets are between those of ordinary paper and cellophane film. It is possible that properties similar to those of cellophane film could be achieved by full dissolution of the paper with ionic liquids in combination with controlled drawing of the film during preparation. Additionally, as with cellophane film, properties such as flexibility and water sorption could be adjusted by additives and coatings. However, from the application point of view, partial dissolution of the fibers resulting in sheets with the properties of both

paper and cellophane film may have more interesting practical potential. With the use of ionic liquids, it may be possible to manufacture paper-like, white, printable material that has oxygen and grease barrier properties and moldability similar to cellophane film. Development of industrial manufacturing methods for such 'paperfilm' materials is an interesting challenge of further studies.

and 318891 (Competence Center for Materials Bioeconomy, FinnCERES).

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