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Towards natural-fibre-based thermoplastic films produced by conventional papermaking†

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Materials based on cellulose are predicted to be of great importance in a sustainable society. However, for materials such as paper to replace materials with a higher ecological footprint, they need to be strong, ductile, provide a gas barrier, and, sometimes, also be transparent. Improved properties, or even novel properties, are also important for use outside the conventional markets. This paper describes how cellulose fibres partly derivatised to dialcohol cellulose can be used to fabricate high-density materials by conventional papermaking techniques that simultaneously display all the above-mentioned features. The materials produced were characterised with respect to X-ray diffraction, dynamic mechanical thermal behaviour, visual appearance, oxygen permeability and tensile properties. The highest degree of modification studied, resulted in a material with thermoplastic features, a tensile strength of 57 MPa, a strain-at-break of 44% and an oxygen permeability at 80% RH of 23 ml µm (m^2 kPa 24 h)$^{-1}$. At a thickness of 125 µm, these films have a total light transmittance of 78% (87% haze). However, by hot pressing the film for 2 min at 150 °C under a pressure of 16 MPa, and thereby increasing the density, the total transmittance increases to 89% (23% haze). The hot pressing can also be used to fuse individual pieces together, which is useful in many modern packaging applications. Altogether, this work shows how chemical modification of cellulose fibres can be used to induce novel properties and improve the range of application, and consequently provide an interesting bio-based material with a good potential to replace less sustainable materials.

Introduction

Our society is gaining an increased environmental awareness at the same time as producers are continuously focusing on production efficiency and customers are demanding better product and material performance. Cellulose, which is the most abundant polymer on earth, is a fascinating and versatile biopolymer which in different forms can be expected to be extremely important in a sustainable bioeconomy.[1] However, for cellulose really to be a competitive option in advanced applications, it cannot be used directly in its natural state but needs to be refined or chemically modified to attain suitable properties. An example of such a refinement is to individualise the strong and highly ordered cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) constituting the native cellulose fibre, an approach that has resulted in thousands of scientific papers over the last 15 years.[2–5] In several of these papers, CNFs and CNCs have been applied in advanced electronic devices, film and barrier applications, and nanocomposites.

Since all forms of native cellulose have limited ductility and are non-thermoplastic, the material processing is typically limited to particle-in-water systems. However, since cellulose is also hydrophilic and has a high propensity to form high-viscosity slurries and hydrogels, especially in the molecular or nanoparticle form, wet processing into the above-mentioned nano- and mesostructured materials can be very complicated on a large scale. It is therefore desirable to find a cellulose-based system which benefits from the high strength of native cellulose, but can be processed by large-scale water-based papermaking-type processes followed by dry-state processing such as hot pressing or hydroforming.

Recently, we have shown that a heterogeneous conversion of cellulose to dialcohol cellulose, presumably by forming a shell of dialcohol cellulose that surrounds the crystalline core of each CNF, can be an interesting way to form an *in situ* composite with high strength and ductility.[6,7] If the modified CNFs

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† Electronic supplementary information (ESI) available: FTIR spectra of the final materials. Light transmittance and density of modified papers pressed under various pressures, temperatures and times. Full spectrophotometer data in support of Fig. 5b. Additional information regarding the *t*-peel test. See DOI: 10.1039/c5gc03068d

are individualised, oxygen-barrier films with high ductility and formability can be fabricated.[7] However, since pure dialcohol cellulose is thermoplastic,[8,9] it is of interest to study whether a core–shell structure is sufficient to induce thermoplastic features in the material while retaining the good mechanical properties of the native cellulose. The present study therefore aims at exploring a higher degree of derivatisation, and characterising the mechanical properties, thermoplastic behaviour and structure of papers and films made by a conventional papermaking technique, with the deliberate goal to produce high-performance materials from cellulose without the energy-consuming liberation of the fibres into CNFs, and to apply a simple form of heat processing, in this case hot pressing, to prepare highly transparent and strong films.

Experimental

Fibres

Bleached softwood kraft fibres (K46) were supplied by SCA Forest Products (Östrand pulp mill, Timrå, Sweden). One part of the material was left unbeaten and one was mechanically beaten in a Voith mill to an energy input of 160 W h kg^{-1} (about 30 SR). This increases the swelling of the fibres and makes them more flexible. Mechanical beating also produces small-particle material, so called fines. To ensure that only long macroscopic fibres were used during the modification, thereby easing the processing and data interpretation, the small-particle material was removed from both the non-beaten (3–4%) and the beaten (8–10%) fibres by filtration through a 200 mesh metal screen, using a Britt Dynamic Drainage Jar (Paper Research Materials, Seattle, USA).

Chemicals

Sodium (*meta*)periodate was provided by Alfa Aesar (98%), and sodium borohydride and hydroxylamine hydrochloride were supplied by Sigma-Aldrich. Other chemicals such as hydrochloric acid, sodium hydroxide, isopropanol (≥99.8% purity) and sodium phosphate were all of analytical grade.

Fibre modification

Cellulose fibres were sequentially oxidised and reduced according to an earlier established protocol.[6] The fibres were partly oxidised to dialdehyde cellulose by adding 5.4 gram of periodate per gram of fibre to a gently stirred beaker at a fibre concentration of 4 g l^{-1}. To limit the formation of radicals and unwanted side reactions, the reaction was performed in the dark. After the desired time of oxidation, 6, 12 or 24 h, the reaction was stopped by filtration and washing of the fibres. The fibres were then suspended to 4 g l^{-1} and the dialdehyde cellulose formed was reduced to dialcohol cellulose by adding 0.5 g sodium borohydride per gram of fibres. To limit the pH increase to about pH 10 upon addition of sodium borohydride, monobasic sodium phosphate was added together with the borohydride in an amount corresponding to 0.01 M. The reduction time was kept constant at 4 h, followed by filtration and thorough washing.

Carbonyl content determination

The carbonyl content of the oxidised fibres was determined by reaction with hydroxylamine hydrochloride.[6,10] The fibres were suspended in water and adjusted to pH 4, followed by dewatering to a gel-like consistency. Then, approximately 0.25 g (dry basis) of these fibres were stirred with 25 ml of 0.25 M hydroxylamine hydrochloride solution at pH 4 for at least 2 h before the fibres were separated from the solution by filtration using a pre-weighed filter paper. The exact mass of the fibres was then determined by oven drying of the filter paper and the carbonyl amount was determined by titration of the filtrate back to pH 4 with 0.10 M sodium hydroxide. Two to three independent oxidations were performed at each oxidation time, and each reaction with hydroxylamine hydrochloride was performed in triplicate.

X-ray diffraction

The crystallinity of the non-modified and modified materials was evaluated by collecting X-ray diffraction (XRD) patterns using a PANalytical X'Pert PRO X-ray diffraction system. Data were recorded in the reflection mode in the angular range of 5–50° (2θ) using CuKα radiation (1.5418 Å). The XRD data were analysed by calculating the ratio between the diffraction of the (002) lattice peak at about 22.5° and the minimum found between the (002) and (101) lattice peaks at about 18.5°, commonly referred to as the crystallinity index,[11] and the crystallite width was estimated using the Scherrer formula on the (002) lattice peak, assuming a shape factor of 0.9.

Paper preparation

Handsheets with an approximate grammage of 150 g m^{-2} were prepared using tap water in a Rapid Köthen sheet former (Paper Testing Instruments, Austria). The dewatering time ranged from 20 to 40 s. The sheets were dried at 93 °C under a reduced pressure of 95 kPa, first for 15 min between 400 mesh woven metal wires attached to regular sheet-former carrier boards, and then for 2 min between ordinary carrier boards. The sheets were then stored at 23 °C and 50% RH until further testing.

Pressing

Circular samples with a diameter of 40 mm were hot pressed between two bright annealed steel discs in a Fontijne TP400 press (Fontijne Grotnes, The Netherlands) for all further analysis, except for peel testing where rectangular (20 mm wide and 63 mm long) steel plates of the same area were used. The typical combination of pressure, temperature and time was 16 MPa, 150 °C and 2 min, but other combinations were also tested (see ESI†).

Thickness and density

Thickness was determined, before and after pressing, as the average structural thickness according to the SCAN-P 88:01

standard. This thickness value was then used together with the area and the mass of the test piece to calculate the material density.

Dynamic mechanical thermal analysis

DMTA was performed with a TA Instruments Q800 operating in the tensile mode. The oscillation frequency and amplitude were 1 Hz and 10 μm, respectively, and temperature scans were performed at a rate of 3 °C min^{-1} in the temperature range of 20–300 °C (or until sample failure). For each degree of modification, four replicates were tested; using test pieces that had an approximate width of 3 mm, a thickness of 100–180 μm and a distance between the clamps of about 8 mm.

Tensile and peel testing

Tensile and *t*-peel testing were performed with an Instron 5944, equipped with a 500 N load cell, in a controlled climate of 23 °C and 50% RH.

For tensile testing, test pieces, 5 mm wide and 100–180 μm thick, were clamped with a free span of 20 mm and strained at a rate of 2 mm min^{-1}. The strain was determined by measuring the grip displacement; the Young's modulus was calculated as the initial linear slope of the stress–strain curve, and the yield point was determined by the offset method, using an offset of 0.3%.[12] A total of ten pressed and ten non-pressed test pieces were tested at each degree of modification.

Prior to *t*-peel testing, two 20 mm wide strips of modified cellulose were hot pressed as described above, fusing them in the middle and leaving four free ends (see ESI† for further information). The fused strips were then cut in half to give two T-shaped test pieces with a 20 mm wide and approximately 30 mm long fused area. *t*-Peel testing was performed using a strain rate of 20 mm min^{-1}. A total of four test pieces were evaluated.

Electron microscopy

A Hitachi S-4800 high-resolution field-emission scanning electron microscope (SEM) was used to acquire micrographs of the pressed and non-pressed papers. In order to suppress specimen charging during imaging, the specimens were sputtered (208 HR Cressington Sputter Coater) for 20–30 s using a platinum–palladium target.

Cross-sections of modified samples were prepared using a microtome (RMC MTXL, Boeckeler Instruments Inc., AZ, USA) equipped with a glass knife. The papers were first clamped between two 0.8 mm polystyrene plates and the assembly was then "polished" by cutting 50 nm thin sections for a total thickness of a few micrometres. This procedure could unfortunately not be used for the reference papers due to their high porosity and low stiffness and a sharp knife was therefore used for cross-sectioning of these samples.

To study whether the hot pressing damages the macroscopic fibres, papers were soaked in water and gently strained until failure. After drying, the failure zone was then imaged as top view micrographs.

Optical properties

The optical properties of the papers were studied with a Shimadzu UV-2550 UV-vis spectrophotometer equipped with an integrating sphere accessory. Each sample was studied at three random positions, and three non-pressed and two pressed samples were evaluated for each degree of modification.

Oxygen permability

The oxygen permeability was evaluated on 5 cm^2 samples using a MOCON OX-TRAN 2/21 according to the ASTM D3985 standard. The oxygen permeability measurements were performed at 23 °C and 50% RH or 80% RH, using the same relative humidity on both sides of the sample. For samples exhibiting measurable barrier properties, four samples were evaluated at each relative humidity.

Results and discussion

Molecular and supra-molecular characterisation

Non-beaten and beaten cellulose fibres were oxidised with sodium periodate, which is known to selectively oxidise vicinal diols, for up to 24 h. Fig. 1 shows that the rate of conversion was relatively slow and remained fairly constant throughout the studied time frame, decreasing only slightly as the degree of oxidation increased. This is well in accordance with other studies on the periodate oxidation of cellulose.[6,13–15] The results also indicate that the oxidation rate is slightly higher in beaten fibres, which is plausible since beating is known to soften the fibre wall and to increase the swelling and hence the accessibility of cellulose molecules inside the fibre wall.[15,16] It should, however, also be stressed that periodate oxidation is significantly faster and more industry-applicable at high temperature, and that the sodium periodate is not to be considered as a consumable, but would in an industrial process be regenerated.[14,17,18]

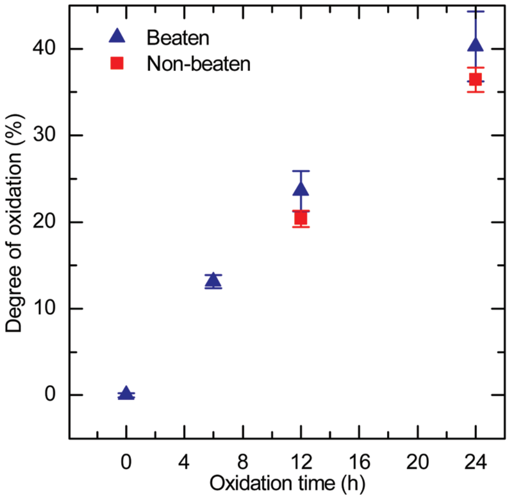

Fig. 1 Degree of oxidation as a function of reaction time at room temperature for beaten and non-beaten fibres.

Directly after the periodate oxidation, the fibres partly containing dialdehyde cellulose were reduced with borohydride (complete reduction was concluded by a non-measurable reaction with hydroxylamine and further supported by the absence of a carbonyl peak in the FTIR spectra of the final papers; the spectra can be found in the ESI†), which in the same way as the sodium periodate would be regenerated in an industrial process,[19] to dialcohol cellulose. According to our earlier findings,[6,7] this gives fibres in which the CNFs constituting the fibre wall have been modified into a core–shell structure, *i.e.* as periodate works its way into the CNF, its surface is transformed into a shell of highly derivatised and amorphous cellulose surrounding the inert and highly ordered CNF core. Papers were rapidly made from the modified fibres by a conventional laboratory technique and analysed by XRD. Fig. 2 shows how the X-ray diffraction and crystallite width decreased with increasing degree of oxidation, in line with the core–shell hypothesis. Fig. 2a also shows that the ordered structure was unaffected by further hot pressing.

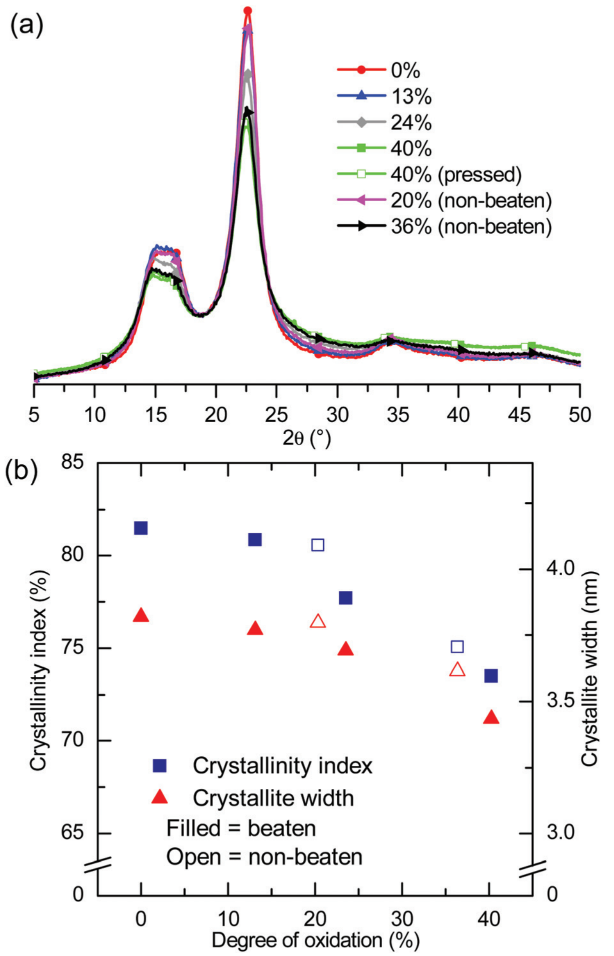

Fig. 2 XRD data of oxidised-reduced fibres; (a) diffractograms, (b) crystallinity index and crystallite width as functions of the degree of oxidation.

Thermoplasticity, pressability and structure

Cellulose is an example of a technically non-thermoplastic polymer, *i.e.* it decomposes before it readily softens. However, there are cellulose derivatives that are thermoplastic, typically various cellulose esters,[1] but also dialcohol cellulose.[8,9,20] Therefore it is interesting to study how cellulose fibres partially transformed into dialcohol cellulose are affected by temperature. Fig. 3 shows DMTA of the different samples and clearly shows that the untreated material is more or less unaffected by temperature while the thermoplasticity increases with increasing degree of modification. For samples with a degree of oxidation of 24% or greater, Fig. 3 shows two rather sudden changes in storage modulus, one at 70–120 °C and one at 160–180 °C, where the first change can presumably be linked to the glass transition of dialcohol cellulose and the latter to its flow region.[9] Furthermore, Fig. 3 shows that hot pressing at 150 °C prior to the DMTA did not affect the thermoplastic behaviour of the material, *i.e.* such a pre-treatment did not induce any significant permanent chemical or structural

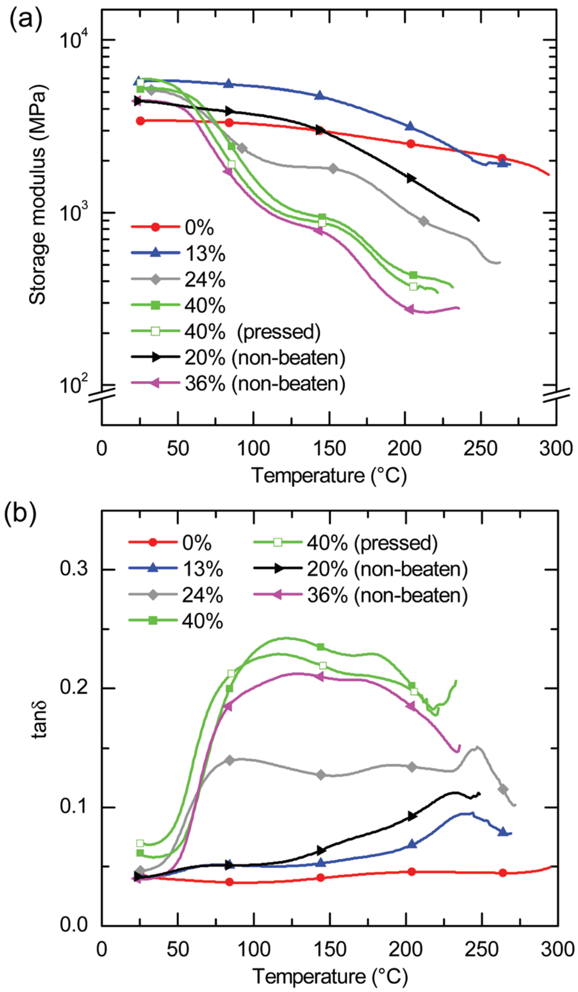

Fig. 3 DMTA of papers and films made of oxidised-reduced fibres; (a) storage modulus, (b) tan δ. Each curve is the average of four measurements.

changes affecting the thermoplasticity. This also implies that the mechanical properties of the non-pressed samples are controlled predominantly by the properties of the fibre wall, and not by the fibre network. Altogether, the data in Fig. 3 indicate that the material can be heat processed in different ways, such as hot pressing.

To further study and utilise the thermoplastic features of the modified cellulose materials, samples were hot pressed between two smooth steel plates. The optimal pressing conditions, in terms of visual appearance and light transmittance, were found to be 16 MPa and 150 °C for 2 min (all the conditions tested can be found in the ESI†). Fig. 4 shows the material density before and after hot pressing of the differently modified materials. The density of the modified papers/films was high already before hot pressing, ranging from 1100 to 1300 kg m^{-3}, which by far exceeds the density of conventional papers, including greaseproof papers,[21] and was similar to the density of fibre materials subjected to extended hot pressing at high pressures (45 MPa for 20 min).[22] The densities of the papers presented here is, to the best of our knowledge, surpassed only by so-called nanopapers made from CNFs or CNCs, which can have densities of about 1500 kg m^{-3}, *i.e.* close to that of solid cellulose.[23,24] However, compared to nanopapers, the current papers were formed and dewatered by conventional papermaking methods in a matter of a few tens of seconds whereas it takes hours to dewater (or solvent cast) a nanopaper.[25,26] When the papers were hot pressed, the density increased by 10–20% to densities greater than 1400 kg m^{-3} for the papers with a degree of oxidation greater than 24%, *i.e.* densities not far from that of solid cellulose. This indicates that the modified fibres are soft and flexible and form a novel, highly consolidated type of paper, more resembling a transparent film.

Another indicator of a highly consolidated paper is a high optical transmittance, which is an indicator not only of a high density of a cellulose-based material but also of good barrier properties. In this work, a spectrophotometer equipped with an integrating sphere was used to measure both direct and diffuse transmittance. The visual appearance and optical transmittance of the different papers are shown in Fig. 5, where Fig. 5a shows how the fibre modification transforms the papers from being opaque to being fairly transparent. This transparency of the modified samples was further improved by hot pressing, especially for the beaten, most modified fibres which resulted in a more or less homogeneously transparent paper/film. Fig. 5 (and Fig. S3†) also shows that the non-beaten fibres were not as susceptible to the hot pressing as the beaten fibres, indicating a synergetic effect between beating and the oxidation-reduction treatment of the fibre, where both treatments soften the fibre wall and facilitate a good consolidation

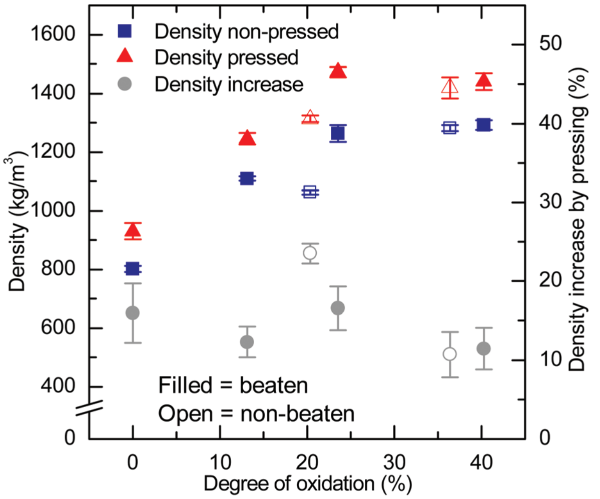

Fig. 4 Density before and after hot pressing for 2 min at 150 °C and 16 MPa. Values are means of at least eight measurements and are given with 95% confidence limits.

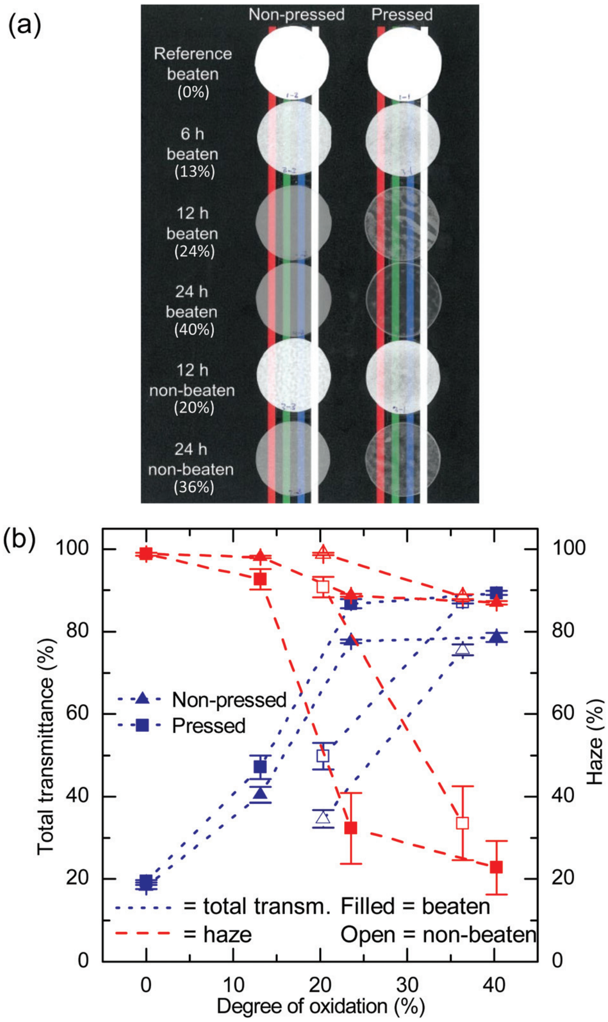

Fig. 5 Optical appearance of non-pressed and pressed samples; (a) scanned image, (b) total transmittance and haze, *i.e.* percentage of diffuse transmittance, measured at a wavelength of 550 nm (full spectra can be found in the ESI†). The average sample thickness was 183 and 150 µm for the non-pressed and pressed reference, respectively, and the thickness of all the modified samples was in the range of 120–150 µm before pressing and 100–120 µm after pressing.

during drying. Fig. 5b shows that the total light transmittance increased significantly upon chemical modification; the three most modified samples had a total transmittance of about 80% at a sample thickness of about 120 µm. However, most of the transmitted light, about 90%, was measured as diffuse light. After hot pressing the total transmittance increased to nearly 90%, and the transmittance mode was changed into mainly direct transmittance, with a haze value of only 20–40%. This possibility of tailoring the optical haze indeed open the way for applications outside the traditional pulp, paper and packaging arena. Recently, hybrid materials between highly beaten fibres and CNFs were identified as interesting materials in solar cell devices due to their combination of high total transparency and high haze.[25]

The structure of the papers was further studied by SEM. Fig. 6 shows micrographs of reference papers and papers made from the most modified fibres and, as can be seen, the pressing had little effect on the structure of the reference paper (first and second column). However, if the reference and modified paper, both before and after pressing, are compared, remarkable differences can be observed (first row): the reference fibres form an expected ribbon-like structure where individual fibres can easily be identified, whereas the modified fibres are merged together making it difficult to distinguish individual fibres from each other (the repeating pattern, that can be mistaken for individual fibres, are imprints from the drying mesh). Upon hot pressing, the uneven structure of the modified paper is more or less completely transformed to a smooth film surface without distinct features (at higher magnification, however, nanofibrils can be seen; results not shown), which largely explains the significant decrease in haze upon pressing since haze is in many materials largely due to surface roughness.[27–29] Quite remarkably, if the non-pressed or pressed, modified papers are soaked in water and strained until failure, fibres become clearly visible as they protrude from the failure surface (Fig. 6g and h), showing that the modification and hot pressing do not significantly affect the macroscopic fibre structure but makes possible a very close contact between individual fibres, still leaving the fibres as discrete entities. The last row in Fig. 6 shows cross-section images and agrees well with the densities and transmittance values reported in Fig. 4 and 5, showing a porous reference sheet and a basically non-porous modified paper.

Barrier properties

High density (Fig. 4), high transparency (Fig. 5) and a highly consolidated network structure (Fig. 6) are typical traits of a polymer-based gas barrier. Therefore, and since non-porous

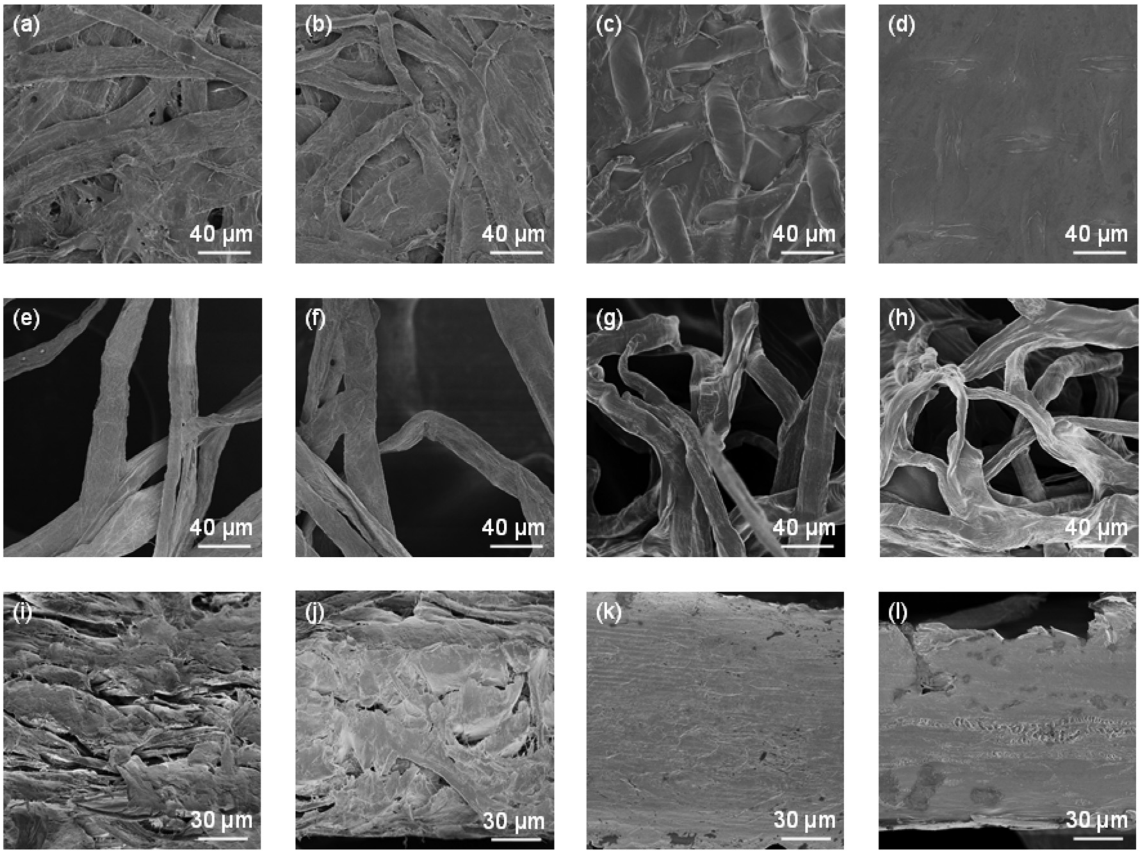

Fig. 6 Micrographs of the reference paper and the most modified paper; the first and second columns are non-pressed and pressed reference papers, respectively, the third and last columns are non-pressed and pressed modified papers, respectively. (a–d) Top-view images, (e–h) top-view images of the failure surface of wet-strained papers, (i–l) cross-section images.

cellulose materials are known to be good oxygen barriers,[4,30,31] especially at low relative humidity, oxygen permeability measurements were performed before and after pressing. The results are presented in Table 1 and, as expected, the non-modified papers did not provide an oxygen barrier but the papers formed from beaten fibres with a degree of modification greater than 24% did indeed provide an oxygen barrier. Since greaseproof papers do not provide any measurable gas barrier,[32] this is, to the best of our knowledge, the first report of a non-coated paper produced by conventional papermaking methods that constitutes a gas barrier.

Hot pressing did not improve the (non-existing) barrier properties of the reference paper; but, pressing of the modified paper sheets tended to further decrease the oxygen permeability. As long as the pressing does not cause any damage to the fibre network, it is expected that an increase in density (Fig. 4) and hence a decrease in void fraction should lower the permeability. Interestingly, pressing of papers made of the most modified non-beaten fibres transformed the paper from a non-barrier to a barrier. This not only shows that hot pressing of the modified papers leads to a smaller void fraction, but also supports the above-mentioned observation of a synergetic effect between beating and chemical modification (since the modified beaten fibres provided a barrier already before pressing).

The oxygen permeability of all the papers/films exhibiting oxygen-barrier properties increased with increasing relative humidity. This is a well-known phenomenon, not only for cellulose and dialcohol cellulose but for polysaccharides in general.[7,31,33,34] It is also interesting to note that the barrier films made from beaten fibres with a degree of oxidation of 24% had a lower permeability than films made from beaten fibres having a 40% degree of oxidation. Apparently 24% oxidation is enough to soften the fibres enough to facilitate a film without interconnected pores, providing a gas barrier, and presumably due to the higher degree of crystallinity (Fig. 2) these films also exhibit lower oxygen permeability than the more modified samples. Regardless, the oxygen permeability at 80% RH was, both for the 24 and 40% oxidised papers, still below a level allowing the material to be used in, for example, packaging applications, especially considering the rapid dewatering and the presumably good and fast processability in a paper machine, which is a prerequisite for economic large-scale material production.

Mechanical performance

Dialcohol cellulose in its pure form is very ductile, but unfortunately it is also very weak.[8,9,20] However, our earlier studies have shown that it was possible to combine both ductility and strength by a heterogeneous modification of CNFs in a core–shell structure.[6,7] Fig. 7 shows that this approach can be taken even further by the extended modification described here. As shown in Fig. 7b, an increasing degree of modification results in a steadily increasing strain-at-break whereas the ultimate strength, Young's modulus, yield stress and hardening modulus pass through a maximum at a degree of modification of 10–25%, reflecting the increasing influence of the more ductile, but weaker, dialcohol cellulose. It is also worth emphasising that the chemical modification has a dramatic effect on the tensile strength of the papers made from fibres subjected to the lowest degree of modification (13%), where the strength is about three times greater than that of the untreated reference. Interestingly, the toughness defined as the work of fracture, *i.e.* the area under the stress–strain curve, reached about 21 MJ m^{-3} for the most modified papers, which surpasses not only all kinds of conventional paper grades by about an order of magnitude but also most nanopapers and nanocomposites made from CNFs.[35,36] This emphasises the remarkable properties of this new material, which would presumably facilitate the advanced hydroforming and deep-drawing of the papers into complex 3D structures.

Table 1 Oxygen permeability of oxidised-reduced papers/films before and after hot pressing. Permeability values are means of four measurements given with 95% confidence limits

Beaten fibres	Pressed/non-pressed	Degree of oxidation (%)	Average sample thickness (μm)	Permeability (ml μm (m^2 kPa 24 h)$^{-1}$)	
				50% RH	80% RH
Reference	Non-pressed	0	185 ± 15	Over range	Not measured
	Pressed	0	158 ± 13	Over range	Not measured
6 h oxidation	Non-pressed	13	139 ± 1	Over range	Not measured
	Pressed	13	115 ± 4	Over range	Not measured
12 h oxidation	Non-pressed	24	118 ± 5	<0.6[a]	11.8 ± 0.9
	Pressed	24	99 ± 2	<0.5[a]	9.6 ± 0.9
24 h oxidation	Non-pressed	40	118 ± 4	<0.6[a]	22.9 ± 2.1
	Pressed	40	113 ± 5	<0.6[a]	20.5 ± 2.0
Non-beaten fibres					
12 h oxidation	Non-pressed	20	144 ± 2	Over range	Not measured
	Pressed	20	118 ± 3	Over range	Not measured
24 h oxidation	Non-pressed	36	118 ± 1	Over range	Not measured
	Pressed	36	107 ± 4	< 0.6[a]	23.4 ± 3.4

[a] Below the detection limit of the instrument.

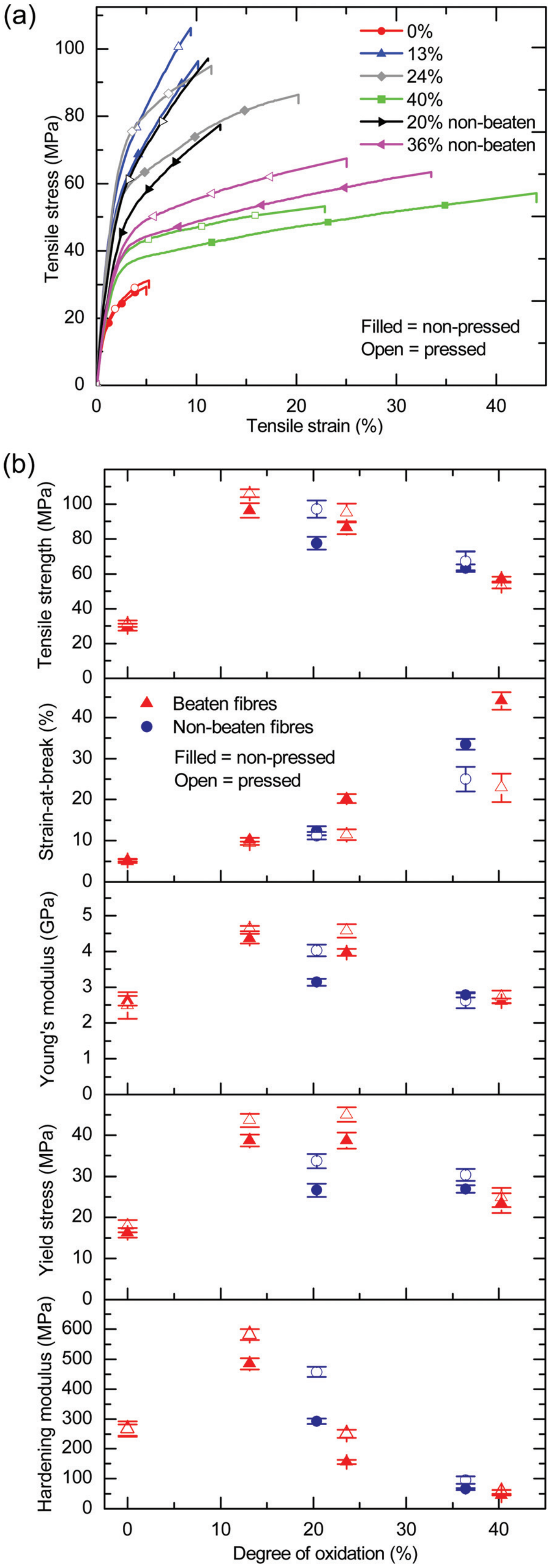

Fig. 7 Tensile data for oxidised-reduced papers/films; (a) average stress–strain curves, (b) tensile strength, strain-at-break, Young's modulus, yield stress and hardening modulus as functions of the degree of oxidation. Values are the means of ten test pieces given with 95% confidence limits.

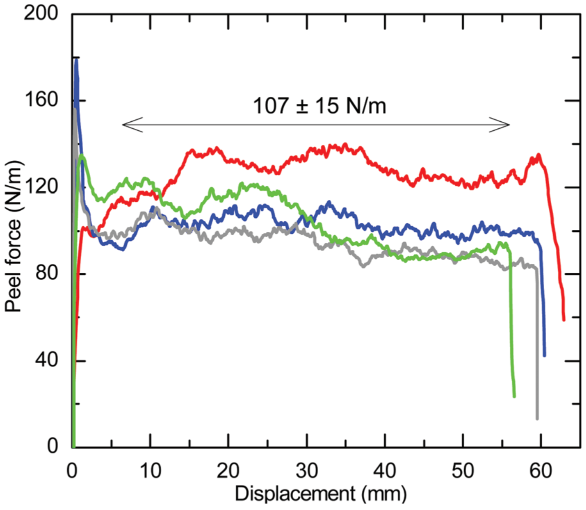

Fig. 8 *t*-Peel force-displacement curves for the separation of two strips made of the most modified fibres fused together by hot pressing for 2 min at 150 °C and 16 MPa.

Hot pressing of the papers affected the mechanical properties in the opposite way to an increasing degree of oxidation, *i.e.* the strain-at-break decreased and the strength, modulus, yield stress and hardening modulus increased in papers that had been hot pressed (Fig. 7). There are at least two possible explanations of this observation: heat-induced chemical degradation, supported by the earlier sample failure seen in Fig. 3 for the modified samples, or a significant decrease in the free volume in the material.[37] Regardless of mechanism, the hot pressed material still shows a very high ductility for a wood-fibre-based network.

From the DMTA data (Fig. 3) and the SEM micrographs (Fig. 6) it can be concluded that the modified cellulose has an increased molecular mobility. This implies that it is possible to fuse two separate pieces by hot pressing. Therefore two paper strips placed on top of each other were hot pressed, followed by a *t*-peel test to quantify the force needed to separate the strips. A force of about 110 N m^{-1} was needed for separation (Fig. 8), showing that it was indeed possible to "weld" two modified papers by hot pressing. Besides showing good adhesion, the merged strips were highly transparent (Fig. S4†). These features demonstrate how the material, in combination with 3D forming, could, for example, be a biorenewable alternative to the often difficult-to-open heat-sealed blister and clamshell packages made of plastic.

Conclusions

Cellulose fibres were heterogeneously converted to different contents of dialcohol cellulose, where the modified cellulose forms an amorphous shell surrounding an intact core of highly ordered cellulose of each nanofibril. Papers and films can then be formed from these fibres in a few tens of seconds by conventional papermaking methods, ultimately resulting in dry materials with tensile strengths ranging from 50–100 MPa and a strain-at-break of up to 44%; the highest work of fracture observed being almost 21 MJ m^{-3}, which surpass by far any earlier reported paper. Materials made of fibres with a degree of modification of at least 24% showed distinct thermoplastic features in DMTA and could be hot pressed so that the fibres were completely fused together, after which no individual fibres could be seen by SEM, demonstrating a high molecular mobility upon heating. This indicates that these novel thermoplastic papers and films can find a use in new value-added applications such as complex-shaped, heat-sealed 3D-formed packaging. Furthermore, films from highly modified fibres had a high density and high transparency, and both properties were further increased by hot pressing; the most modified material had a density of 1450 kg m^{-3} and a light transmittance of 89% after hot pressing. In fact, the densities of the most modified materials were so high that they could act as oxygen barriers. Films with a degree of oxidation of 24 and 40% showed, at 80% RH, oxygen permeabilities of 12 and 23 ml μm $(m^2kPa24\ h)^{-1}$, respectively. This is, to the best of our knowledge, the first report of an oxygen barrier formed by a conventional (laboratory) papermaking protocol, with production times similar to those of the reference papers, which presumably facilitates large-scale industrial production of this novel high-performance cellulose material.

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Notes and references

1 D. Klemm, B. Heublein, H.-P. Fink and A. Bohn, *Angew. Chem., Int. Ed.*, 2005, **44**, 3358–3393.
2 S. J. Eichhorn, A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A. N. Nakagaito, A. Mangalam, J. Simonsen, A. S. Benight, A. Bismarck, L. A. Berglund and T. Peijs, *J. Mater. Sci.*, 2010, **45**, 1–33.
3 D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray and A. Dorris, *Angew. Chem., Int. Ed.*, 2011, **50**, 5438–5466.
4 N. Lavoine, I. Desloges, A. Dufresne and J. Bras, *Carbohydr. Polym.*, 2012, **90**, 735–764.
5 R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, *Chem. Soc. Rev.*, 2011, **40**, 3941–3994.
6 P. A. Larsson, L. A. Berglund and L. Wågberg, *Cellulose*, 2014, **21**, 323–333.
7 P. A. Larsson, L. A. Berglund and L. Wågberg, *Biomacromolecules*, 2014, **15**, 2218–2223.
8 T. Morooka and M. Norimoto, *Sen'i Gakkaishi*, 1991, **47**, 328–333.
9 T. Morooka, M. Norimoto and T. Yamada, *J. Appl. Polym. Sci.*, 1989, **38**, 849–858.
10 H. Zhao and N. Heindel, *Pharm. Res.*, 1991, **8**, 400–402.
11 L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *Text. Res. J.*, 1959, **29**, 786–794.
12 W. D. Callister, *Fundamentals of materials science and engineering: an interactive e-text*, Wiley, New York, 2001.
13 N. Guigo, K. Mazeau, J.-L. Putaux and L. Heux, *Cellulose*, 2014, **21**, 4119–4133.
14 J. Sirviö, U. Hyväkkö, H. Liimatainen, J. Niinimäki and O. Hormi, *Carbohydr. Polym.*, 2011, **83**, 1293–1297.
15 S. H. Zeronian, *Sven. Papperstidn.*, 1963, **18**, 707–710.
16 J. E. Stone, A. M. Scallan and B. Abrahamson, *Sven. Papperstidn.*, 1968, **71**, 687–694.
17 S. Koprivica, R. Scholz, W. Bauer, W. Roggenstein, T. Rosenau and A. Potthast, Regeneration of aqueous periodate solution from dialdehyde cellulose production by ozone treatment determined by RPHPLC with UV detection, in *8th ISWFPC International Symposium on Wood, Fibre and Pulping Chemistry Conference*, Vienna, Austria, ed. J. Hell, S. Böhmdorfer, A. Potthast and T. Rosenau, Vienna, Austria, 2015.
18 H. Liimatainen, J. Sirviö, H. Pajari, O. Hormi and J. Niinimäki, *J. Wood Chem. Technol.*, 2013, **33**, 258–266.
19 T. Kemmitt and G. J. Gainsford, *Int. J. Hydrogen Energy*, 2009, **34**, 5726–5731.
20 W. Kasai, T. Morooka and M. Ek, *Cellulose*, 2014, **21**, 769–776.
21 K. M. Furuheim, D. E. Axelson and T. Helle, *Nord. Pulp Pap. Res. J.*, 2003, **18**, 168–175.
22 H. Nilsson, S. Galland, P. T. Larsson, E. K. Gamstedt, T. Nishino, L. A. Berglund and T. Iversen, *Compos. Sci. Technol.*, 2010, **70**, 1704–1712.
23 M. Nogi, S. Iwamoto, A. N. Nakagaito and H. Yano, *Adv. Mater.*, 2009, **21**, 1595–1598.
24 J. Sugiyama, R. Vuong and H. Chanzy, *Macromolecules*, 1991, **24**, 4168–4175.
25 Z. Fang, H. Zhu, Y. Yuan, D. Ha, S. Zhu, C. Preston, Q. Chen, Y. Li, X. Han, S. Lee, G. Chen, T. Li, J. Munday, J. Huang and L. Hu, *Nano Lett.*, 2014, **14**, 765–773.
26 H. Sehaqui, A. Liu, Q. Zhou and L. A. Berglund, *Biomacromolecules*, 2010, **11**, 2195–2198.
27 V. Kanniah, E. A. Grulke and T. Druffel, *Thin Solid Films*, 2013, **539**, 170–180.
28 P. F. Smith, I. Chun, G. Liu, D. Dimitrievich, J. Rasburn and G. J. Vancso, *Polym. Eng. Sci.*, 1996, **36**, 2129–2134.

29 F. C. Stehling, C. S. Speed and L. Westerman, *Macromolecules*, 1981, **14**, 698–708.
30 W. L. Hyden, *Ind. Eng. Chem.*, 1929, **21**, 405–410.
31 Q. Yang, H. Fukuzumi, T. Saito, A. Isogai and L. Zhang, *Biomacromolecules*, 2011, **12**, 2766–2771.
32 H. Kjellgren, L. Stolpe and G. Engström, *Nord. Pulp Pap. Res. J.*, 2008, **23**, 272–276.
33 P. A. Larsson, T. Pettersson and L. Wågberg, *Green Mater.*, 2014, **2**, 163–168.
34 C. Aulin and T. Lindström, in *Biopolymers – New Materials for Sustainable Films and Coatings*, ed. D. Plackett, John Wiley & Sons, Ltd, Chichester, UK, 2011, pp. 255–276.
35 K. Prakobna, C. Terenzi, Q. Zhou, I. Furo and L. A. Berglund, *Carbohydr. Polym.*, 2015, **125**, 92–102.
36 H. Sehaqui, Q. Zhou and L. A. Berglund, *Soft Matter*, 2011, **7**, 7342–7350.
37 C. A. Daniels, *Polymers: Structure and Properties*, Taylor & Francis, 1989, ch. 4.