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Melt processing of chemically modified cellulosic fibres with only water as plasticiser: Effects of moisture content and processing temperature

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ABSTRACT

To replace petroleum-derived polymers with cellulose fibres, it is desirable to have the option of melt processing. However, upon heating, cellulose degradation typically starts before the material reaches its softening temperature. Alternatives to plastics should also, ideally, be recyclable via existing recycling streams. Here, we address the problem of melt processing cellulose as fibres while preserving recyclability. Native cellulose fibres were partially modified to dialcohol cellulose to impart thermoplastic characteristics. We demonstrate melt processing of these modified fibres with only water as plasticiser. Processability was investigated at selected processing temperatures and initial moisture content by monitoring the axial force of the extruder screws as a rheological indicator. The effects on molecular structure, fibre morphology and material properties were characterised by NMR spectroscopy, microscopy, tensile testing, fibre morphology analysis and X-ray diffraction. When comparing the melt-processed extrudate with handsheets, the already exceptional ductility was further increased. Moderate losses in tensile strength and stiffness were observed and are attributable to a loss of crystallinity and fibre shortening. This is the first report of strong and durable extrudates using cellulosic fibres as the only feedstock. Finally, the potential for recycling the processed material with unmodified fibres by paper recycling procedures was demonstrated.

1. Introduction

Cellulose has been identified as a promising renewable alternative to petroleum-derived synthetic polymers. However, native cellulose has a high glass transition temperature, and upon heating, it degrades before it appreciably softens or melts (Goring, 1965; Salmen & Back, 1978; Shafizadeh & Bradbury, 1979). Thus, native cellulose cannot be melt processed, which limits the range of applications within which cellulose can replace synthetic thermoplastics such as polyethylene and polypropylene.

Native cellulose is commonly available from the pulp and paper industry as mechanically and/or chemically refined wood fibres (which may still contain a significant fraction of hemicellulose and lignin). If it were possible to melt process cellulose in fibre form, this would allow for ready access to raw materials and cost-effective adaptation of existing

equipment and techniques within pulp and paper industry instead of requiring the design of new equipment and techniques.

Melt processing of non-fibrous cellulose derivatives, such as cellulose acetate and other cellulosic esters is known but this has been limited to narrow processing windows, usually in the presence of synthetic plasticizers (Mohanty et al., 2003; Quintana et al., 2012).

Here we make a substantial contribution to addressing the problem of melt processing cellulose in the form of fibres. Our solution presents an opportunity for industrial-scale continuous manufacturing and the manufacture of complex three-dimensional cellulosic parts by well-established processes such as twin-screw extrusion, compression moulding and injection moulding, while preserving recyclability by repulping with conventional, unmodified fibres.

Cellulose can be converted to dialcohol cellulose by periodate oxidation, followed by borohydride reduction (Fig. S1 of the electronic

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supplementary material)(Larsson et al., 2014b; Zeronian et al., 1964). This reaction can be carried out heterogeneously, on native cellulose fibres suspended in water. Previous work in our group has demonstrated that native cellulose fibres partially converted to dialcohol cellulose, by heterogeneous chemical modification, exhibit remarkable hygroplastic and thermoplastic features (Larsson & Wågberg, 2016; Linvill et al., 2017; López Durán et al., 2018). Here, we refer to such fibres (of a specified degree of modification) as modified fibres or dialcohol fibres. Chemical and materials characterisation of dialcohol fibres has supported the hypothesis that a core-shell structure exists at the cellulose nanofibril (CNF) level, where individual CNFs comprise a crystalline native cellulose core (unpenetrated by chemical modification) surrounded by an amorphous dialcohol cellulose shell (Larsson et al., 2014b; Leguy et al., 2018; Leguy et al., 2019; Matsumura et al., 2000). Furthermore, double-curved structures have been prepared from core-shell dialcohol CNFs by exploiting their hygroplasticity and thermoplasticity (Larsson et al., 2014a; Linvill et al., 2017).

We recently reported that dialcohol fibres can be melt processed with ethylene acrylic acid at very high fibre content (Lo Re et al., 2023). In the same paper, we demonstrated that dialcohol fibres at 38 % and 55 % degree of modification, when conditioned at high humidity, could be melt extruded even without a synthetic polymer, but the resulting materials were very brittle. The facilitated processability was also corroborated by molecular dynamics simulations (Mehandzhyski et al., 2022; Mohanty et al., 2003; Quintana et al., 2012).

The aim here is to systematically investigate the hygroplasticity and thermoplasticity of dialcohol fibres by melt processing, with a focus on processing fibres without additional polymer or additive that remains in the final material. We hypothesise that an increased moisture content or an increased temperature, or the two in combination, reduce the torque required to extrude modified fibres, i.e. improves the melt processability, resulting in materials that are both stiff and tough. Furthermore, we hypothesise that such processed fibres can be resuspended in water and recycled by processing into paper. A successful test of this hypothesis would be a first demonstrator of the possibility to produce mechanically strong, recyclable cellulose fibre materials using paper as the feedstock in conventional melt processing equipment.

Melt processability was assessed by monitoring axial force during extrusion, as an online rheological assessment (axial force is proportional to viscosity at the processing condition) and material characterisation was carried out using scanning electron microscopy, tensile testing, fibre morphology analysis and X-ray diffraction.

2. Materials and methods

2.1. Materials

Bleached softwood kraft fibres (<0.5 % Klason lignin) with a molecular weight of 492 kDa ($\bar{M}_w = 11$) from Norwegian spruce and Scots pine (same as characterised and used in earlier studies by Larsson et al., 2014b and López Durán et al., 2016) were supplied by SCA Forest Products (Östrand pulp mill, Timrå, Sweden). Sugar composition and molecular weight distribution (Fig. S2) can be found in the electronic supplementary material. The pulp was mechanically beaten in a Voith mill to an energy input of 160 W h kg⁻¹. Small-particle material generated during beating (5–10 % by mass), commonly referred to as fines, were removed from the beaten fibres by filtration through a 200 mesh-equivalent metal screen, using a Britt Dynamic Drainage Jar (Paper Research Materials, Seattle, USA).

Sodium metaperiodate was supplied by Alfa Aesar (98 %), sodium borohydride and hydroxylamine hydrochloride were supplied by Sigma-Aldrich. Other chemicals, such as hydrochloric acid, sodium hydroxide, sodium phosphate, isopropanol and ethanol were all of analytical grade.

2.2. Chemical modification of cellulose fibres

Beaten cellulose fibres (fines removed) were partially modified to dialcohol cellulose (Fig. S1). The fibres were firstly partially oxidized to dialdehyde cellulose using sodium metaperiodate, followed by total reduction of aldehydes to hydroxy groups by treatment with sodium borohydride, in a similar manner to earlier protocols (Larsson et al., 2014a; Larsson & Wågberg, 2016). Nuclear magnetic resonance (NMR) spectroscopy has been used to show that dialcohol cellulose was the product of the modification (see Fig. S3–S4 and the electronic supplementary material for more details).

One batch at 47 % degree of modification was prepared at lab scale. For the oxidation reaction, 120 g of fibres were suspended in 8 L of 6.3 % (v/v) isopropanol in water to give a concentration of 15 g L⁻¹. Isopropanol served as a radical scavenger to limit unwanted side reactions (Painter, 1988). The fibres in suspension were then partially oxidized with 162 g of sodium metaperiodate (1.35 g per g of fibre), under constant stirring, for 38 h. The oxidation reaction was stopped by washing the fibres with deionized water until the filtrate conductivity was 10 $\mu\text{S cm}^{-1}$ or lower. The fibres were then resuspended to 15 g L⁻¹ in 0.1 M sodium phosphate monobasic (to prevent the pH from increasing beyond pH 10, limiting alkaline depolymerisation upon addition of sodium borohydride) and treated with 0.5 g sodium borohydride per gram of fibres, under gentle, constant stirring, for 2 h. The reduction reaction was stopped by washing as for the oxidation reaction.

A larger batch of modified fibres at 45 % degree of modification was prepared in an industrial lab using a moderately scaled-up version of the above protocol, using non-beaten instead of beaten fibres as starting material.

2.3. Estimation of degree of modification

Degree of modification was estimated by determining the aldehyde content after periodate oxidation. Aldehyde content was determined by a well-established protocol based on reaction with hydroxylamine hydrochloride (Larsson & Wågberg, 2016; Zhao & Heindel, 1991). Since all aldehydes are finally reduced (assessed by reaction with hydroxylamine), the degree of modification after periodate oxidation is taken as the final degree of modification to dialcohol cellulose.

2.4. Preparation of handsheets and cast films

Handsheets with a grammage of 100–150 g m² were prepared using tap water in a Rapid Köthen sheet forming machine (Paper Testing Instruments, Laakirchen, 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. Moisture content of the conditioned, modified sheets was 6.3 %, measured gravimetrically using a conventional forced air oven for drying, confirming agreement with previously published measurements (Linvill et al., 2017).

Alternatively, films were cast from aqueous suspensions by pouring onto a Teflon sheet and drying in a forced air oven at 50 °C.

2.5. Lab-scale melt processing trials

Melt processing was done using a DSM Xplore Micro 5 cc twin-screw mini extruder (Heerlen, The Netherlands). Handsheets of dialcohol fibres were cut into strips. These strips were fed into the extruder within 6 min at a screw speed of 30 rpm and allowed to recirculate for an additional 5 min. During the recirculation step the screw speed was increased from 30 rpm to 100 rpm.

Extrusion was carried out at a temperature of 70 °C or 100 °C. Prior to extrusion, handsheet strips were conditioned at high relative

humidity (in a desiccator over liquid water for at least 12 h to ensure RH of >95 %), achieving an initial moisture content of 25 wt%, or liquid water was added to the materials to achieve an initial moisture content of 63 wt%. These moisture contents were measured in triplicate using halogen light moisture analyser (Mettler Toledo HB43-S). Samples were labelled **70 deg-25 %**, **100 deg-25 %**, **70 deg-63 %** and **100 deg-63 %** according to the temperature of extrusion and initial moisture content.

In one experiment to probe the effect of higher temperature, a sample was conditioned to approx. 60 % moisture content and extruded at 120 °C (Fig. S14).

2.6. Scanning electron microscopy and optical microscopy

Scanning electron micrographs were collected using a Hitachi TM-1000 tabletop scanning electron microscope (Tokyo, Japan) and a Hitachi S-4800 high-resolution field-emission scanning electron microscope (Tokyo, Japan).

Samples of non-extruded fibres were prepared by suspending these fibres in water, followed by solvent exchange with absolute ethanol and drop casting onto conductive carbon tape. In the case of extruded materials, these were resuspended in deionized water for at least 48 h. After resuspending in water, the materials were either solvent exchanged with ethanol three times and drop cast onto conductive carbon tape or flash-frozen in liquid nitrogen followed by freeze drying and depositing on conductive carbon tape. All samples were sputter coated for 20 s using a Pt-Pd target to minimize charging (208 HR Cressington, Watford, UK).

Optical microscopy was carried out using a Carl Zeiss Standard 25 ICS transmission light microscope equipped with a cross polarization filter and lambda retardation plate.

2.8. Tensile testing

Tensile testing was carried out on samples conditioned at 23 °C and 50 % RH using a single column Instron 5944 (Norwood, Massachusetts, USA). All samples were tested with a span of 20 mm at a strain rate of 2 mm min⁻¹.

Samples were either rectangular strips cut from standard handsheets (five replicates) or cylindrical filaments obtained directly from twin screw extrusion (eight replicates). The rectangular strips cut from handsheets were 5 mm wide and 90–180 μm thick (precise thickness was determined for each test piece before testing). The cylindrical extruded filament samples were approximately 2 mm in diameter with a span of 20 mm between the clamps. Ends of approximately 5 mm were fixed to rectangular pieces of sandpaper to facilitate clamping. For the cylindrical samples of extruded materials, **100 deg-25 %** (diameter of approx. 2 mm) was tested without polishing because the surface was already sufficiently smooth. For **100 deg-63 %** polishing the surface to a reduced diameter of approx. 1.5 mm was necessary to achieve uniform samples.

2.9. Density measurements

Samples were conditioned at 23 °C and 50 % RH before making measurements. For the extruded materials, samples of 20–70 mg were cut from the intact filament. For handsheets, square samples were cut. The volumes of these samples were determined by measuring their dimensions using callipers and the masses determined by weighing on an analytical balance. Density values were determined in triplicate.

2.10. Repulping

Repulping experiments were carried out by resuspending extruded material in water for at least 48 h. This resuspended material was mixed in 1, 2 and 5 wt% ratio of extruded material to unmodified fibres (either beaten or unbeaten fibres) in a pulp disintegrator by Paper Testing Instruments (Laakirchen, Austria) at a concentration of 5 g L⁻¹ and total

dry content of 10 g. In each instance, the pulp disintegrator was run for 10 min at the default propeller speed of 3000 rpm. After mixing in the pulp disintegrator, handsheets were prepared as before.

3. Results and discussion

Dialcohol cellulose is known to be more hygroscopic than native cellulose and at least partially soluble in water (Painter, 1988; Salmén & Larsson, 2018). We have found that dialcohol fibres at 47 % degree of modification, suspended in deionized water, exhibit distinct morphological features, such as extensive swelling and so-called ‘balloon-and-collar’ structures (Fig. 1 and Fig. S5). Such features are well-known for native fibres in solvent systems such as aqueous *N*-methylmorpholine *N*-oxide (Fig. S6)(Le Moigne & Navard, 2010) and charged fibres, such as carboxymethylated cellulose in water (Gorur et al., 2020; Sim et al., 2014). A core-shell CNF model of dialcohol fibre has been described previously (Larsson et al., 2014b; Larsson & Wågberg, Leguy et al., 2018; Leguy et al., 2019), where an intact crystalline native CNF core is surrounded by a highly modified amorphous dialcohol shell, which is associated with reduced total crystallinity. Based on this model, the swelling behaviour observed here for dialcohol fibres (Fig. 1b, Fig. 1d and Fig. S5) can be attributed to the highly modified hydrophilic dialcohol shell, which has a greater tendency to interact with moisture, as evidenced by greater equilibrium moisture content when compared with unmodified cellulose fibres. (Salmén & Larsson, 2018) The simultaneous presence of modified fibres that are uniformly swollen, i.e. those that *do not* exhibit ‘balloon-and-collar’ structures, is attributable to the inherent polydispersity of pulp fibres combined with the heterogeneity of the chemical reaction. In fibres that swell with ‘balloon-and-collar’ structures it has been suggested that the S1 layer of the fibre wall remains intact and concentrated at the collars, where it restrains swelling of the fibres (Sim et al., 2014). Dialcohol fibres were also suspended in 1 M NaCl solution. By optical microscopy, there was no observable difference when comparing the morphology of the swollen fibres in this high ionic strength (data not shown) against those in deionized water, suggesting that this swelling is not osmotically driven due to charged moieties (dialcohol cellulose has no charge). The swelling can be reasonably ascribed to the higher solubility of the amorphous dialcohol cellulose in water compared to native cellulose.

It has been shown previously that the degree of modification of dialcohol fibres can be controlled by varying the periodate oxidation

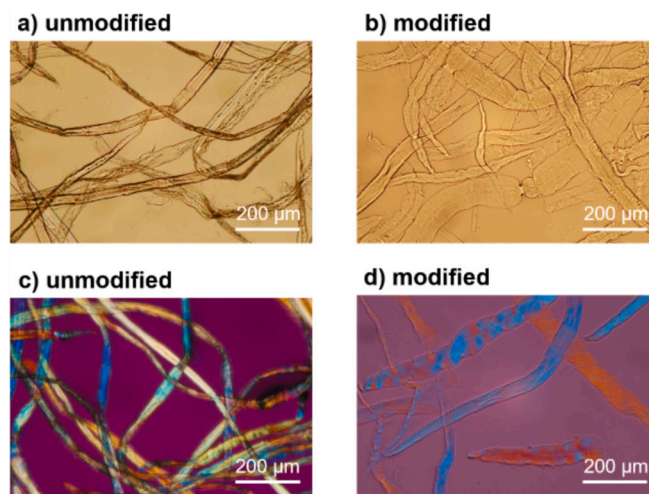


Fig. 1. Optical micrographs of unmodified and modified fibres (47 % degree of modification) allowed to swell in deionized water for at least 48 h: a) unmodified fibres and b) modified fibres via an ordinary polarising filter; c) unmodified fibres and d) modified fibres via both a polarising filter and a retardation plate, where ‘balloon-and-collar’ structures are observable.

reaction time, while maintaining other relevant parameters constant (Larsson et al., 2014b; Larsson & Wågberg, 2016; Leguy et al., 2019). The degree of modification is the estimated number of moles of modified anhydroglucose units as a fraction of the total number of moles of anhydroglucose units. In the present work, 47 % degree of modification was reached after 38 h of periodate oxidation at 15 g L⁻¹ fibre concentration and 1.35 g sodium metaperiodate per gram of fibre.

The heterogeneous reaction employed here inherently produces modified fibres that are polydisperse both in morphology and, possibly, degree of modification. At very high degree of modification (ca. 60 % and above) the total yield of the reaction drops off rapidly because the highly modified cellulose polymer chains are soluble. Matter is lost as dissolved chains when washing by filtration. As a further consequence, the fibres swell and break into smaller fragments such as CNF aggregates and individual CNFs, and probably other shapes of particles, which then are lost during washing by filtration (Painter, 1988).

Melt processability of dialcohol fibres is highly dependent on the degree of modification. It was found that at lower degree of modification (ca. 30 % and lower) dialcohol fibres only could not be processed by lab-scale twin-screw extrusion. The mini extruder employed here has an axial force limit of 5000 N, which is rapidly exceeded when attempting to melt process dialcohol fibres of 30 % or lower degree of modification, regardless of temperature or water content. At ca. 40 % degree of modification and higher, melt processing was consistently achieved. Dialcohol fibres at 47 % degree of modification were prepared for melt processing trials because this degree of modification falls well between the lower limit determined by poor melt processability and the upper limit above which reaction yields are very poor.

The hygro- and thermoplasticity of dialcohol cellulose has been previously noted (Kasai et al., 2014; Larsson et al., 2014a; Larsson & Wågberg, 2016; Linvill et al., 2017; Salmén & Larsson, 2018). Thus, for melt processing by twin-screw extrusion, temperature of processing and initial moisture content were the variables investigated. All other parameters of processing were maintained essentially constant. Four batches of extruded materials were prepared by processing at either 70 °C or 100 °C with an initial moisture content of either 25 wt% or 63 wt%: **70 deg-25 %**; **70 deg-63 %**; **100 deg-25 %** and **100 deg-63 %**.

Fig. 2 shows photographs of the extrudates obtained from melt processing and a graph of the online axial force registered during melt processing. Irregular texturing of the extrudate and opacity are observed in **70 deg-25 %**, **70 deg-63 %** and **100 deg-63 %**. A high proportion of bulk water is retained in the mini extruder because the instrument is not specifically designed to vent gases. A high degree of surface roughness, observable by the naked eye, and opacity in the batches processed at 63 wt% initial moisture content are presumably attributable to retention of water vapour in the extruder, which leads to rapid expansion of steam as the material exits at the die. Previous evidence showed that storage modulus decreases rapidly with increasing temperature, above the T_g of approximately 60 °C for fibres modified to approximately 40 % dialcohol cellulose. (Larsson & Wågberg, 2016) Additional data has been reported on the thermal softening of dialcohol cellulose fibres as a function of degree of modification and relative humidity (Linvill et al., 2017; Salmén & Larsson, 2018) In the case of **70 deg-25 %**, at this temperature the material is too solid-like to avoid the irregular texturing feature and opacity. It is worth noting that the diffusivity in a polymeric material increases substantially beyond its T_g (Welle, 2021). The **100 deg-25 %** batch is within a processing window where the material is sufficiently liquid-like, and initial moisture content is low enough to avoid the adverse effects of steam expansion. The **100 deg-25 %** extruded material is thus translucent and does not exhibit undesirable surface texture.

The measured axial force serves as an indication of viscosity during processing. The axial force stabilised at approx. 3800 N for **70 deg-25 %**, approx. 3200 N for **100 deg-25 %**, approx. 900 N for **70 deg-63 %** and approx. 700 N in the case of **100 deg-63 %**. A higher temperature of processing or higher initial moisture content results in lower viscosity

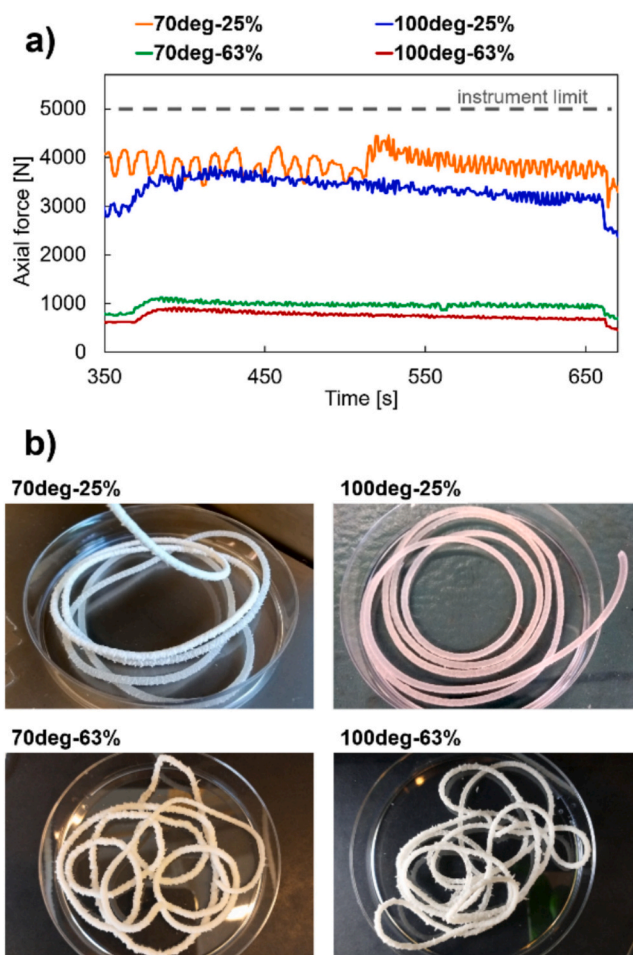


Fig. 2. Melt processing by lab-scale twin-screw extrusion at a temperature of 70 °C or 100 °C and initial moisture content of 25 wt% or 63 wt%: a) Online axial force as function of time during melt processing and b) photographs of the extrudates obtained from melt processing.

during processing, which is consistent with previous evidence of hydroplasticity and thermoplasticity in dialcohol fibres (Larsson et al., 2014b; Larsson & Wågberg, 2016). Increasing the temperature from 70 °C to 100 °C reduces the viscosity only modestly. An increased moisture content from 25 wt% to 63 wt%, instead, had a large effect - the axial force was reduced fivefold. A vented extruder, as the conventional twin-screw extruder already at pilot scale, allowing for higher initial moisture content and in situ removal of water, could be used to further optimize the melt processing (Sessini et al., 2021).

An experiment to probe higher temperature of processing showed that, for 45 % degree of modification dialcohol fibres, at 120 °C and approx. 60 % moisture content, the measured axial force was higher than expected and increased rapidly, reaching the instrument limit before processing could be completed (Fig. S14). We inferred that at 120 °C, drying occurs too rapidly to obtain a meaningful result from the available equipment.

Thermogravimetric analysis indicated no degradation associated with mass loss (although chemical degradation without mass loss is not detectable by this method alone) of the materials after melt processing (Fig. S7). The thermograms of the melt processed samples are near-identical to the thermogram of the modified fibres (of a specified degree of modification), before processing, as reference.

Melt-processed materials could be reswollen (Fig. S8) and the fibres resuspended in water. SEM images of the melt processed materials after resuspending them in water (and further sample preparation details) are provided in Fig. 3, and at higher magnification in Fig. S9. Images of the

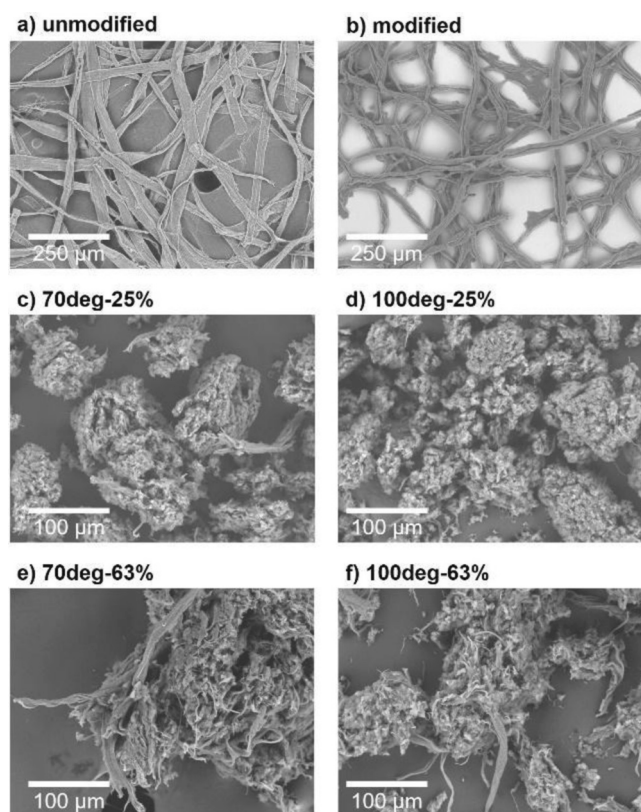


Fig. 3. SEM images of samples deposited on conductive carbon tape unless otherwise specified. Fibres prior to melt processing: a) unmodified beaten fibres; b) modified fibres (deposited on silicon wafer). Materials obtained from melt processing: c) 70 deg-25 %; d) 100 deg-25 %; e) 70 deg-63 %; f) 100 deg-63 %. The melt processed materials were resuspended in water, solvent exchanged with ethanol and dried in air prior to mounting as SEM samples.

unmodified fibres (Fig. 3a) and modified fibres before processing (Fig. 3b) indicate that their structure as macroscopic fibres are largely preserved during the chemical modification. The unmodified fibres are collapsed, appearing as ribbons and adhered to the surface via the carbon tape adhesive, whereas the modified fibres are more curled as a result of solvent exchange with ethanol and partially spread onto the untreated silicon wafer surface (mainly SiO₂) by adhesion of dialcohol cellulose to the surface. Micrographs of the melt processed samples (Fig. 3c–f), however, reveal that the fibres are severely damaged, and aggregates persisted, despite resuspension for at least 48 h and vigorous agitation using a vortex mixer. Previous research involving hot-pressing of dialcohol fibre sheets showed that the hot-pressed fibres could be separated as largely intact fibres by rewetting the pressed films and applying tensile strain until breakage (Larsson & Wågberg, 2016). However, it was not possible, here, to fully separate the melt processed fibres by agitation in water suspension because of damage of the fibres and fibrillation. Although the method applied previously to handsheets is similar to the method applied here, to separate melt processed fibres, the outcomes are rather different. Aggregation is more severe in the lower moisture content samples, 70 deg-25 % and 100 deg-25 %, and is less pronounced in 70 deg-63 % and 100 deg-63 %, where more fibres and free fibril aggregates are observable. Damaged fibres and fibrillation are evident in all processed samples, especially at lower moisture content, and is unsurprising given the severe shear stresses, i.e. axial forces, that the fibres were subjected to during processing. However, it should be noted that the melt processing did not change the NMR-assessed molecular structure of the cellulosic material (Fig. S2).

Additionally, changes in fibre size and morphology, related to shear stresses applied during melt processing, were assessed by an optical

method using a commercial fibre analyser, assuming that it properly can detects the highly swollen fibres. Shear stresses varied according to the conditions of melt processing, as indicated by variations in axial forces (Fig. 2a). The fibre length distribution and the percentage of fines (defined here as 10–200 μm in length) at the different processing conditions are represented in Fig. S10. Fibre shortening is evident from the reduced number of longer fibres (Fig. S10a), while the percentage of fines generated (10–200 μm) increases after processing (Fig. S10b). These results are attributable to high shearing during extrusion and are consistent with the images of the fibres after processing in the mini extruder (Fig. 3).

Tensile testing was performed directly on the extruded filaments (extrudates) and compared to unprocessed modified and unmodified fibres. Typical stress–strain curves are shown in Fig. 4a. The exceptional ductility associated with dialcohol-modified fibres – five times higher than the unmodified fibres – was further doubled by melt processing, which suggests the effect of increased amorphous content (as reported previously, Larsson & Wågberg, 2016) is dominant over fibre shortening (which would result in lower strain at break) and may also be supported by alignment of fibres. Alignment has been previously observed for dialcohol fibres extruded with ethylene acrylic acid (Lo Re et al., 2023). A remarkable mean strain-at-break of 67 ± 6 % was measured for the 100 deg-25 % sample. Sheets of modified fibres show about 80 % higher Young's modulus and tensile strength compared to unmodified fibres (Fig. 4b and c, respectively). Considering the decreased crystallinity associated to the modified fibres (Fig. S11 and Fig. S12), one can hypothesize a change in the fibre networking, i.e. in the materials density. Losses in Young's modulus (approx. 60 % loss) and maximum strength (approx. 20 % loss) were observed in the melt processed materials compared to the unprocessed modified fibres and are possibly attributable to reduction in not only crystallinity, but also fibre length (Fig. S10).¹³

The assessment of density (Fig. 4c) partly supports the hypothesis based on higher density in unprocessed modified fibres. These exhibit 80 % higher density (1355 ± 15 kg m⁻³) than sheets from the pristine fibres (766 ± 3 kg m⁻³), which enhances the stiffness and strength of the material. The measured density of the extruded materials was 1357 ± 16 kg m⁻³ for 100 deg-25 % and 1173 ± 32 kg m⁻³ for 100 deg-63 %. The origin of this difference in density between the extruded samples is presumably the difference in moisture content. In the case of 100 deg-63 %, melt processing generated steam as the material exited the die, resulting in greater porosity, which is also observable as increased opacity of the extrudate (Fig. 2b).

Crystalline native cellulose is known to exhibit high strength (Mariano et al., 2014; Saito et al., 2013). Amorphous dialcohol cellulose has been associated with improved ductility in core-shell fibres and CNF as well as regenerated films (Kasai et al., 2014; Larsson et al., 2014a; Larsson & Wågberg, 2016). The combination of reduced strength and enhanced ductility as observed here for the extruded materials (Fig. 4) may be attributable to amorphization that occurs during processing in the extruder, where the materials are subjected simultaneously to elevated temperature and mechanical shear forces. Furthermore, fibre-fibre shear stress reduces with increasing degree of modification, which can be inferred at the fibre level from evidence of reduced shear stress at the nanoscale (Mehandzhyski et al., 2022), given that the fibres comprise such nanoparticles. Reduced crystallinity, in all melt processed samples, was indeed observed by X-ray diffraction (Fig. S11 and Fig. S12), observable as reduced intensity of the (1–10) and (200) diffraction peaks (French, 2014).

Repulping experiments were carried out, using material prepared at larger scale (Fig. S13), to investigate the potential of recycling dialcohol fibre products with conventional fibres by existing recycling procedures (Fig. 5). In one set of experiments, the extruded material (0–5 wt%) was repulped with unmodified *beaten* fibres, while in a second set of experiments unmodified *unbeaten* fibres were used. After resuspending the extruded material in water and mixing with unmodified fibres, no

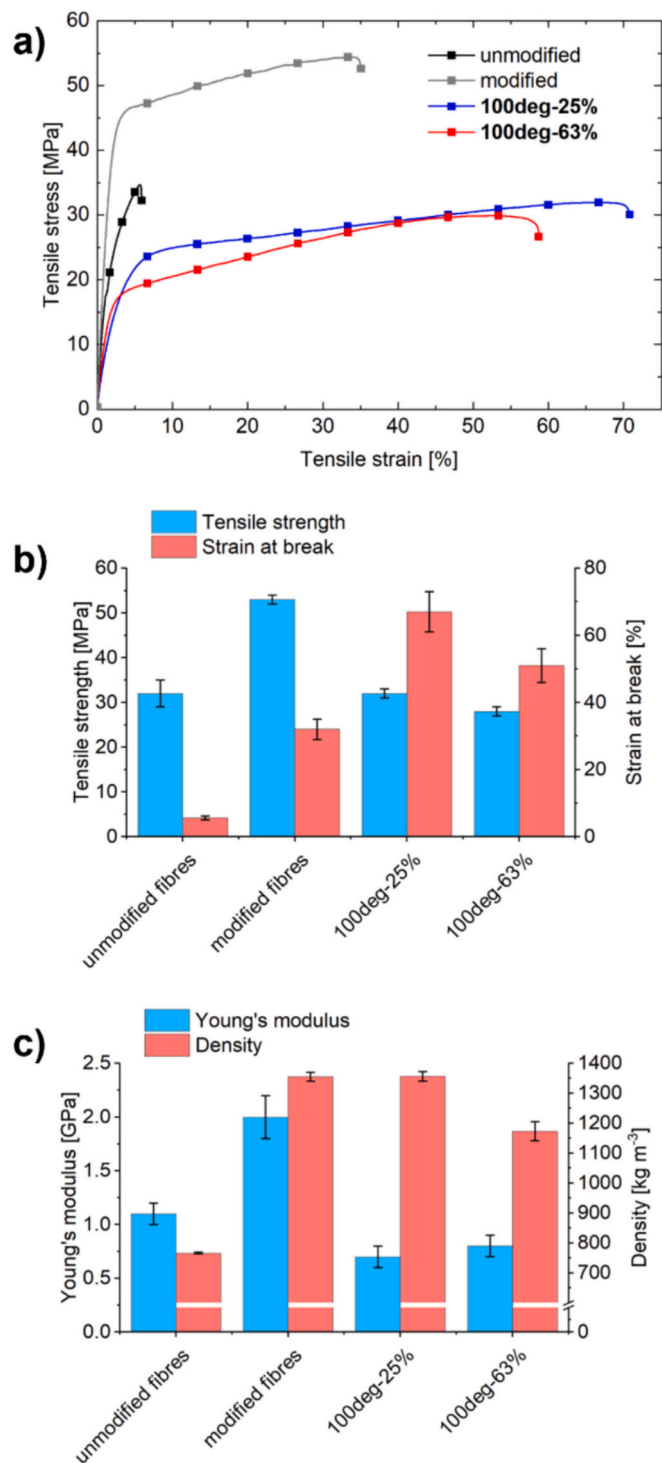


Fig. 4. a) Representative stress–strain curves of unmodified and modified fibres as handsheets, and 100 deg-25 % and 100 deg-63 % in extruded filament form; b) tensile strength and strain at break and c) Young's modulus and density.

difficulties were experienced when preparing handsheets. In particular, no substantial increase in dewatering time was observed. The resultant handsheets incorporating unmodified *beaten* fibres exhibited near identical mechanical properties to the reference sheet containing only unmodified fibres (Fig. 5a), which could indicate that the resuspended extruded material was not retained in the sheets. However, in the experiment with *unbeaten* fibres as reference, the resultant handsheet mechanical properties improved towards values observed for beaten

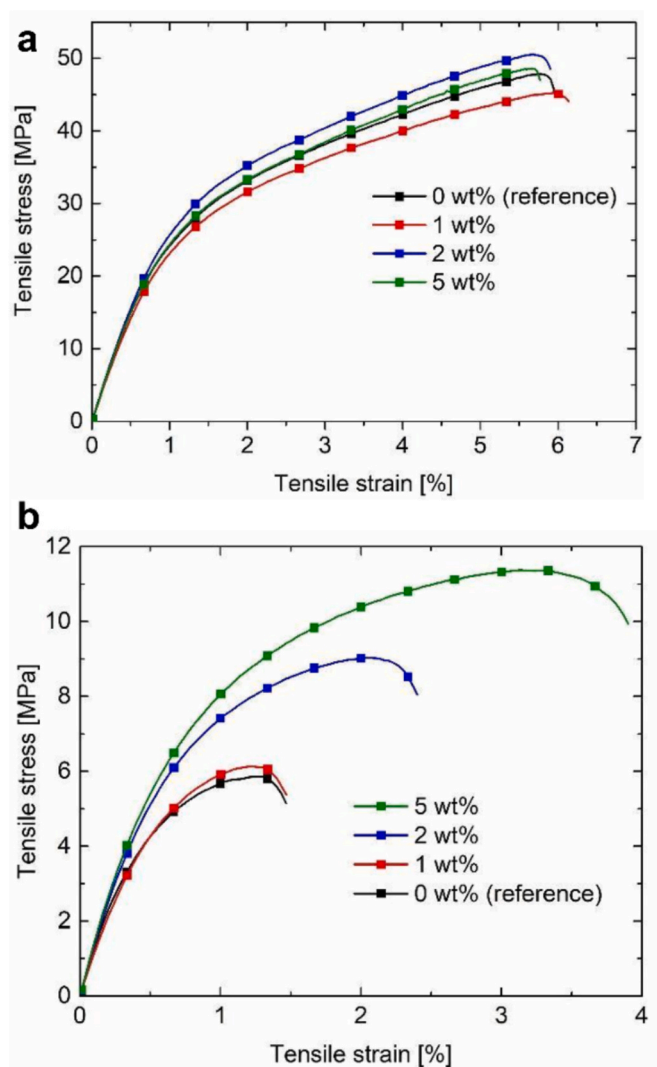


Fig. 5. a) Stress–strain curves for handsheets prepared by repulping 0–5 wt% extruded material with unmodified beaten fibres. b) Stress–strain curves for handsheets prepared by repulping 0–5 wt% extruded material with unmodified unbeaten fibres.

fibres (Fig. 5b). This implies that a significant portion of the extruded material is indeed retained. Taken together, these results suggest that the extruded material can potentially be recycled with conventional unmodified fibres, i.e. within the established recycling system for paper and board. However, further studies are needed to establish more accurately to what extent the extruded fibres are retained and how the addition of extruded fibres affects the properties of the resultant paper.

4. Conclusion

Beaten cellulose fibres were partially converted to dialcohol cellulose at 47 % degree of modification. The modified fibres are more hydrophilic than the unmodified version and exhibit heterogeneous swelling with ‘balloon-and-collar’-type structures in deionised water, despite their low charge, as is reminiscent of native cellulose fibres in alternative solvent systems, such as *N*-methylmorpholine *N*-oxide/water or charged cellulosic fibres in water.

The results of melt processing trials demonstrate that water is an adequate plasticiser for melt processing of dialcohol-modified fibres, at relatively high degree of modification, without the addition of a synthetic polymer. By lab-scale extrusion, 100 °C and 25 wt% initial moisture content were adequate for obtaining translucent extruded

filaments free of undesired surface texture. No indications of significant chemical degradation or supramolecular changes were observed and the melt processed material could be reswollen and resuspended in water. However, non-fibrous aggregates remained, despite agitation by vortex mixing.

Although shearing damages the fibres during twin-screw extrusion, resulting in moderate losses in tensile strength and modulus, an enhancement in the already exceptional ductility of dialcohol fibres was observed after melt processing. The enhancement of ductility, and the loss in strength and modulus, may be attributable to reduced crystallinity and increased molecular/polymer mobility.

Facile resuspension of the melt processed material in water allowed for repulping in combined suspensions with unmodified beaten or unbeaten fibres, as well as the preparation of handsheets, using standard lab equipment.

The melt processing of dialcohol fibres, with water as the only additive, represents an important step towards exploiting cellulose, as an alternative to thermoplastics derived from fossil carbon, in challenging applications such as the moulding of complex three-dimensional parts. As a novel bio-source material with potential to be more sustainable than petroleum-based counterparts, it is additionally encouraging that extruded dialcohol fibres can potentially be recycled together with unmodified cellulose fibres using conventional repulping and papermaking equipment.

CRedit authorship contribution statement

Emile R. Engel: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Giada Lo Re:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Per A. Larsson:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

The following additional material, and descriptions thereof, is freely available online: chemical composition and molecular weight distributions, NMR spectra, optical and SEM images, thermograms, Kajaani fibre analysis, X-ray diffraction patterns. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.carbpol.2024.122891>.

Data availability

Data will be made available on request.

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