Klar, Ville; Orelma, Hannes; Rautkoski, Hille; Kuosmanen, Petri; Harlin, Ali

Spinning Approach for Cellulose Fiber Yarn Using a Deep Eutectic Solvent and an Inclined Channel

Published in:
ACS Omega

DOI:
10.1021/acsomega.8b01458

Published: 30/09/2018

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
Unspecified

Please cite the original version:
Spinning Approach for Cellulose Fiber Yarn Using a Deep Eutectic Solvent and an Inclined Channel

Ville Klar, Hannes Orelma, Hille Rautkoski, Petri Kuosmanen, and Ali Harlin

Department of Mechanical Engineering, Aalto University School of Engineering, P.O. Box 16300, Aalto, FIN-00076 Espoo, Finland
VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, 02044 VTT Espoo, Finland

ABSTRACT: We developed a spinning approach for a dope produced by treating softwood pulp with a deep eutectic solvent (DES). The DES enables formation of a sufficiently viscous spinnable gel-like suspension of fibers, which solidifies upon the removal of the DES. This solidification, however, requires a longer time compared to most conventional wet spinning processes. Consequently, the continuity of the spinning process has been constrained in previous work. Moreover, the ability to draw the incipient yarn to increase orientation has been limited. Here we present a continuous spinning approach where the fiber yarn properties and processability can be improved using an inclined channel. A combination of an air gap and an inclined ethanol stream transports and draws the incipient fiber yarn during spinning. The influence of syringe tip diameter, angle of the channel, ethanol flow rate, and twisting were studied experimentally. The improvements in the spinning process resulted in an increase in load bearing capability and ability to reduce the linear density of the fiber yarn.

INTRODUCTION

Environmental issues such as the accumulation of microplastics in the marine environment and carbon emissions from production of plastic goods have been ushering material research into bio-based options for the past decades. In the context of fibers and yarn, exploration of new raw materials is essential as their demand is expected to dramatically increase because of the global increase in both population and prosperity. Arguably, cellulose-derived and based materials are among the most potential candidates to meet this future demand.

Numerous spinning technologies and approaches have been developed for cellulose-derived and based raw materials to form them into various fibers, filaments, and yarns. While a plethora of different options exist, spinning approaches for forming low-aspect-ratio native cellulose fibers directly into monofilaments or staple fibers without dissolution lack commercial adoption. To lower the barrier for commercial development and adoption, research of new continuous spinning approaches and machinery is necessary.

Cellulose-based yarns are typically manufactured either from natural or regenerated fibers. Naturally high-aspect-ratio fibers such as cotton or flax are spun into yarn retaining the natural fiber structure by using carding and, for example, ring or rotor spinning. In brief, the main issue with increasing the production of most natural fibers is that it impinges on farming of comestible crops.

Several established technologies exist to produce high-tenacity regenerated cellulose fibers through dissolution and subsequent regeneration. Dissolution of the natural cellulose fiber enables the use of lower-aspect-ratio fibers such as pulp fibers as feedstock in the spinning process. Regenerated cellulose fibers such as viscose have been prominent fibers on the global market since the 1930s. Because of the high cost of environmentally friendly production of viscose, alternative dissolution routes such as the CarbaCell and BioCelSol process have been explored. Non-derivatizing dissolution methods using for example N-methylmorpholine-N-oxide or ionic liquids have enabled production of filaments with both a reduced environmental impact and improved tensile properties.

Recently, spinning of native tensile components of wood, namely nanofibers and pulp fibers, has received scientific attention. Spinning without dissolution preserves the native cellulose I structure, which has a higher modulus and tensile strength compared to the cellulose II structure in regenerated cellulose fibers. Furthermore, omitting dissolution reduces the number of process steps in yarn or filament production.

Several successful demonstrations of cellulose nanofiber (CNF) wet spinning and dry spinning have been reported. Specialized techniques, such as flow focusing, have been utilized to achieve impressive tensile strengths (490 MPa) and Young’s moduli (18 GPa). Flow focusing aligns
the nanofibrils axially within the filament. Such an alignment is typically achieved through drawing, which is why most conventional solvent and melt spinning techniques contain a drawing phase after the spinneret. Drawing improves tensile strength and stiffness in both regenerated cellulose fibers and CNF filaments.

In addition to CNF spinning, research has been conducted into using pulp fibers in spinning. Fiber yarn preparation without dissolution using wood pulp as the main raw material has been demonstrated by Tenhunen et al., Spoljaric et al., and Salmela et al. These structures are dissimilar to conventional cellulosic monofilaments or yarns, and therefore, we refer to them as fiber yarns.

Tenhunen et al. successfully spun a wood fiber-based suspension into fiber yarn by pretreating the fibers with a deep eutectic solvent (DES). DESs have similar physiochemical qualities to ionic liquids and some of them, such as a choline chloride and urea mixture (ChCl/urea), are biodegradable and have relatively low toxicity and vapor emissions. The DES pretreatment of softwood pulp fibers results in a stable gel-like spinnable suspension. In a further research, Tenhunen et al. researched the interaction of pulp fibers and ChCl/urea extensively. They found that a ChCl/urea treatment (16 h at 100 °C) had no significant influence on the pulp fiber structure. Furthermore, there was no evidence of derivatization of the cellulose and only negligible changes in monosaccharide contents.

In the context of spinning, the DES keeps the wood fibers separate which enables their extrusion into a yarn-shape. The resulting structure solidifies when the DES is removed with a suitable solvent, such as ethanol. Ethanol removes the DES without interrupting the bonding between the cellulose fibers. To increase the poor water stability of the natural cellulose fiber network, Tenhunen et al. cross-linked the cellulose fibers with heat activatable polyacrylic acid (PAA).

Regarding the spinning process, one key difference compared to conventional wet spinning techniques is spinneret orifice diameter. To produce sufficiently stable dope flows, the spinneret diameter needs to be larger (0.5−1 mm) compared to diameters used in conventional wet spinning processes (10−300 μm). This diameter constraint stems from the flow behavior of the spinning dope. Similarly to aqueous cellulose fiber suspensions, the DES-cellulose fiber suspension exhibits a propensity to form agglomerates of fibers, often referred to as flocs. This agglomeration behavior results in clogging with smaller spinneret orifices. The larger spinneret diameter influences the solidification of the structure and thusly governs the subsequent spinning process phases.

In the early phases of development, we observed that using rolls or godets to draw the incipient fiber yarn was challenging because of the slow solidification and poor wet strength of the incipient fiber yarn. Alternative drawing approaches were tested, and an inclined channel with an ethanol stream was most promising in early testing. We found that by adjusting the angle of the spinning channel and flow rate of ethanol in it, yarn could be continuously spun. Similarly to dry-jet wet spinning, initial drawing occurs in an air gap before the spinning dope comes in contact with ethanol. The angle of the inclined channel and flow rate of ethanol in it can be used to adjust the external force applied to the yarn, that is, extent of drawing. We evaluated the spinning approach by

- constructing a modular prototype spinning line (shown in Figure 1), where process critical parameters could be measured and controlled;
- studying the influence of three parameters; spinneret diameter, the combined effect of angle and flow rate in the inclined channel, and twisting of the spun yarn;
- comparing the structure and tensile properties of yarns spun with different parameters through microscopy and load-strain measurements.

**EXPERIMENTAL SECTION**

**Materials.** Never-dried, bleached softwood pulp was supplied by a mill in central Finland. PAA (M₄ 450 000 mol/
g), urea, and choline chloride (ChCl) were purchased from Sigma-Aldrich, Finland. Ethanol used in the spinning trials contained a maximum of 0.5 wt % of water. All chemicals and solvents were of analytical grade and used as received.

**Preparation of Spinning Dope.** The spinning dope was prepared according to Tenhunen et al.\(^2\) ChCl and urea were mixed together in a molar ratio of 1:2. The mixture was heated to 100 °C under constant stirring in a closed system until a clear homogeneous liquid was formed. The pulp was washed twice; first to Na⁺ form according to Swerin et al.\(^3\) and second several times with excess acetone to remove water from the pulp. Prior to dispersing the pulp into the DES, it was dried at 40 °C overnight in a vacuum.

The spinning dope was prepared by dispersing the water free pulp in the ChCl/urea (1:2 mole ratio) mixture at 100 °C under constant stirring overnight as described by Tenhunen et al.\(^2\) Once the dispersion had cooled to room temperature, 10 wt% of PAA was mixed into it with a SpeedMixer (FlackTek Inc., UK) in a vacuum at 800 rpm for 2 min and at 1500 rpm for 8 min. The resulting spinning dope had a cellulose content of 4.4 wt%. Its gel-like consistency is shown in Figure 2a.

**Spinning of Fiber Yarn.** The modular spinning system consists of three main sections: the syringe pump, the channel, and the spinning bath. A custom syringe pump with sufficient torque was used to extrude the dope. The syringe piston was pushed with a screw-based linear actuator that was driven by a stepper motor with a planetary gear. The piston force was measured with a force transducer.

The inclined channel was a 1.8 m long polypropylene pipe with the top section cut off. It had a circular cross section with a diameter of 50 mm. The channel was mounted between the syringe pump and spinning bath. The angle of the channel was adjusted and measured with a digital angle gauge. The spinning bath had a total volume of 7 L. The spinning bath was emptied and refilled with fresh ethanol between each 60 mL syringe refill. Ethanol was circulated with a centrifugal pump from the bottom of the spinning bath to the top of the channel. The ethanol flow rate was adjusted with a flow regulating valve and measured with a flow meter. A schematic illustration is shown in Figure 1 and the modular spinning system is shown in Figure 2b.

The spinning dope was charged into a 60 mL syringe equipped with a tapered dispensing tip. All tests were run with a spinning rate of 0.1 m/s. The volumetric flow rate for each syringe diameter was set according to this spinning rate. Tapered dispensing tips purchased from Drifton, UK with diameters 0.41 mm (22 gauge), 0.63 mm (20 gauge), and 0.84 mm (18 gauge) were used. Fiber yarn was spun both with and without the inclined channel. All three diameters were used without the channel to research the influence of the syringe tip diameter separately. The 0.63 mm tip was used in all spinning trials with the channel.

Two ethanol flow rates (200 and 400 mL/min) and two angles (5° and 7°) were tested resulting in 4 different angle configurations. The nomenclature and production parameters of the prepared yarns are summarized in Table 1, where ID is the inner diameter of syringe tip, \(V_{\text{DES}}\) is the volumetric flow rate of the DES suspension, \(V_{\text{ethanol}}\) is the flow rate of ethanol, and \(\alpha\) is the channel angle. All spinning trials were performed at room temperature.

After spinning, all yarn samples were placed in a fresh bath of ethanol for a minimum of 24 h. Finally, the yarns were disentangled manually and the PAA was cross-linked with the pulp fibers in an oven at 140 °C for 30 min.

Additional twisting and washing was performed on G20-7-200 yarns. Three different posttreatments were studied: washing, dry twisting, and wet twisting, which we denote as W, DT, and WT, respectively. All posttreatments were performed before cross-linking. The first posttreatment (W) was a short immersion in distilled water, which was also performed by Tenhunen et al.\(^2\) The immersion time was extended from the previously used 5–30 s. The second posttreatment (DT) included washing, air drying, and twisting once the yarn was dry. The third posttreatment (WT) included washing and twisting immediately after the immersion while the yarn was still wet. Twisting was performed with a stepper motor-driven twisting device. Yarn samples (20 cm long) were twisted 50 revolutions.

**Scanning Electron Microscopy (SEM).** SEM (MERLIN FE-SEM, Carl Zeiss NTS GmbH, Germany) was used to study the morphology and structure of the fiber yarns. Samples were prepared on double-sided carbon adhesive discs attached to aluminum specimen stubs. Prior to imaging, the samples were sputter-coated (Agar Auto Sputter Coater, UK) with gold (Au) to improve specimen conductivity. The imaging was conducted using 3.0 keV electron energy and 30 pA probe current. The pixel resolution was 2048 × 1536. The approximate dimensions of the yarns were measured from the SEM images using ImageJ.\(^3\)

**Mechanical Properties of Fiber Yarn.** An Instron 5944 Single Column, Tabletop Universal Testing System operating in tensile mode was utilized to analyze the tensile properties of the yarns. Specimens (20 mm long) were analyzed using an extension rate of 1 mm min⁻¹ and a 5 N load cell. Specimens were analyzed in three conditions: dry, wet, and after prolonged immersion in water. The wet specimens were immersed in water for 24 h at 23 °C prior to tensile testing. The prolonged immersion samples were immersed in water for 70 h at 23 °C and dried at 23 °C and 50% relative humidity for a minimum of 24 h prior to testing. All samples were stored in 23 °C and 50% relative humidity for a minimum of 24 h before being measured. The results presented are the average of ten parallel measurements.

Linear densities of selected samples were measured by first measuring 1 m lengths of yarn and weighing the lengths with a precision scale (METTLER, Switzerland). The diameters of selected yarn samples were also measured with a pressure sensitive micrometer (Lorentzen & Wettre, Sweden). Tenacities (cN/tex), linear densities (tex), and elongation at break (%) of 10 wet and dry twisted specimens were also measured using Lenzing Instrument devices; Vibroskop and Vibrodyne 400 using a pretension weight of 7 g. Only dry samples were measured with the Lenzing Instrument devices.

<table>
<thead>
<tr>
<th>Table 1. Process Parameters Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>name</td>
</tr>
<tr>
<td>G22</td>
</tr>
<tr>
<td>G20</td>
</tr>
<tr>
<td>G18</td>
</tr>
<tr>
<td>G20-5-200</td>
</tr>
<tr>
<td>G20-5-400</td>
</tr>
<tr>
<td>G20-7-200</td>
</tr>
<tr>
<td>G20-7-400</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

In this research, we manufactured a modular spinning line for continuous production of fiber yarn. The modular system was used to produce fiber yarn by using DES as a spinning medium for softwood pulp fibers. While DES enables formation of a spinnable gel-like suspension, the time required for solidification is longer compared to most solution spun dopes. The use of an inclined channel enabled gentle drawing and transportation of the incipient yarn without breaching. The yarn structure and properties can be influenced by using different process parameters. Herein, we discuss the influence of syringe tip diameter, ethanol flow rate, angle of the inclined channel, and three different posttreatments.

**Determination of Spinning Parameters.** While the DES-cellulose fiber suspension can be extruded and spun, the fiber kinetics constrain the use of smaller diameters. In the context of this research, 0.41 mm (22 gauge) was the smallest usable syringe tip size with the chosen spinning dope composition and extrusion method. Smaller sizes could not be used because of the propensity of cellulose fibers to flocculate, resulting in clogging and unstable spinning.

The steady state forces measured at the piston of the syringe (syringe inner diameter 26 mm) for the used extrusion rates were approximately 600, 350, and 150 N for the 0.41, 0.63, and 0.84 mm syringe tip diameters, respectively. Continuous spinning with the inclined channel was not achieved with the 0.41 mm syringe tip. The smaller diameter incipient yarn was too weak for stable spinning using the inclined channel approach.

Fluctuations in the extrusion velocity of the dope were observed, which were attributed to the aggregation and disaggregation behavior of the fibers. Fibers agglomerated in the tapered tip, resulting in an increase of pressure in the syringe. Upon discharge, the extrusion velocity momentarily increased before returning to a steady-state as the pressure stabilized. The authors consider it likely that the flow profile velocity of the spinning dopes fluctuates during extrusion despite a constant piston speed.

Continuous spinning rates ranged from approximately 0.05 to 0.3 m/s with the 0.63 mm (20 gauge) syringe diameter. The spinning rate of 0.1 m/s was chosen as it could be matched with the flow velocity of a laminar ethanol stream with the chosen channel geometry. The chosen spinning rate was higher than the previously used 0.075 m/s by Tenhunen et al.\(^1\) Slowing the spinning rate below 0.05 m/s resulted in an unsteady flow and discontinuities in spinning because of breaching in the air gap and channel. Increasing the spinning rate beyond 0.3 m/s increased extrusion pressures and resulted in an inconsistent flow. While spinning rates above 0.1 m/s were possible, their influence on yarn properties was not systematically tested.

As the fibrillar suspension is extruded, shear forces induce alignment of the fibers in the axial direction. In their review, Lundahl et al.\(^5\) showed that, in CNF wet spinning, high shear rates in the spinneret (on the order of hundreds of s\(^{-1}\)) are typically coupled with high stiffness and tensile strength. Given a single orifice spinneret with a circular cross section, the mean shear rate, \(\dot{\gamma}\), can be estimated using the following equation

\[
\dot{\gamma} = \frac{v}{r}
\]

where \(v\) is the average flow velocity and \(r\) is the spinneret radius.

As the yarns were all spun with the same flow velocity, 0.1 m/s, the shear rates for the 0.41, 0.63, and 0.84 mm spinnerets were 488, 318, and 238 s\(^{-1}\), respectively. These shear rates are in the range suggested by Lundahl et al.\(^5\) but the values are not entirely comparable as the average dimensions of fibers used in this research are not in the nanoscale. Moreover, these shear conditions are localized resulting in a low total induced shear.

Similarly to Ioncell-F or Lyocell fibers, the fiber yarns produced in this research are spun through an air gap. This technique, known as dry-jet wet or air-gap spinning, typically results in highly oriented structures as the incipient structure is stretched in an air gap before de-solvation.\(^40\) Such a spinning technique requires the incipient structure to be able to transmit the external force, which in turn means high viscosities are necessary for continuous high draw-ratio spinning. For example, the zero shear viscosities of dopes used in the Ioncell-F process are between 5000 and 30 000 Pa s at spinning temperature.\(^26\) Within a stable force region, the orientation can be increased without compromising the stability of the spinning process.

While dry-jet wet spinning is an established spinning process and extensively researched, it is, to the author’s best knowledge, exclusively used with dissolved polymers. The fiber yarn spinning process discussed in this research is not based on a solution but rather a fibrillar gel-like suspension. Because of this fundamental difference, process parameters utilized in established dry-jet wet spinning processes cannot be directly compared to the ones reported in this research.

In the domain of fiber suspensions, a slightly analogous situation can be found in papermaking, where the influence of shear conditions and fiber orientation on sheet properties has been studied extensively. In Fourdrinier forming, the fiber orientation can be influenced through the jet-to-wire speed ratio. For example, Svensson and Osterberg\(^41\) showed that an increased jet-to-wire speed difference led to increased anisotropy in the formed sheet.

Unlike typical dry-jet wet spinning or papermaking where the external force is controlled with pick-up rolls or wires, in the inclined channel approach it is controlled via the channel angle and flow rate of ethanol. The main forces involved in the inclined channel approach are illustrated in the free body diagram that is shown in Figure 3.

![Figure 3. Free-body diagram of the incipient fiber yarn.](image)

First, the rheological force (\(F_{\text{rheo}}\)) determines the maximum external force (\(F_{\text{ext}}\)) that can be applied without breaching the incipient fiber yarn. The net external force (extent of drawing) is composed of the ethanol transporting it (\(F_{\text{fluid}}\)), the friction between the yarn and the channel (\(F_f\)), the buoyancy of the...
yarn ($F_y$), the weight of the yarn ($G$), and the normal force ($N$). The magnitude of the external force can be adjusted with the channel angle ($\alpha$) and flow rate of ethanol in it. Naturally, the forces are distributed along the length of incipient yarn. The vectors in Figure 3 are not drawn as distributions to maintain legibility.

Similarly to other spinning processes, the control parameters are interdependent. For example, the friction between the incipient yarn and the channel surface is not only influenced by the mass and geometry of the incipient fiber yarn but also the ethanol flow rate as it lubricates the contact. Naturally, the ethanol flow speed changes with the channel angle as well. The steepness of the channel and length of air gap were kept moderate in this research to decrease the likelihood of the yarn breaching in the channel. Because of the semi-buoyant nature of the incipient yarn, measuring the ethanol flow velocity alone is not sufficient to determine draw ratios.

Different channels with different cross sections, lengths, and materials were tested. A polypropylene pipe with a circular cross section (diameter of 50 mm and length of 1.8 m) was chosen. Of all geometrical shapes, a circle has the shortest length of wetted perimeter for a given cross-sectional area. This means that for a given volumetric flow rate a circular channel results in the highest maximum depth of the flow profile. Furthermore, a more even distribution of ethanol was possible with the circular cross section. Increasing the channel length above 2 m resulted in frequent breaching of the incipient yarn.

The time that it takes for the incipient yarn to travel down the channel (10–15 s) is insufficient to remove all the DES. The ethanol flow did, however, appear to expedite the removal. While this was not verified through measurements, the wet strength of the yarn after the channel was sufficient for it to be picked with a rotating roll, unlike fiber yarns samples spun directly into a bath after the same amount of time. In this research, the incipient yarns were placed in a second ethanol bath for 3 h to remove the remaining DES. It is likely that this time could be significantly reduced. For example, Tenhunen et al.\textsuperscript{37} placed the yarns in an ethanol bath for approximately 10 min.

**Yarn Morphology and Structure.** The influence of the spinning parameters on the topographical properties of the spun fiber yarns was investigated with a SEM system. Micrographs of eight different yarn samples spun with different spinning parameters are shown in Figure 4. Samples spun with different syringe tips into a stationary bath are shown on the top row (Figure 4a–c), samples spun with two different channel conditions are shown on the middle row (Figure 4d,e), and posttreated samples are shown on the bottom row (Figure 4f–h). The name of each sample is shown below the corresponding micrograph.

Fiber yarns spun with the smaller tip diameter displayed a more tightly packed structure as well as smaller external dimensions. The yarns spun with larger syringe orifices had a more hairy surface with individual fibers protruding out as seen on Figure 4c. Channel spinning (Figure 4d,e) had no visible influence on the morphology of the fiber yarn. Posttreated yarns also displayed a more tightly packed structure. The influence of the twisting can be seen in Figure 4g,h. Wet-twisted fiber yarn specimens displayed a more tightly wound structure compared to dry-twisted samples.

Table 2 shows the approximate maximum and minimum diameters of fiber yarn samples measured from the SEM micrographs as well as their linear density. The difference between maximum and minimum values indicates a variation in the cross-sectional geometry of the yarn. The cross-sectional geometry of the yarn is neither circular nor constant, which makes the determination of area and therefore stress challenging. The fiber yarn displays similar inherent irregularity and variation as other yarns produced from natural fibers. Naturally, the SEM micrographs cannot be used to accurately measure the three-dimensional shape of the yarn. Therefore, linear density and tenacity are applied instead of cross-sectional area and tensile stress. Approximate tensile stress values are given in Supporting Information Figure S2.
Fiber yarn thicknesses between 50 and 100 μm were measured with a pressure sensitive micrometer. These results were omitted as measurements from the SEM micrographs (shown in Table 2), indicate significantly larger external dimensions. This discrepancy was attributed to the yarn’s loosely packed structure which is compressible. Such challenges are typical in the field of yarn thickness measurements and further studies are necessary to establish a more robust process for analyzing the geometry of fiber yarn.

**Tensile Properties.** The tensile testing data from all measured fiber yarn samples are illustrated in Figure 5. Figure 5 is composed of two sections: tenacities are shown on the top and elongation at break on the bottom. The bars are grouped with a vertical line. The three different conditions, that is, dry, wet, and prolonged immersion (denoted as 70 h) are distinguished by color. Additionally, the dry linear density value for each specimen is shown below the specimen name.

The error bars shown in Figure 5 do not take into account the error in linear density measurements. The same linear density measurements and further studies are necessary to establish a more robust process for analyzing the geometry of fiber yarn.

**Influence of the Syringe Tip Diameter.** Samples G22, G20, and G18 were spun with different syringe tip diameters without the channel. While fiber yarn spun with the largest syringe tip (G18, 0.84 mm inner diameter) withstood the highest maximum load, their linear density was larger resulting in low tenacity values. Load at break values for yarn samples are shown in Supporting Information Figure S1 and Table S1. The measured linear densities of yarns spun without the channel positively correlate with the cross-sectional area of the used syringe tip. The load bearing capability, however, did not scale in the same relation. Fiber yarns spun with the G20 (0.63 mm) syringe tips had the highest tenacity of fiber yarns spun without a channel.

The thinnest yarns were more water-stable compared to thicker yarns. The reduction in maximum load between a dry and wet state was 21% with G22 samples, whereas it was 39 and 45% with G20 and G18 samples, respectively. As stated by Tenhunen et al. it is likely that PAA becomes the main load bearing component when the yarns are exposed to water as interfibrillar bonding is compromised. The more tightly packed structure is more water-stable as the water cannot penetrate the structure easily.

Prolonged immersion samples (70 h water bath followed by drying) retained or even increased in tenacity. The highest increase in load at break (73%) between dry and prolonged immersion samples was observed with the samples spun with a G18 syringe tip. Thinner yarns did not exhibit the same increase in maximum load after a prolonged immersion in water.

The thinnest yarn (G22) was stiffer with a 4.6 ± 0.4% elongation at break compared to the 7.5 ± 0.6 and 7.6 ± 0.9% of G20 and G18, respectively. The samples exhibited similar elongation values in a wet state. The prolonged immersion resulted in increased stiffness in all samples spun without the channel.

**Influence of Channel Conditions.** Samples G20-5-200, G20-5-400, G20-7-200, and G20-7-400 demonstrate the influence of the channel. The channel spinning approach reduced the linear density by 22–29% compared to samples spun with the same syringe tip diameter without the channel. From the non-posttreated channel spun samples, the highest increase in maximum load of 13.7% was measured between samples G20 and G20-7-200. The highest increase in tenacity of 61%, however, was measured between samples G20 and lower linear density G20-7-400.

The non-posttreated channel spun samples exhibited lower wet strength compared to samples spun without the channel. Similarly to fiber yarn spun without the channel, the channel-spun samples retained their tenacity after the prolonged immersion. The yarns that had been spun onto the channel were on average stiffer than the yarns spun without a channel. Increasing the ethanol flow rate from 200 to 400 mL/min increased the tenacity by 13.2% with a 5° channel and by 8.2% with a 7° channel. Similarly, increasing the angle from 5° to 7° increased the tenacity by 14.8% with a 200 mL/min flow rate and by 9.7% with a 400 mL/min flow rate. The results indicate...
that increasing the angle or the flow rate results in increased tenacity. Increasing the angle or the ethanol flow rate beyond these values, however, resulted in unstable spinning. The observed reductions in linear density while maintaining or even improving load bearing capability indicate that the channel approach induces drawing. More detailed research on the orientation and structure of the fiber yarn would be necessary to confirm this hypothesis.

The spinning trials carried out in this research suggest that channel spinning is more advantageous compared to spinning without a channel. The tenacities achieved through channel spinning are, however, modest compared to the influence of twisting. Additionally, the differences in tensile properties between the four different channel configurations are marginal. This suggests that the main benefits of the channel lie in enabling the gentle transportation of the incipient yarn into subsequent processing phases rather than substantial improvements in the fiber yarn structure or properties.

**Influence of Posttreatments.** The three tested posttreatments had a more substantial influence on the yarn’s tensile properties. Washing the yarn prior to cross-linking improved load bearing capability and reduced the linear density. A similar posttreatment was reported by Tenhunen et al.\(^\text{27}\)

Twisting the fiber yarn before cross-linking resulted in the highest increases in tenacity in the context of this research. While twisting the yarn both wet and dry increased its tenacity, a higher tenacity was achieved by twisting the fiber yarn directly after washing without allowing it to dry first. The WT samples exhibited both highest load bearing capability and smallest dimensions of the posttreated samples. Furthermore, the WT fiber yarn was more water-stable. The reduction in load bearing capability between dry and wet samples was 45% for WT samples and 80% for G20-7-400 samples. Similarly to decreasing the syringe diameter, the wet twisting appears to decrease mean interfibrillar distance and therefore results in more cross-linking. As a consequence, the fiber yarn has higher tenacity both in a wet and dry state.

Samples DT and WT were also measured with the Vibrodyn and Vibroskop devices. The results are shown in Table 3. The Vibroskop device measures the linear density by setting the fiber is set into its natural vibration by an electronic delta impulse. The applicability and accuracy of this measurement method for fiber yarns was not verified in the context of this research, but the results agree with the caliper and scale-based measurements.

Comparing to the results reported by Tenhunen et al.\(^\text{27}\) the linear densities were reduced from 21 to 24 tex to approximately 13 tex. Tenacities were improved from the previously reported 5.3 ± 1.8 to 7.5 ± 0.3 cN/tex. Given the range of attainable properties, the yarns can be further developed in an application-oriented approach. For example, Orelma et al.\(^\text{43}\) produced fiber yarns with a similar process. The open inner structure and good water absorption capability of the fiber yarns enabled their use in cyclodextrin-based capture of synthetic estrogen hormones from water.

### CONCLUSIONS

A continuous spinning scheme was demonstrated with a prototype spinning line. Cellulose fiber yarns were spun from a spinning dope produced by treating cellulose fibers with a DES. The DES enabled production of a spinning dope with sufficient viscosity for spinning without affecting the ultrastructure of the wood fibers. Water stability was achieved with a 10 wt% addition of PAA which was cross-linked with the cellulose fibers after spinning.

The novel feature of the spinning line is that unlike traditional wet spinning or dry-jet wet spinning, the dope is extruded into an inclined channel instead of a stationary bath. The channel approach enables flow-induced drawing of the incipient yarn, expedites the removal of DES, and transports the incipient yarn into another bath where final solidification takes place. Values, enabling continuous spinning, were determined for syringe tip diameter, dope flow rate, channel angle, and ethanol flow rate through successive testing.

SEM micrographs revealed that the syringe tip diameter influences both the diameter and packing density of fibers in the yarn. Despite tighter packing with smaller syringe tips, the highest tenacity values were measured for the yarns produced with a 0.63 mm diameter syringe tip. Yarn samples spun with the optimal channel configuration had a lower linear density and a higher load at break compared to yarn samples spun directly into a spinning bath. Wet twisting the yarn before cross-linking resulted in a further increase in both dry and wet strength. The highest tenacity was obtained by using a 0.63 mm syringe tip diameter with the inclined channel and an added wet twisting posttreatment. This resulted in yarns with a linear density of 13.2 tex, tenacity of 7.5 cN/tex, and modulus of 35.78 cN/tex.

The improved spinning technique coupled with inexpensive and environmentally friendly raw materials presents an opportunity to produce yarns suitable for use in for example nonwoven structures. The achieved controllability of yarn properties with the developed spinning approach encourages further investigation of the process.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01458.

Numerical load and elongation values at break; load at break values of different fiber yarn samples; and approximate stress at break values of the fiber yarn samples (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**
*E-mail: ville.klar@aalto.fi (V.K.).
E-mail: hannes.orelma@vtt.fi (H.O.).

**ORCID**

Ville Klar: 0000-0003-3827-6638
Hannes Orelma: 0000-0001-5070-9542

**Notes**
The authors declare no competing financial interest.

Table 3. Tenacities of DT and WT Yarn Samples, Measured with the Vibroskop Device

<table>
<thead>
<tr>
<th>linear density (tex)</th>
<th>tenacity (cN/tex)</th>
<th>elongation (%)</th>
<th>modulus (cN/tex)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT</td>
<td>13.7 ± 0.2</td>
<td>6.5 ± 0.3</td>
<td>5.2 ± 0.5</td>
</tr>
<tr>
<td>WT</td>
<td>13.2 ± 0.5</td>
<td>7.5 ± 0.3</td>
<td>4.3 ± 0.3</td>
</tr>
</tbody>
</table>

10924 DOI: 10.1021/acsomega.8b01458
ACS Omega 2018, 3, 10918–10926
ACKNOWLEDGMENTS

This work was conducted as part of the Design Driven Value Chains in the World of Cellulose (D沃C) project. The authors wish to thank TEKES (Finnish Funding Agency for Technology and Innovation) for financial support. We would like to acknowledge the contribution of Vuokko Liukkonen, Kirsi Kale, and Tiia-Maria Tenhunen for help in designing the spinning line prototype. Furthermore, we thank Marja Kärkkäinen and Steven Spoljaric for help with yarn measurements.

REFERENCES


