# Method for Forming Pulp Fibre Yarns Developed by a Design-driven Process

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A simple and inexpensive method for producing water-stable pulp fibre yarns using a deep eutectic mixture composed of choline chloride and urea (ChCl/urea) was developed in this work. Deep eutectic solvents (DESs) are eutectic mixtures consisting of two or more components that together have a lower melting point than the individual components. DESs have been previously studied with respect to cellulose dissolution, functionalisation, and pre-treatment. This new method uses a mixture of choline chloride and urea, which is used as a swelling and dispersing agent for the pulp fibres in the yarn-forming process. Although the pulp seemed to form a gel when dispersed in ChCl/urea, the ultrastructure of the pulp was not affected. To enable water stability, pulp fibres were crosslinked by esterification using polyacrylic acid. ChCl/urea could be easily recycled and reused by distillation. The novel process described in this study enables utilisation of pulp fibres in textile production without modification or dissolution and shortening of the textile value chain. An interdisciplinary approach was used, where potential applications were explored simultaneously with material development from process development to the early phase prototyping.

## INTRODUCTION

To add value to materials, a material-oriented design approach is often employed, focusing on a multidimensional perspective of the material properties. In addition to technical parameters, perceptual qualities are also considered, *e.g.*, tactility and visual appearance (Ashby *et al.* 2009; Ashby and Johnson 2010). A design-driven approach can positively contribute to every step of the research process and steer the material development in a more user-oriented direction to enhance its future potential in novel applications. A sustainable design-driven approach in the development of new materials requires a holistic life cycle perspective.

Wood-based pulp is commonly used to produce two-dimensional web structures such as paper and paperboard. However, in this study, it was utilised to produce a one-dimensional structure: fibre yarn. Utilisation of pulp fibres without dissolution would decrease the number of processing steps needed to produce the fibre yarns and enable the exploitation of natural wood fibre properties.

Forming fibre yarn from wood pulp is not as simple as it is with other fibrous materials. The long fibres of flax or staple fibres of cotton naturally form strong yarns, whereas short, wood-based cellulose fibres cannot be spun using current methods and have a tendency to disintegrate in water. Therefore, wood fibres are commonly used to form yarn through dissolution and regeneration processes. These processes result in man-made cellulosic textile fibres, *e.g.*, viscose, modal, and lyocell (Woodings 2001). Fibre yarn preparation without the dissolution of cellulose has been demonstrated using normal pulps (Salmela *et al.* 2014) and cellulose nanofibrils (CNF) (Iwamoto *et al.* 2011; Walther *et al.* 2011; Håkansson *et al.* 2014).

Environmental concerns are important when designing a new process or product. Fibre yarns prepared from wood pulp are considered to be more environmentally friendly than cotton, for example, which can consume up to 11 $m^3$ water/kg during production. It has also been predicted that by 2030, one-third of textile fibres must be produced with cellulose fibres, and cotton production cannot be increased because of the limited availability of arable land (Hämmerle 2011). Therefore, infrastructure for wood-based cellulose fibre yarns in applications that traditionally use cotton is needed.

This method for fibre yarn production was designed to use an environmentally friendly and easily recyclable choline chloride and urea mixture (ChCl/urea) as a solvent. ChCl/urea is a deep eutectic solvent (DES): a eutectic mixture with a melting point lower than that of its individual components. DESs have comparable physicochemical qualities to ionic liquids, but are much cheaper and more environmentally friendly (Abbott *et al.* 2004; Jhong *et al.* 2009; Zhang *et al.* 2012a). Recyclability of the ChCl/urea was evaluated by studying the recycled solvent after fibre yarn production.

In the method described in this paper, fibre yarns were prepared from dope, where ChCl/urea acted as a rheology modifier. The suspension of ChCl/urea and pulp became gel-like and could be extruded into a solvent bath. Rheology could be further modified with a small addition of polyacrylic acid (PAA), which also functioned as a crosslinking agent that provided water stability to the fibre yarns. The effects of PAA addition on morphology and mechanical properties were analysed.

In design-driven development of materials, the final product is not considered the driving force of research. Possible applications are determined by the intrinsic properties of the developed material. The novel pulp fibre yarns demonstrated in this study can be used not only in textiles but also in composite applications.

## EXPERIMENTAL

### Materials

Never-dried, bleached softwood pulp was supplied by a mill in central Finland. Polyacrylic acid (PAA) ($M_v$ ~450 000 mol/g), urea, and ChCl were purchased from Sigma-Aldrich, USA. All chemicals and solvents were of analytical grade and used as received.

### Preparation of Dope

ChCl/urea was prepared using a modified procedure according to Abbott *et al.* (2003). ChCl and urea were mixed together in a molar ratio of 1:2, respectively, and heated at 100 °C with constant stirring (in a closed system) until a clear homogenous liquid was formed.

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The pulp was washed with excess acetone and dried before preparation of the dope. Washed pulp, PAA, and ChCl/urea were dried at 40 °C overnight in vacuum and stored in a desiccator.

Dopes were prepared by dispersing pulp in ChCl/urea overnight at 100 °C with constant stirring. Dispersions were then cooled to room temperature and mixed in a SpeedMixer (FlackTek Inc., UK) in a vacuum (800 rpm for 2 min and 1500 rpm for 8 min). PAA was added to the suspension and mixed with the SpeedMixer. Dopes with a dry matter content of 4.5 wt% were prepared with varying PAA concentrations (0%, 5%, 10%, and 25%). Dopes were stored in a desiccator until use.

*Capillary viscometry*

Viscosity average molecular weights of the untreated pulp sample and pulp sample after ChCl/urea and were determined by capillary viscometry according to ISO 5351 (2004). Prior to measurement, samples were washed and filtrated (1 µm) using distilled water and dried in a vacuum at 40 °C.

*$^{13}$C CP MAS NMR spectroscopy*

$^{13}$C cross polarisation magic angle spinning (CP MAS) NMR spectrometer (Bruker AVANCE-III 400 MHz, Bruker BioSpin, Germany) was used to measure spectra from the untreated reference sample and a pulp sample kept in ChCl/urea overnight (~16 h) at 100 °C. Both samples were washed thoroughly with acetone and dried in a vacuum oven (40 °C, overnight) prior to measurements.

CP MAS NMR spectroscopy was used to characterise the solid-state structures of the untreated pulp and pulp sample after dispersing and washing procedures. For each sample, 10,000 scans were collected using 8 kHz spinning frequency, 2 ms contact time, and 5 s delay between pulses.

## Formation of Pulp Fibre Yarn

Pulp fibre yarns were produced using a laboratory-scale device (assembled at VTT). Dope was extruded at a constant speed (~1.4 mL/min) into ethanol from a 5-mL syringe through a tapered tip with a 0.63-mm diameter nozzle. Fibre yarns were washed in ethanol in order to remove DES for at least 10 min and dried in ambient conditions. Subsequently, fibre yarns were dipped in room temperature distilled water for 5 s and placed in an oven at 140 °C for 30 min. The process is illustrated in Fig. 1.
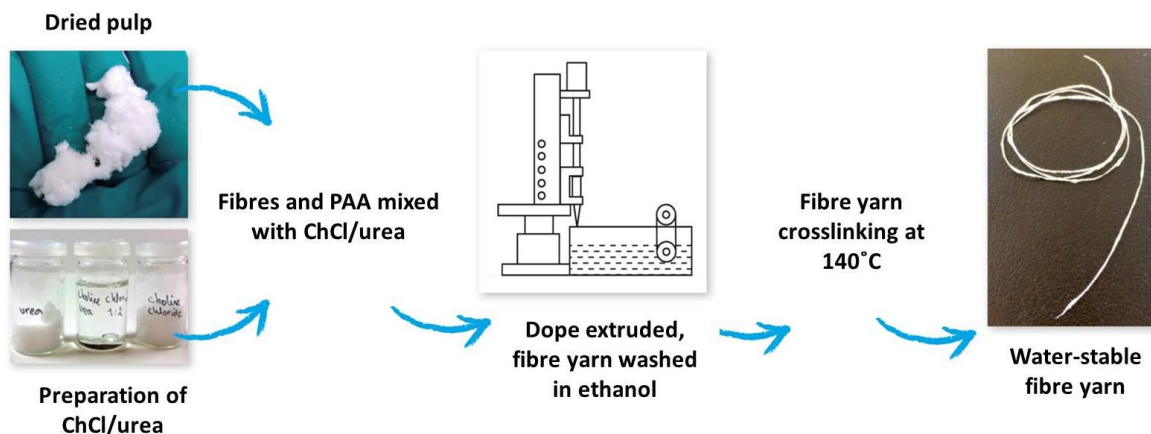


**Fig. 1.** Process chart for producing the fibre yarn

*Tensile testing of fibre yarns*

A C-Impact fast strain rate tensile tester (assembled at VTT) was used for the tensile testing. The span length of the sample was 50 mm. The strain rate was 1 mm/s (2 %/s). The accuracy of displacement and force measurements were better than 6 μm and 15 mN, respectively.

Prior to tensile testing the dry fibre yarn, samples were stored at 23 °C in 50% relative humidity (RH) for at least 24 h. Some of the fibre yarns were immersed in water for 24 h to analyse the wet strength. Tenacity (cN/tex) values were calculated dividing ultimate breaking force of the fibre yarns by the linear density, tex (g/km). The weight of all the fibre yarns were measured at 50% RH and 23 °C temperature.

*SEM*

Scanning electron microscopy (SEM) (Merlin® FE-SEM, Carl Zeiss NTS GmbH, Germany) was used to study the morphology of the fibre yarns with various pulp:PAA ratios. Samples were prepared on double-sided carbon adhesive discs attached to aluminium specimen stubs. Prior to imaging, the samples were sputter-coated (Agar™ Auto Sputter Coater, England) with platinum (Pt) to improve specimen conductivity. The imaging was conducted using 3.0 keV electron energy and 30 pA probe current. The pixel resolution was $2048 \times 1536$.

*FT-IR*

An FT-IR spectrometer with ATR diamond (Thermo Scientific™ Nicolet™ iS™50 FT-IR Spectrometer, United States) was used to study the chemical structure of crosslinked and non-crosslinked fibre yarns with 10% PAA. Spectra of pure cellulose and DES were acquired for references. The spectrum for PAA was acquired from Aldrich FT-IR collection edition II. All spectra were obtained from 32 scans with a resolution of 4 cm$^{-1}$ and transmission mode from 350 to 4000 cm$^{-1}$.

## Recycling ChCl/urea

Four millilitres of dope (ChCl/urea 95.5%, pulp 4.05%, PAA 0.45%) was extruded in ethanol (50 mL) that was evaporated in ambient conditions overnight to study the recycling of ChCl/urea; the remaining liquid fraction was studied using FT-IR and compared to the measured pure ChCl/urea.

## RESULTS AND DISCUSSION

## Effect of ChCl/Urea on Pulp Properties

The fibre yarn preparation process that utilises cellulose has a tendency to form a highly viscose gel-like suspension with ChCl/urea. The formation of cellulose gel is commonly associated with swelling and dissolution. It has been proposed that ChCl/urea interacts with cellulose; however, there are no studies on how ChCl/urea affects the structure of cellulose (Abbott *et al.* 2006; Sirviö *et al.* 2015).

Changes in the cellulosic structure caused by ChCl/urea treatment were analysed using capillary viscometry and $^{13}$C CP MAS NMR, which can be used to distinguish different crystalline allomorphs of cellulose. The $^{13}$C CP MAS NMR spectrum of the pulp did not change after being dispersed in ChCl/urea overnight at 100 °C (Fig. 2). Spectra of both samples resembled the spectrum of native form cellulose I reported in the literature

(Atalla and Vanderhart 1984). This indicates that the crystalline structure and chemical composition remained mostly unchanged by the ChCl/urea, which is in the agreement with previous studies (Zhang *et al.* 2012b; de Olivieira Vigier and Jerome 2014). In addition, no new peaks were observed, which indicates a lack of degradation products.
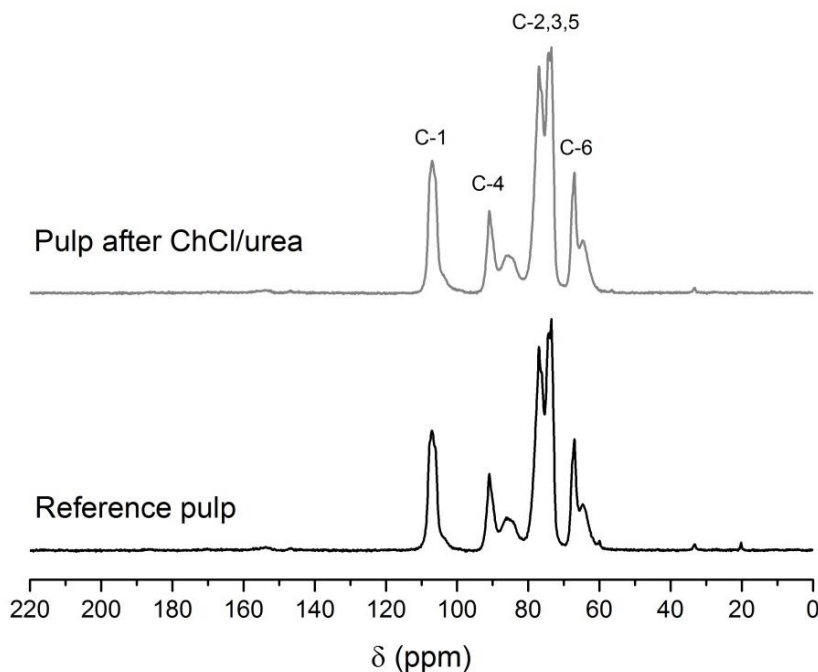


**Fig. 2.** $^{13}$C CP MAS NMR spectrum of bleached softwood pulp before (bottom) and after (top) dispersing in ChCl/urea at 100 °C overnight

The degree of polymerisation (DP) of cellulose was approximated from the intrinsic viscosity of cellulose dissolved in cupriehylenediamine measured with a capillary viscometer (da Silva Perez and van Heiningen 2002; ISO 5351 2004). According to the measurements, the DP of cellulose decreased only slightly after being dispersed in ChCl/urea overnight at 100 °C, from 1226 ($\pm$ 0.5%) to 1194 ($\pm$ 0.8%). Such a difference could be the result of mechanical damage caused by stirring, for example.

**Fibre Yarn Morphology and Chemical Crosslinking**

SEM micrographs of the fibre yarns (Fig. 3) show that most of the pulp fibres became well aligned along the fibre yarn axis. Good fibre orientation can be assumed to have a positive effect on the strength properties of fibre yarn. The structure of fibre yarns, according to SEM micrographs, appears to be porous. Fibres had not been packed tightly together and voids can be seen between them. Such a structure is likely to be caused by the solvent used to wash the ChCl/urea. The polarity of the solvent has a significant effect on shrinkage and formation of hydrogen bonds during cellulose drying (Klemm *et al.* 1998).

The PAA concentration of the dope does not seem to have affected the morphology of the fibre yarns. Even up to the addition of 25 wt% of PAA, pulp fibres can be clearly distinguished. The PAA content did not affect the linear densities of the fibre yarns, which were between 21 and 24 tex.
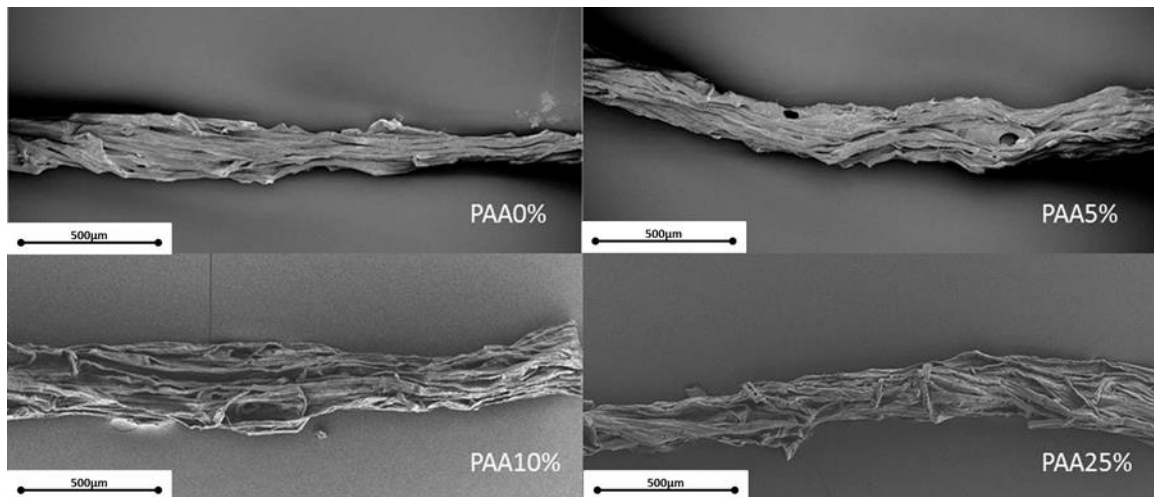
**Fig. 3.** SEM micrographs of pulp-PAA fibre yarns

Pulp fibres were crosslinked with different amounts of PAA using heat-initiated esterification (Fig. 4a), where carboxyl groups of PAA form ester bonds with hydroxyl groups of cellulose (Spoljaric *et al.* 2013; Hakalahti *et al.* 2015) to provide water stability to fibre yarns and increase tensile strength. This process was enhanced by quickly immersing the dried fibre yarns into water prior to crosslinking at 140 °C.
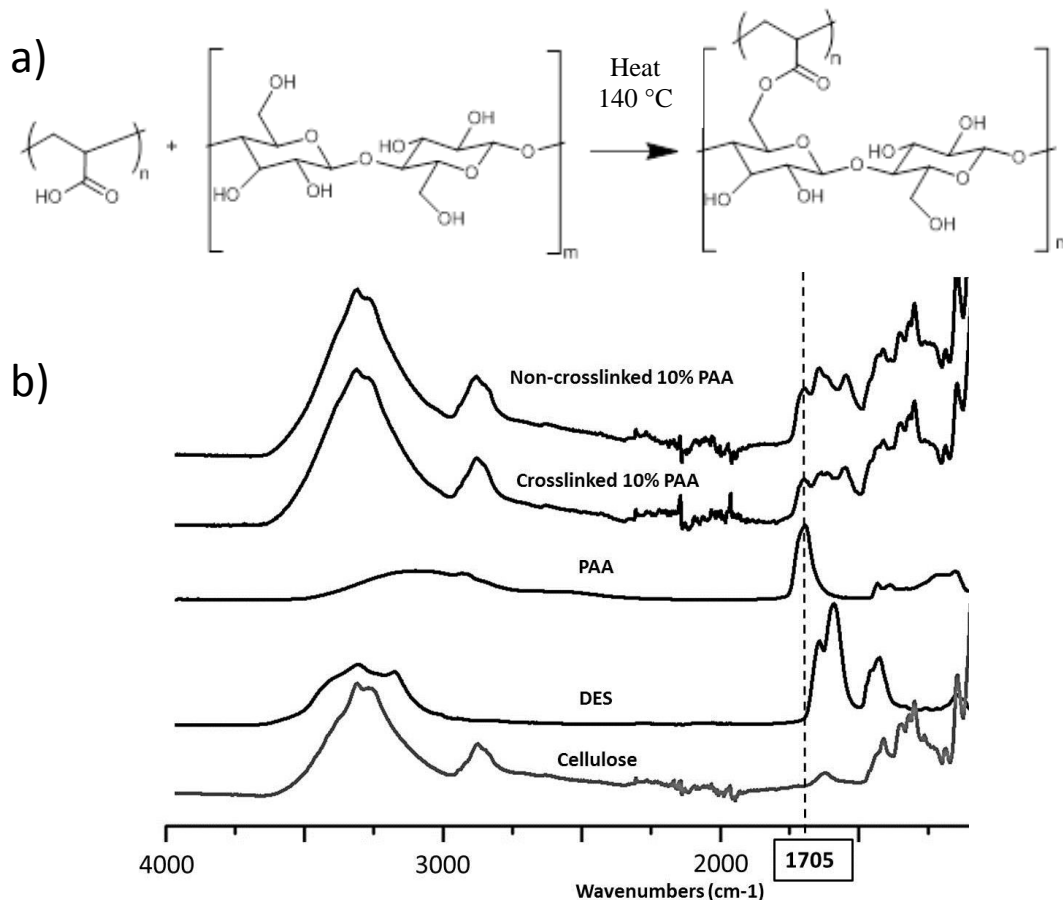


**Fig. 4.** (a) Crosslinking pulp fibres with PAA by heat initiated esterification and (b) IR spectra measured from untreated and crosslinked fibre yarns with 10% PAA

An FT-IR spectrometer was used to analyse the bonding between cellulose and PAA. However, crosslinking could not be distinguished from IR spectra (Fig. 4b). In dense CNF films, structural crosslinking has been seen as a shift of the carbonyl band in the 1705 cm$^{-1}$ region (Spoljaric *et al.* 2013). The amount of linkages formed in the studied fibre yarns is likely to be so low that it cannot be seen from the spectra, but sufficient enough to provide water stability.

## Mechanical Properties of Fibre Yarns

The mechanical properties of the fibre yarns (Fig. 5) were analysed in a dry (RH 50%) and wet state. The reinforcing effect of PAA can be seen from the tenacities of the dry fibre yarns. Tenacity seemed to reach its maximum near 10% PAA content. The declining tenacity curve indicates that above 10%, PAA is left unbound or crosslinked with a single fibre and is not contributing to bridging. Tenacities of cotton and viscose measured using our tensile tester were 16.2 cN/tex and 15 cN/tex, respectively.

A similar trend could also be seen with water-soaked fibre yarns. However, the differences between fibre yarns with different PAA contents were less prominent in this case. Wet fibre yarn without any PAA could not be mounted in the tensile tester. In fibre yarns without PAA, only hydrogen bonds hold the fibres together and they are cleaved upon immersion in water. The wet strengths of the PAA-containing fibre yarns were roughly 1/3 of the dry strengths, which indicates that in addition to crosslinking by PAA, hydrogen bonding between fibres also played an important role in a dry state.
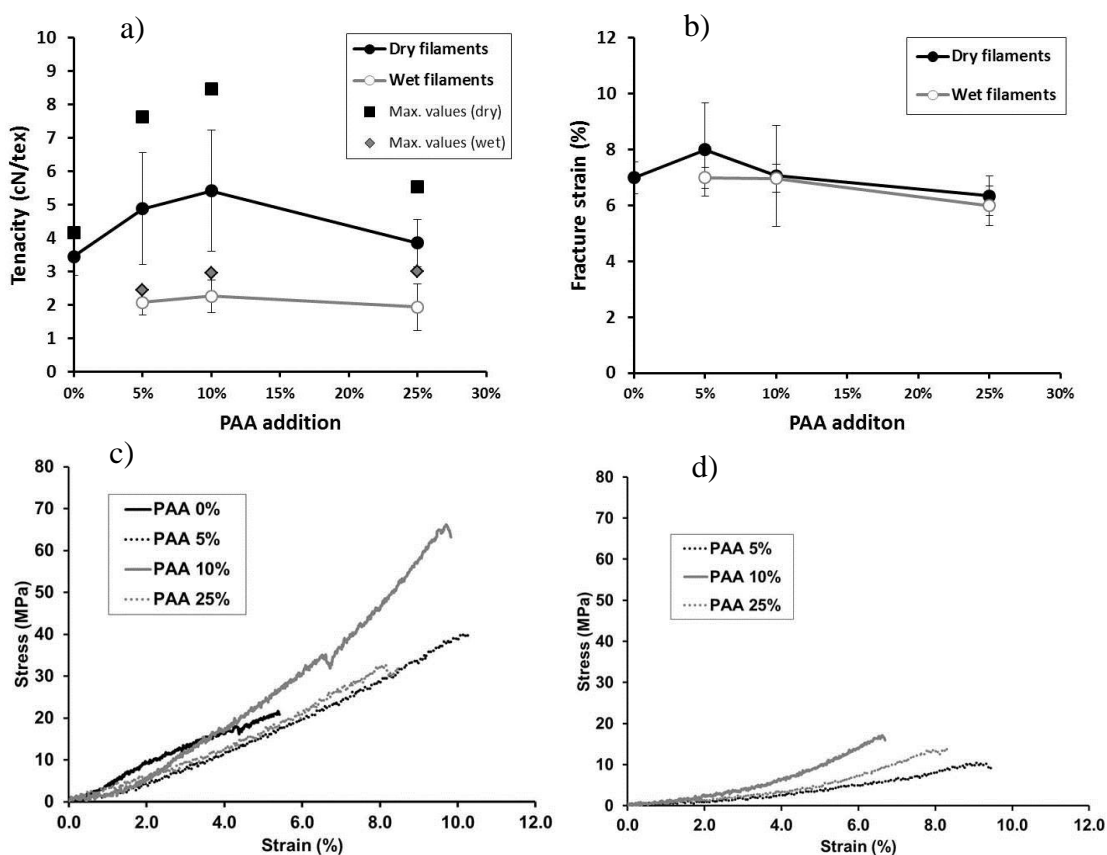


**Fig. 5.** Average tenacities and measured maximum tenacity values (a) and fracture strain (b) measured from dry and wet samples. Stress-strain curves from dry (c) and wet (d) from most presentable fibre yarns

The fracture strain of the fibre yarns seemed to decrease with increasing PAA content, which could be an indication of decreasing PAA bridging between fibres. The fracture strain values for the fibre yarns were at a similar level as cotton (8.5%) and approximately half the value of viscose (16.4%). Imperfect shape and defects in the fibre yarn affected the mechanical strength values negatively, which can be observed from the long error bars. No marked differences could be seen between the fracture strains of the dry and wet samples. This could indicate that PAA plays an important role in tensile load bearing.

Stress strain curves of the most presentable fibre yarns (no weak spots) were chosen to Fig. 5c (dry) and 5d (wet). The stress-strain behaviour of the studied yarns was non-linear and strain hardening phenomenon was clearly detectable in the stress-strain curves of the yarns with addition of PAA. This can be considered as an indirect implication that crosslinking is improving the strength after hydrogen bonding. In wet fibre yarns, where interfibre hydrogen bonding plays a minor role, the strength is provided by PAA-cellulose bonds. Average tensile strengths are presented in Table 1.

**Table 1.** Average Tensile Strengths and Standard Deviations

|  | Tensile strength, MPa | Tensile strength SD, MPa |
|---|---|---|
| PAA 0% | 13.35 | 3.78 |
| PAA 5% | 23.81 | 8.80 |
| PAA 10% | 33.55 | 15.60 |
| PAA 25% | 20.35 | 7.17 |
|  |  |  |
| PAA 5% WET | 9.49 | 1.73 |
| PAA 10% WET | 13.13 | 2.87 |
| PAA 25% WET | 8.61 | 3.12 |

Because the tensile strength values of fibre yarns were noticeably lower than values of individual pulp fibres (~1 000 MPa) (Faruk and Sain 2013), it seems that inter-fibre bonding dominated in the mechanical properties of the fibre yarns. Using more fibrillated fibres or enhancing the fibre-fibre bonding area by other means, the mechanical properties of fibre yarns could be improved significantly. According to the literature (Häyrinen 1973), twisting even a single filament improves tenacity values, and plying and cabling several filaments improves those values even more. Improving the mechanical properties of the fibre yarns will be in the scope of following studies.

## Recycling the Chemicals

Recyclability of the process chemicals is an important factor in designing a new process. Recycling the process chemicals not only decreases the environmental impact of the process, but also makes it economically more attractive.

FT-IR spectra (Fig. 6) of freshly prepared and recycled ChCl/urea collected from ethanol used for washing DES from fibre yarns were identical, and no bands arising from PAA or pulp could be observed. This indicates that recycling ChCl/urea can easily be done by evaporating the ethanol used for regeneration. There are also studies where ChCl/urea has been successfully recycled in different processes (Singh *et al*. 2011; Azizi and Gholibegloa 2012; Lobo *et al.* 2012). The ethanol can also be reused using fractional distillation.
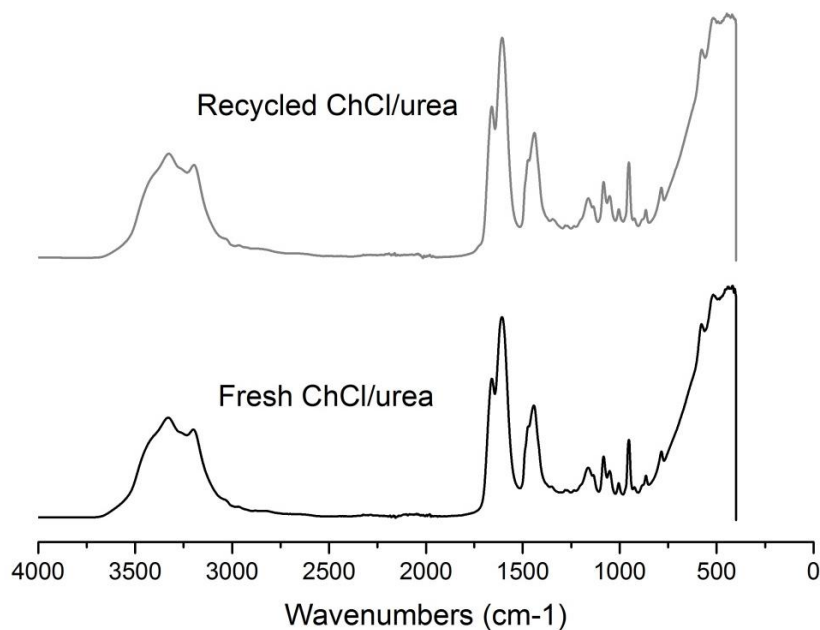
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**Fig. 6.** FT-IR spectra of recycled and fresh ChCl/urea

In the sustainable design approach, the whole life cycle of the fibre yarn from manufacturing to recycling is taken into consideration. Cellulose, which is the main component of the fibre yarns, is easily recyclable. However, PAA, with a molecular weight over ~700 Mw is not biodegradable. Despite this fact, PAA has been used for decades in cleaning products and detergents and can be efficiently removed during wastewater treatment. Additionally, its toxicity to aquatic and terrestrial organisms is low (Freeman and Bender 1993; Larson *et al*. 1997). Replacing PAA with bio-based crosslinkers will be in the scope of future studies.
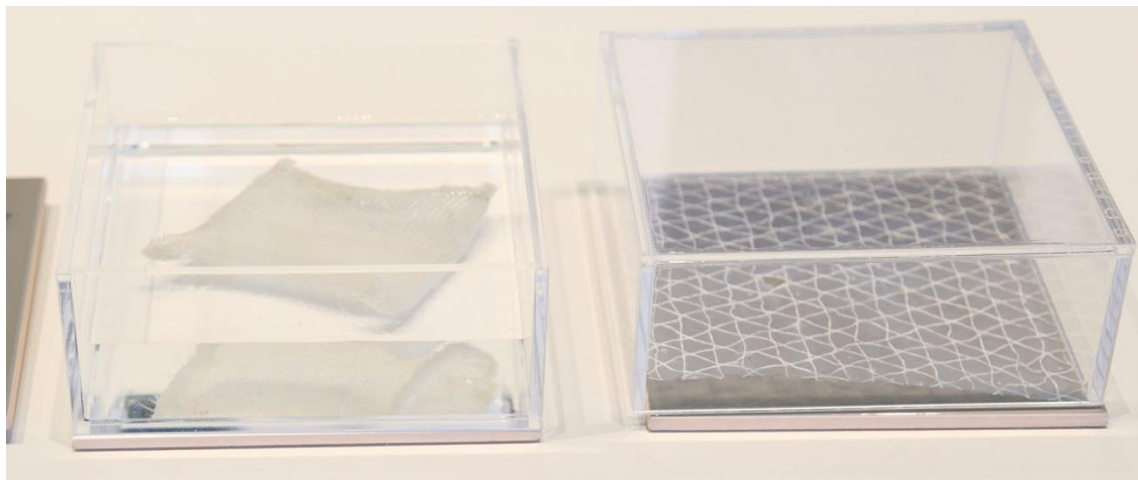


**Fig. 7.** Early phase prototyping: knitted sample in water (left), composite structure: fibre yarn embedded into a nanocellulose film (right), photo: Eeva Suorlahti

Novel pulp fibre yarn has applications in textiles as well as composites. From a design-driven perspective, the inherent properties of the materials should be well utilised in its intended applications. As cellulose has good affinity to itself, fibre yarns can be used

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as reinforcement in all-cellulose composites (Fig. 7). By embedding a textile structure prepared from the fibre yarn into a nanocellulose film structure, the inherently brittle nanocellulose films could be made easier to handle.

## CONCLUSIONS

1. A new, simple, and inexpensive method for producing water-stable pulp fibre yarns using a DES composed of choline chloride and urea was developed.

2. ChCl/urea can be used as a dispersion medium for fibre yarn formation without affecting the pulp ultrastructure. The method allows the cellulose I crystalline structure to remain in the fibre yarn.

3. All of the process chemicals are recyclable and reusable.

4. The novel process enables shortening of the textile value chain.

## ACKNOWLEDGMENTS

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