Nanocellulose Production from Walnut Pruning Wastes Using Hydrated Deep Eutectic Solvent as Paper Strength Additives

Hakan Fidan,* and Nihat Sami Çetin

The valorization potential of industrial walnut pruning wastes was investigated as a value-added product. Nanofibrillated cellulose (NFC) was prepared from walnut pruning wastes *via* hydrated choline chloride-lactic acid deep eutectic solvent (ChCl-LA DES) pretreatment followed by grinding, and these were used as paper strength additives. The effect of reaction time on NFC properties were investigated and compared. The structure of nanocellulose was determined by Fourier transform infrared, scanning electron microscopy (SEM), and rheological analysis. The results show that carboxylated NFC having high aspect ratio could be successfully isolated after DES-pretreatment with the average diameter of 39 to 77 nm. Prepared NFC was added to the bulk suspensions of papermaking slurries at various percentages (up to 8%) together with poly(diallyldimethylammonium chloride). The drainage and electrokinetic properties of the pulp and mechanical properties of fabricated handsheets were analyzed and compared. The addition of 1% NFC to the bulk suspensions increased tensile index by 14.2% and burst index by 6.3%. There were further increases observed up to 71.8% in tensile index and up to 72.3% in burst index at 8% NFC addition. Results indicate that DES pretreated cellulose nanofibrils have great potential as reinforcing agent in papermaking.

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Keywords: Cellulose nanofibers; Deep eutectic solvent; Choline chloride; Lactic acid; Hydrated DES; Papermaking

*Contact information: Department of Wood Chemistry and Technology, Faculty of Forestry, İzmir Kâtip Çelebi University, 35620, İzmir, Turkey; *Corresponding author: hakan.fidan@ikc.edu.tr*

INTRODUCTION

Studies on the use of nanofibrillated cellulose in both scientific and industrial areas are accelerating drastically due to its numerous advantages. Among the advantages of using nanofibrillated cellulose are the high abundance of cellulose, as well as its renewability, sustainability, high specific surface area, and excellent mechanical properties (Dufresne 2019). Nanocelluloses can be divided into three different classes as their production methods and dimensions: micro- *vs.* nanofibrillated (MFC, NFC), cellulose nanocrystals (CNCs), and bacterial nanocellulose (BNC). These three main types of nanocelluloses possess similar chemical features; however, they exhibit different physical characteristics like crystallinity, particle size, morphology, and are primarily determined by their preparation technique (Hubbe *et al.* 2017; Balea *et al.* 2020). Because of its intriguing properties, NFC has found applications in several high-end fields such as drug delivery (Li *et al.* 2021a), tissue engineering (Padhi *et al.* 2023), polymer composites (Liu *et al.* 2021), food packaging (Hashemzehi *et al*. 2022), water treatment (Abouzeid *et al.* 2019), and

many others. The production of NFC generally occurs through harsh mechanical disintegration, resulting in particles having both crystalline and amorphous regions. Generally, a dilute suspension of cellulosic fibers is subjected to high shear forces for mechanical delamination of microfibrils. The MFC production was first reported by Turbak *et al.* (1983) as homogenization of cellulosic fibers and until this date, several production techniques are proposed including high intensity ultrasonication (Hong *et al.* 2020), cryocrushing (Alemdar and Sain 2008), grinding (Suopajärvi *et al.* 2017), ball milling (Yu *et al.* 2021), high-pressure homogenization (Li *et al*. 2021b), and microfluidizing (Tozluoğlu *et al*. 2021).

However, these mechanical techniques have some disadvantages such as high energy cost of the process and low efficiency (Yan *et al.* 2021). Therefore, one of the main topics of researchers has been related to the reduction of the energy costs associated with cellulose microfibrillation, so NFC can be an appealing material for commercial uses. For this purpose, various enzymatic or chemical pretreatment techniques are used before the mechanical disintegration of fibers such as phosphorylation, periodate-oxidation, carboxymethylation, and TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) oxidation (Hollertz *et al*. 2017; Lourenço *et al.* 2019; Tozluoğlu *et al.* 2021). Recently, deep eutectic solvents (DES) were proposed as a pretreatment method to enhance microfibrillation of lignocellulosics. For instance, choline chloride-urea mixture was the first DES system used for treating cellulose fibres before microfibrillation by Sirviö *et al.* (2015). Following the DES pretreatment, nanofibrillation of cellulose was successfully achieved with widths of 2 to 5 nm and larger nanofibril bundles with widths ranging from 15 to 200 nm. The DES could be described as a mixture of acids and Lewis or Brønsted bases. They can be also defined as the mixture of hydrogen bond donors (HBD) and hydrogen bond acceptors (HBA). Those made of quaternary ammonium and metal salts or hydrogen bond donor are the most studied systems. These systems are able to swell the fibers and thus break the hydrogen bonds between the cellulose chains but without degrading the polysaccharide (Malaeke *et al.* 2018; Dhali *et al.* 2021; Raza and Abu-Jdayil 2022). In addition, chemical modification of cellulose is also possible according to the acid groups contained in the hydrogen bond donor used in the preparation of deep eutectic solvents (lactic acid, acetic acid, oxalic acid, *etc.*) (Kwon *et al.* 2020). In the reaction medium, the functional groups of cellulose undergo an esterification reaction and transform into carboxylic acid groups, giving the cellulose a stable structure in hydrophobic and colloidal dimensions. In contrast to the dissolution potential of lignin and hemicelluloses, cellulose is not affected by the reaction or is affected at negligible (< 10%) levels even at extended reaction times due to its extremely stable β-1-4 bonds. Therefore, the use of deep eutectic solvents is considered more effective and cost-effective in the pretreatment of cellulosic biomass to facilitate nanofibrillation (Sirviö 2018; Zhang *et al.* 2020a; Dhali *et al.* 2021; Liu *et al*. 2024).

As a natural consequence of their origin, there is also an interest in using NFCs in papermaking as reinforcing agent or coating and packaging applications. Due to its low cost and wide availability, valorization of lignocellulosic biomass in NFC production is a viable approach environmentally and economically (Balea *et al.* 2020). The application of NFC as a reinforcing agent in the bulk suspension of papermaking slurries has recently been employed for improving paper strength (Taipale *et al.* 2010; Djafari Petroudy *et al.* 2014; Delgado-Aguilar *et al.* 2015; He *et al.* 2016; Tozluoğlu *et al.* 2021). The increase in paper strength caused by the addition of reinforcing agents is mainly reflected in the increase in fiber bonding strength, and the formation of hydrogen bonds is particularly important. For instance, both CMF and NFC isolated from cotton linter were used as

strength additives in unbleached kraft paper, and it was found that the tensile strength of CMF- and NFC-added kraft papers significantly increased compared with the control kraft papers (Bharimalla *et al.* 2017). Hollertz and his colleagues compared the effects of four different NFCs on paper properties, namely carboxymethylated NFC, periodate-oxidized carboxymethylated NFC, dopamine grafted carboxymethylated NFC, and CMF made from unbleached kraft paper fibers (Hollertz *et al.* 2017). It is indicated by the authors that an addition of NFC can significantly increase the tensile strength, Young's modulus, and strain fracture of paper, and the addition of polyvinylamine (PVAm) or poly(dimethyldiallylammonium chloride) (p-DADMAC) could significantly enhance the reinforcing effect of NFC. However, due to its high specific surface area, the addition of a high amount of NFC to a bulk suspension decreases the drainage rate, which is undesirable for papermaking (Taipale *et al.* 2010). Drainage is a critical factor in papermaking because it decreases the speed of the paper machine (Su *et al.* 2014; Osong *et al.* 2016). Djafari-Petroudy *et al.* (2017) showed that it is possible to achieve a high tensile index increment by combining NFC and cationic polyacrylamide (cPAM) without increasing the drainage time. Merayo *et al.* (2017) also proved that both tensile index and drainage rate can be enhanced using 1.5 wt% NFC with a dual retention system composed of cPAM and bentonite. In papermaking, the majority of applied NFC as reinforcing agent are obtained from virgin pulps and annual plants and commonly produced *via* TEMPO-mediated oxidation or without any pretreatments. Balea *et al.* (2016) prepared NFC from eucalyptus kraft pulp and bleached pine pulp by TEMPO-mediated oxidation and the addition of obtained NFC at 4.5% increased the tensile and burst indices of recycled papers 46% and 40%, respectively. Furthermore, González *et al*. (2012) prepared NFC from eucalyptus pulps *via* TEMPO-mediated oxidation and evaluated their effect on eucalyptus pulp paper and they reported 100% of increases in tensile index by the addition of 9 wt% of NFC into the bulk suspension of eucalyptus pulp.

The main objective of this study was to evaluate the annual industrial walnut pruning wastes as value-added products. According to that, nanofibrillated cellulose successfully isolated from walnut pruning wastes *via* kraft cooking followed by hydrated deep eutectic solvent pretreatment and grinding. Subsequently, various percentages of prepared NFC (1%, 2%, 4%, 6%, and 8%) were added to the bulk suspensions of pulp slurries as a strength additive with 0.5% high-molecular-mass polyelectrolyte (p-DADMAC), and mechanical properties of both control and NFC added handsheets determined and results are compared.

EXPERIMENTAL

Materials

Walnut pruning wastes (*Juglans regia* L.) were collected from local orchard in İzmir, Turkey. Bleached softwood kraft pulp was kindly supplied from Fiber Kimya Co. (Aydın, Turkey). Choline chloride (90%), (S)-lactic acid (80%), and ethyl alcohol (96%) were supplied from Sigma Aldrich (Taufkirchen, Germany). Sodium hydroxide (99%), sodium sulfide (80%), sodium chlorite (80%), acetic acid (99.9%), formic acid (99%), and hydrogen peroxide (35%) were derived from TEKKIM Co. (Istanbul, Turkey). A 25% (w/w) aqueous solution of p-DADMAC (diallyldimethylammonium chloride) was kindly supplied from Caran Chemical Co. (Izmir, Turkey) with and average molecular weight of

300,000 to 400,000 and it was diluted to 1% (w/w) before its use. All chemicals were used without any further purification.

Methods

Pulping and bleaching

Kraft cooking procedure was conducted, and the cooking results are summarized in Table 1. According to the procedure, kraft cooking was performed at a 1:6 solid to liquid ratio in a 10-L rotating digester (Uniterm Rotary Digester, Uniterm Laboratuvar Cihazları, Ankara, Turkey). The active alkali charge in terms of Na_2O was determined as 18%, with a sulfidity of 28%. The cooking was conducted at 170 °C for 90 min after reaching maximum temperature in 30 min. Subsequently, obtained pulp was washed until the black liquor was removed on a 150-mesh screen and then treated for 10 min in a laboratory-type fiber disintegrator. After disintegration, pulp was screened through a laboratory-type screen (Somerville Flat Screen, Techlab Systems, San Sebastian, Spain) with a slit opening size of 0.15 mm according to TAPPI T275 sp-18 (2018) standard, and the cooking yield and residue yield were determined according to TAPPI T210 om-08 (2013) standard. The Kappa numbers and viscosities of the fibers (650 cm^3/g) were calculated according to the applicable standards (TAPPI T236 om-13 (2013), SCAN-CM 15-62 (1962), respectively). Obtained pulp were bleached with sodium chlorite bleaching procedure. According to this method, the pulp was soaked in a solution of $NaClO_2$ (15%) containing CH_3COONa, (3%), CH3COO- (7%), and CH_2O_2 (0.5%) at 5 wt% at 25 °C for 16 h. After this period, fibers were washed with 200 mL hydrogen peroxide (H_2O_2) solution, and they were dried and stored for further deep eutectic solvent treatment. Bleached kraft walnut pulp was named as BWP.

Table 1. Kraft Cooking Procedure and Properties of Obtained Kraft Pulp

Active Alkali (%)	Sulfidity (%)	Max. Temperature (°C)	Reaching Max. Temp. (min)	Max. Temp. Cooking (min)	Solid to Liquid Ratio	Screened Yield (%)	Residual Yield (%)	Total Yield (%)	Kappa Number
18	28	170	30	90	1:6	38.35	4.06	42.41	22.3

Deep eutectic solvent preparation and pretreatment

Choline chloride (90%) and (S)-lactic acid (80%) were used to prepare hydrated deep eutectic solvent mixture. For this purpose, choline chloride (ChCl) and lactic acid (LA) were added into 1000-mL round bottom flask at 1:9 M ratio (respectively) and then heated up to 80 °C. The reactions were completed in an oil bath at a constant temperature until ChCl and LA completely dissolved into a clear solution. Then, 30% de-ionized water was added into mixture to form hydrated ChCl-LA eutectic solvent. Once DES was synthesized, a certain amount of raw material was added into 1000-mL round bottom flask based on a solid to liquid ratio of 1:8 (30 g of BWP and 240 mL DES.) The reaction was conducted at 120 °C for 3 to 5 h and stirred every 10 min. At the end of the periods, 250 mL ethanol was added to the flask to terminate the reaction. After cooling down, the

mixture was filtered, and the treated fibers were washed with enough ethanol until the filtrate became clear. The DES-treated pulp fibers were named according to reaction time as ChCl-LA3, ChCl-LA4, and ChCl-LA5.

Nanofibrillated cellulose production

Nanofibrillated cellulose production were performed through a Supermass Collider (MKCA6-5J, Masuko Sangyo, Japan) with a 2 wt% suspension concentrations. Initially, untreated and DES-pretreated fibers were disintegrated *via* ultraturrax at 20,000 rpm for about 10 min and suspensions were passed five times through collider. The parameters applied in NFC production are given in Table 2. Following the nanofibrillation, the obtained fiber suspensions were transferred into plastic containers, three droplets of biocide per liter were added to suspensions to prevent bacterial and fungal formation and stored at 4 °C. Prepared NFC samples were named as BWPn, ChCl-LA3n, ChCl-LA4n, and ChCl-LA5n after the nanofibrillation process.

Table 2. Nanofibrillation Process Parameters

Passage Time	Power (kW/h)	Rpm	Disk Gap (µm)
1	0,5	1500	-50
2	0,5	1500	-50
3	0,5	1500	-100
4	0,5	1500	-100
5	0,5	1500	-200

Rheological properties

The rheological properties of untreated and DES-pretreated NFC samples were determined with an RST-CPS Rheometer (Brookfield Corp., Toronto, Canada). For analysis, 1 wt% suspensions were prepared for each sample and the measurements carried out with the 37.5-mm diameter cone-plate and the 25-mm diameter parallel plate at 25 °C.

Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra were recorded by the standard crystal attenuated total reflectance (ATR) method at room temperature on a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). For each sample, a total of 16 scans were conducted at a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1}.

Scanning electron microscopy (SEM)

Scanning electron microscopy was used to characterize the morphology of BWPn, ChCl-LA3n, ChCl-LA4n, ChCl-LA5n, and fabricated handsheets. Prior to that, NFC suspensions were diluted to 1 wt% concentration and oven-dried as films, the NFC films were affixed to metal stubs using double-faced tape and were then coated on the surface with gold with anion sputter instrument. Images were recorded by a scanning electron microscope (QUANTA FEG 250, Japan), and analyzed on Nano Measurer Software (Fudan University Department of Chemistry, Shanghai, China).

Handsheet preparation

Bleached softwood kraft pulp (BSKP) was evaluated as primary raw material for handsheet production and used as received without any further beating. Determination of the freeness level of the pulp was conducted according to ISO 5267-1 (1999). Untreated and pretreated NFC were added to the bulk suspensions of kraft fibers at 1%, 2%, 4%, 6%,

and 8% (oven-dried to fibers). To increase the retention of NFC to the pulp, 0.5% p-DADMAC was added and the suspensions were mixed for 20 min at 3000 rpm. Determination of zeta potential and freeness level were carried on after the addition of NFCs in the papermaking slurries. Handsheets were fabricated with a basis weight of 80 g/m^2 using a Rapid Kothen handsheet former (PTI, Vorchdorf, Austria) according to ISO 5269-2 (2004), and conditioned according to TAPPI T402 sp-13 (2013). Tensile and burst indices of handsheets were determined according to applicable standards (TAPPI T494 om-01 (2006), TAPPI T403 om-15 (2015), respectively). All the data were statistically analyzed (SPSS Statistics, IBM, v23, Armonk, NY, USA) *via* analysis of variance (ANOVA) and Duncan's mean separation tests.

RESULTS AND DISCUSSION

Characterization of Untreated and DES-pretreated Cellulose Nanofibrils

Fourier transform infrared spectroscopy is a crucial tool for characterizing the alterations in the chemical structure of pulp during the DES treatment. The FT-IR spectra of initial kraft and ChCl-LA DES-pretreated pulp are given in Fig. 1. As shown, slight shifts occurred in the infrared spectra of the fibers after DES-pretreatment, indicating that the chemical structure of the pulp changed in some manner. The characteristic peak at 1736 cm^{-1} corresponded to the carbonyl stretching vibrations (C=O), which can be attributed to the presence of lignin. However, the presence of the aromatic C-O-C bonds of lignin should be confirmed by the absorbance peak at 1267 cm^{-1} (Zhang *et al*. 2020b). The absence of the stated peak confirms that the pulp is totally lignin-free.

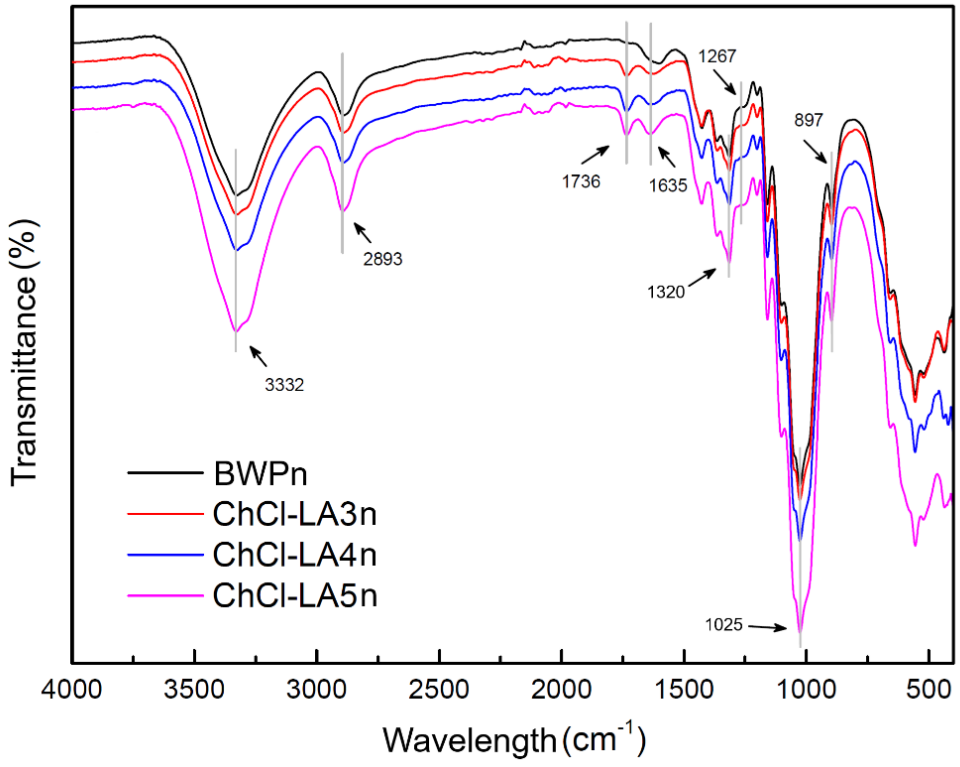

Fig. 1. FT-IR spectra of BWPn, ChCl-LA3n, ChCl-LA4n and ChCl-LA5n samples

Therefore, the absorbance peak that appeared at 1736 cm^{-1} in DES-pretreated samples can be attributed to the carbonyl vibrations of esters, indicating that the cellulose could be successfully esterified *via* the reaction between carboxyl groups and hydroxyl groups during the lactic acid-based DES pretreatment (Li *et al.* 2021b). This shows that the main structure of cellulose was retained, and it reacted with lactic acid and an esterification reaction occurred between cellulose and lactic acid during the pretreatment (Liu *et al.* 2021). Esterification peaks characterized at a wavelength of 1720 cm^{-1} have been reported in several studies as a result of carboxylic acid-based DES pretreatment (Suopajärvi *et al.* 2020; Zhang *et al.* 2020a; Shi *et al.* 2024). The most comprehensive study on this topic was conducted by Liu *et al.* (2021). The authors prepared six different DES systems based on choline chloride (ChCl) using three different carboxylic acid groups (mono-carboxylic, di-carboxylic, and tri-carboxylic acid) (ChCl-acetic acid, ChCl-formic acid, ChCl-lactic acid, ChCl-malic acid, ChCl-oxalic acid, and ChCl-citric acid) and conducted pretreatments on bleached hardwood kraft pulp. At the end of the study, they observed C=O vibration peaks around 1720 cm^{-1} in all pretreated samples, indicating the presence of carbonyl groups. In parallel to that, intensity of the O-H stretching vibrations at 3332 cm^{-1}, C-H stretching vibrations at 2893 cm^{-1} and C-O stretching vibrations of cellulose rings at 1025 cm^{-1} increased due to carboxylation of cellulose. In all samples, an absorbance peak was observed at 1635 cm^{-1}, which can be due to the vibration peak of –OH group and water absorption (Soleimanzadeh *et al.* 2022). In addition, obtained characteristic peaks of cellulose at around 1336 cm^{-1} and 1320 cm^{-1}, O-H in-plane bending and CH_2 rocking vibration (respectively), and 897 cm^{-1}, C-O-C stretching at the β-(1-4) glycosidic linkages, indicating that cellulose was not peeled or dissolved during the reactions.

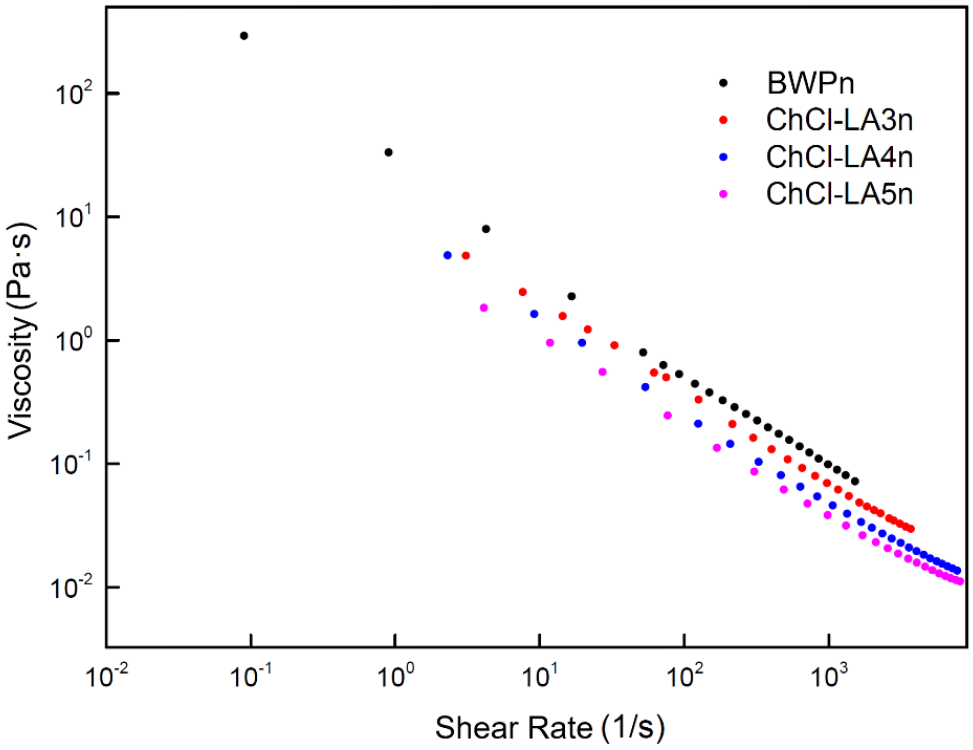

Fig. 2. Viscosity as a function of shear rate of BWPn, ChCl-LA3n, ChCl-LA4n and ChCl-LA5n samples

The SEM images of BWPn, ChCl-LA3n, ChCl-LA4n, and ChCl-LA5n fibers are illustrated in Fig. 3. It was found that the width and length of cellulose fibers decreased significantly with increasing pretreatment time. All NFC samples showed good nanofibril network structures with an average diameter in the range of 39 to 77 nm. However, NFC agglomerates were observed because cellulose nanofibrils tend to coagulate during the drying process. The average diameter of BWPn, ChCl-LA3n, ChCl-LA4n, and ChCl-LA5n was found as 77, 53, 43, and 39 nm, respectively. Compared with the DES-pretreated NFCs, untreated BWPn samples demonstrated the highest aspect ratio, with average width of 77 nm and a length of more than 2 μm. However, prolonged reaction times, especially at higher temperatures, caused a decrease in the cellulose fiber length due to strong hydrolysis at higher temperature, even if diluted DES was used (Liu *et al.* 2021). After the pretreatment, cellulose nanofibrils were cut into shorter fragments and fiber length decreased up to 1.47 μm on average. Further, the degree of polymerizations (DP) of the NFCs decreased from 997 to 895 after DES pretreatments.

The rheological properties of obtained untreated and DES-pretreated NFC are given in Fig. 1b. Untreated BWPn samples exhibited higher viscosity values as a function of shear rate due to higher diameters and lower surface charges. However, ChCl-LA5n samples demonstrated relatively lower viscosity values when compared with other DES-pretreated NFCs.

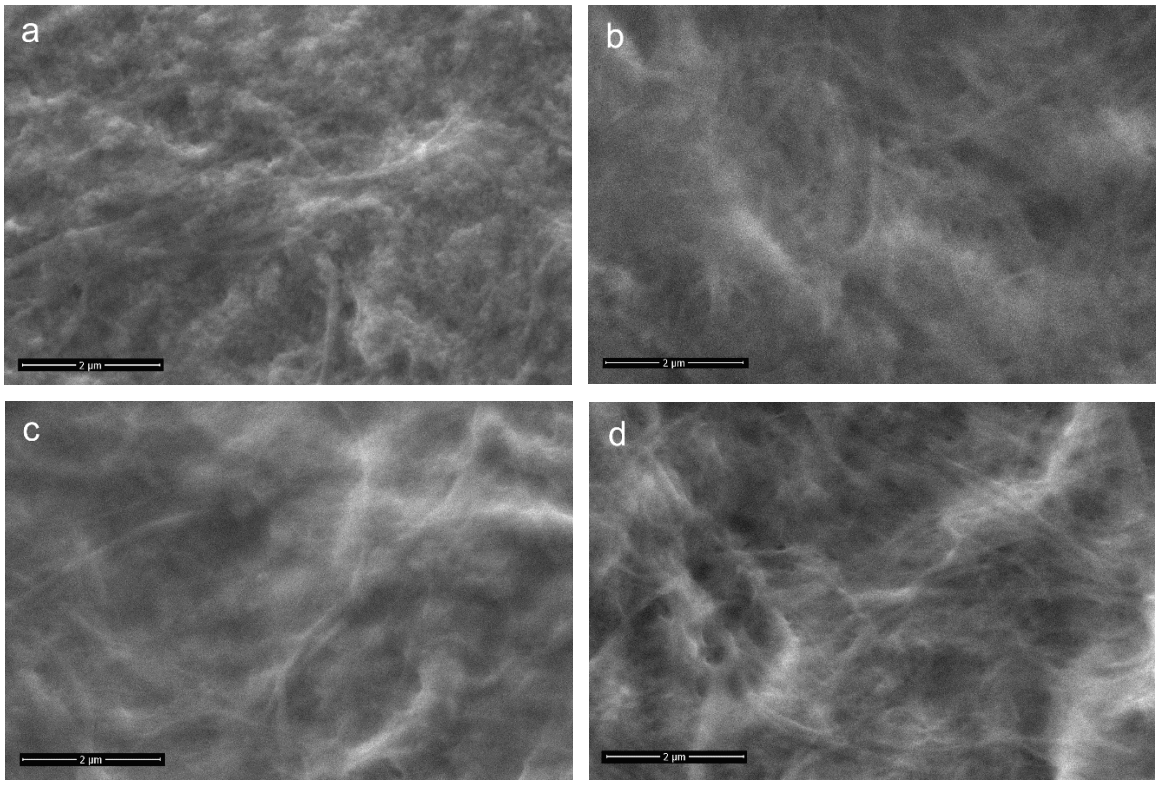

Fig. 3. SEM images of a) BWPn, b) ChCl-LA3n, c) ChCl-LA4n and d) ChCl-LA5n

Pulp Properties

The drainage and electrokinetic properties of prepared pulps are given in Table 3. The additions of NFC to the bulk suspensions of the kraft pulp fibers increased the °SR values. The freeness level of pulp is an important parameter that affects dewatering time,

and it directly affects the energy consumption and the later press and drying processes. Low additions of untreated and pretreated NFC samples to the pulp suspensions had minimal effects on the °SR values of the slurries. However, as the NFC percentage increased in the suspensions, the °SR values increased drastically, and these results are supported by previous studies (González *et al.* 2012). The highest increases in the °SR values were determined with the addition of 8% of BWPn as 161.5% (from 13 °SR to 34 °SR). Similarly, Bharimalla *et al.* (2017) reported a 107.1% increase in °SR values of unbleached kraft pulp by the addition of 10% CMF (14 °SR to 29 °SR). However, the same amount of NFC did not increase the °SR values as CMF addition and it resulted in 50% increase in the °SR values. The authors indicated that NFC samples passed through the screen during the papermaking process due to their small particle size.

Table 3. Untreated and DES-pretreated NFC Effects on the Zeta Potentials and °SR Values of Kraft Pulp

		Zeta Potential (mV)	Freeness Level (°SR)
Control	-	-0.3	13
BWPn	1%	-0.06	14
	2%	-0.09	16
	4%	-0.3	19
	6%	-0.6	30
	8%	-0.8	34
ChCl-LA3n	1%	-0.3	13
	2%	-0.6	17
	4%	-0.5	19
	6%	-0.9	24
	8%	-0.9	29
ChCl-LA4n	1%	-0.4	14
	2%	-0.9	16
	4%	-0.6	21
	6%	-1.0	24
	8%	-1.1	30
ChCl-LA5n	1%	-0.5	13
	2%	-0.6	15
	4%	-0.8	19
	6%	-1.1	22
	8%	-1.1	30

Similar results were also observed by Serra-Parareda *et al.* (2022). The authors noted that the addition of 10% NFC to a pulp suspension, in the presence of 0.5% cationic starch and 0.8% colloidal silica, doubled the freeness level of the pulp (from 22 °SR to 44 °SR). In addition, González *et al.* (2012) reported a 61.1% increase in the °SR values of bleached eucalyptus pulp fibers by the addition of 3% of NFC. However, relatively lower increases were reported by Tozluoğlu *et al.* (2021) as 23.1% after the addition of 4% periodate-pretreated NFC to the recycled pulp, even though 0.5% cationic starch was used as a retention aid. The difference between the present study and earlier studies could be explained due to the fiber sources and initial freeness levels of pulp fibers. According to the authors, evaluated recycled fibers demonstrated 39 °SR values. However, in the present study, unrefined bleached pine kraft pulp exhibited 13 °SR values. In summary, due to its high degree of fibrillation and surface area, the addition of NFC negatively affects the dewatering ability of the pulp, thereby reducing drainage efficiency. Several studies claim that using high amount of NFC increases the mechanical properties of paper; however, high

strength could be achieved without sacrificing drainage efficiency *via* the optimal selection of high-molecular-mass polyelectrolyte (Taipale *et al.* 2010; Balea *et al.* 2016). As a result of NFC additions to the pulp slurries, zeta potentials were measured generally at negative values even cationic retention aid was added. However, NFC additions did not cause major changes in the zeta potential of pulp mixtures. Consequently, coagulation and flocculation of NFC onto the fibers are expected in these stable conditions (Hubbe 2007).

Mechanical Properties

The tensile indices of fabricated handsheets are given in Fig. 4. Fabricated control kraft handsheets exhibited lower tensile index (18.3 N·m/g) due to evaluated fibers initial °SR value (13 °SR) without any further beating process. These results were similar to previous studies. For instance, Torres *et al.* (2005) reported 16 N·m/g tensile index of 13 °SR bleached pine kraft pulp. Due to higher specific surface areas, NFC additions to the papermaking slurries of kraft papers increased the tensile indices of handsheets by increasing the bonding ratios (Djafari Petroudy *et al.* 2014). The addition of untreated and DES-pretreated NFC at various proportions to the bulk suspensions of kraft papers (1%, 2%, 4%, 6%, and 8% o.d.) increased the tensile indices from 18.3 to 31.4 N·m/g ($p < 0.001$). Untreated NFC added handsheets demonstrated relatively higher tensile indices than DES-pretreated NFC added samples at higher concentrations (6% and 8%) and the highest increase was observed in untreated BWPn samples as 71.8%. This result can be explained by the higher viscosity values of untreated NFC samples (Fig. 2). Due to their viscous nature, untreated BWP nanofibrils might bond the unrefined fibers with the help of retention aid and result in a higher increase of the tensile index (Hubbe 2014). Similar results were also reported by Maskhour *et al.* (2015). The authors indicated that the addition of 10% unmodified NFC to bleached pine kraft pulp fibers in the presence of 0.3% C-PAM led to a greater increase in tensile indices of 75 g/m² papersheets when compared 10% acetylated NFC added samples.

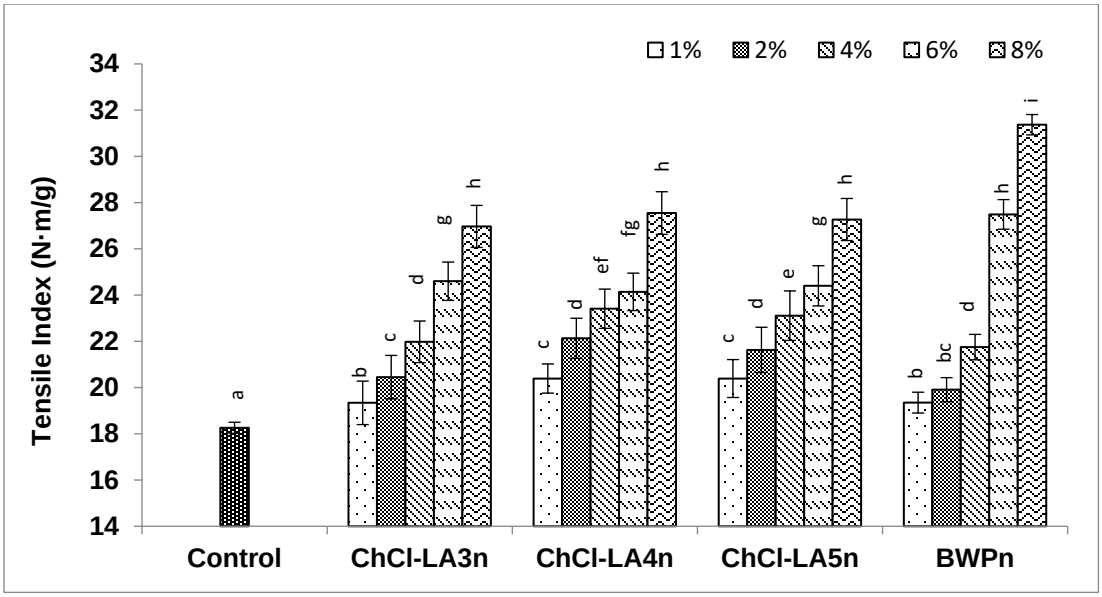

Fig. 4. Untreated and DES-pretreated NFC effects on the tensile index of fabricated kraft handsheets. Factors followed by the same letter were not significantly different (Duncan test at $p < 0.001$).

In papermaking, maintaining charge density and zeta potential is crucial for achieving high levels of retention. For this reason, cationic polyelectrolytes are needed to ensure complete retention of anionic dry strength agents on the fibers in the pulp suspension (Du *et al.* 2021). The effect of NFC addition on the tensile index of handsheets is a controversial issue in the literature. González *et al.* (2012) fabricated bleached eucalyptus pulp handsheets by the addition of 3%, 6%, and 9% TEMPO-pretreated NFC and observed 24.5%, 67%, and 100% increase in the tensile indices of handsheets, respectively.

In contrast, Haunreiter *et al.* (2024) reported only 25.9% increase in the tensile index of bleached softwood kraft pulp even at 10% NFC addition. Further, a 19.5% decrease in tensile index values of 70 g/m^2 handsheets was reported by Bharimalla *et al.* (2017) after the addition of 5% and 10% NFC to the unbleached kraft pulp. In the present study, it can be stated that the use of p-DADMAC as a retention aid provided good bonding between NFC and fibers, hence tensile indices increased as a result of increasing bonding ratio of fibers.

The burst indices of the fabricated handsheets are given in Fig. 5. In parallel to the tensile index, NFC addition increased the burst indices of kraft handsheets. Control samples demonstrated 1.01 kPa·m^2/g burst index and with the addition of untreated and DES-pretreated NFCs to the bulk suspensions, burst indices resulted in the range of 1.02 to 1.74 kPa·m^2/g. Burst index is closely related to the bonding ratio as well as the individual fiber strength. Hence, the burst indices drastically increased due to the increased amount of fiber-fiber bonds *via* the addition of untreated and DES-pretreated NFC to the pulp slurries.

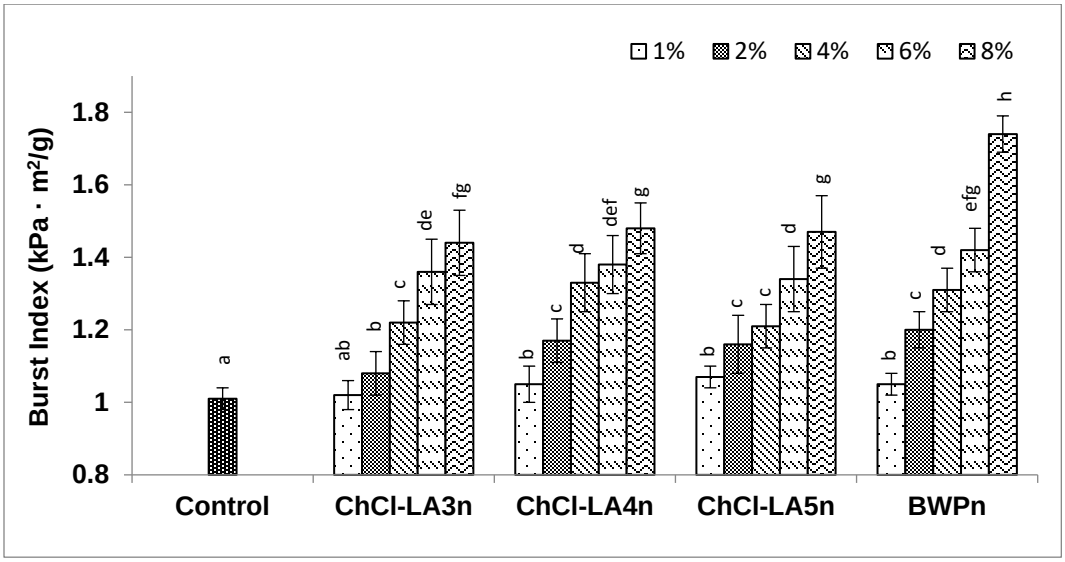

Fig. 5. Untreated and DES-pretreated NFC effects on the burst index of fabricated kraft handsheets. Factors followed by the same letter were not significantly different (Duncan test at $p < 0.001$).

Similarly, 76% increase in the burst index of bleached eucalyptus paper was reported by González *et al.* (2012) after the addition of 3% NFC, and further increases reported by the authors as 172% with the increasing NFC ratio up to 9%. The highest increase in the burst index of the handsheets in the present study was observed in 8% BWPn added samples as 72.3%.

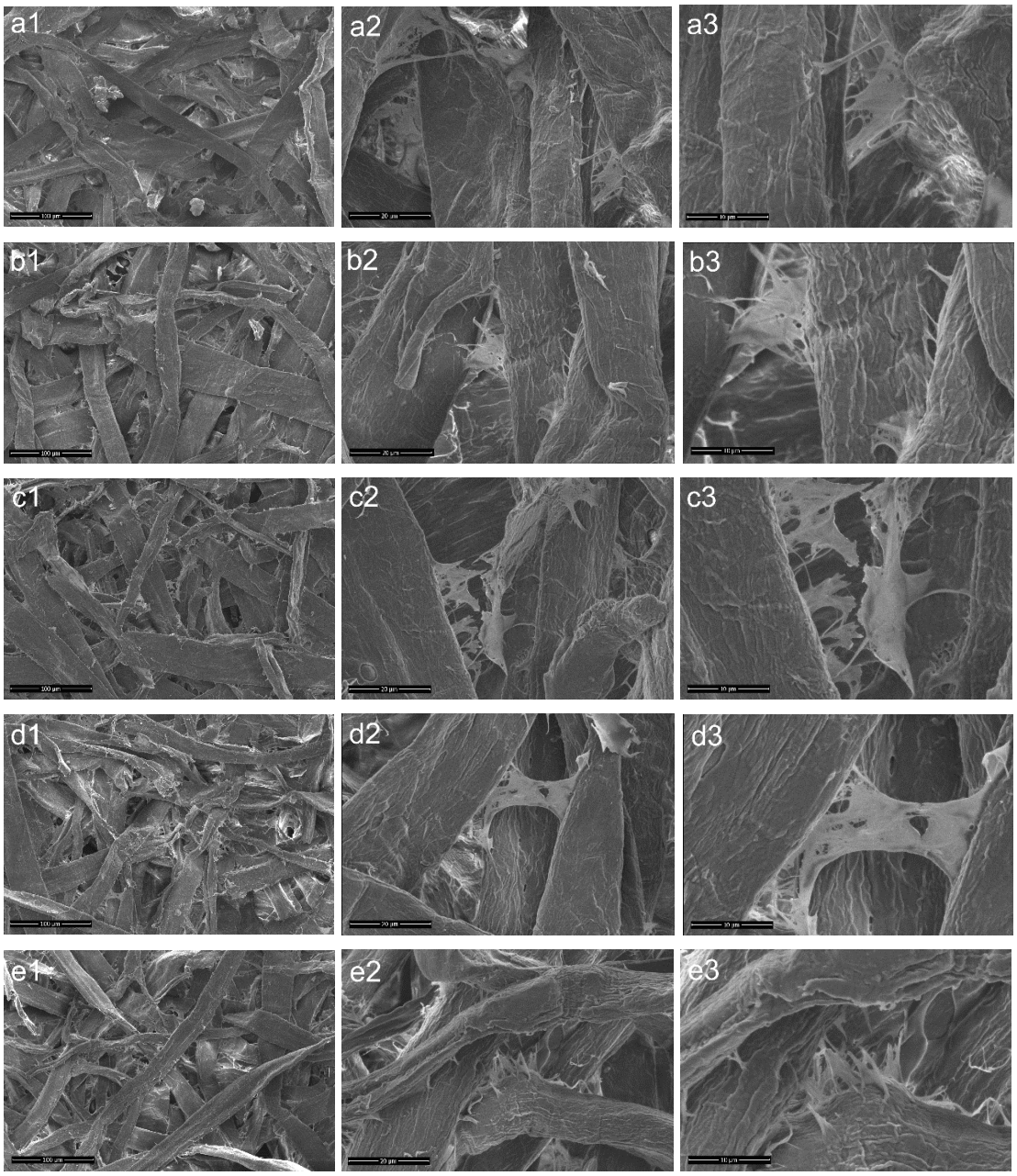

Fig. 6. SEM images of a1 to a3) ChCl-LA3n1, b1 to b3) ChCl-LA3n2, c1 to c3) ChCl-LA3n4, d1 to d3) ChCl-LA3n6, and e1 to e3) ChCl-LA3n8 handsheets at different magnification rates

In parallel to the tensile index, due to BWPn having higher viscosity than the DES-pretreated NFC samples, it increases the number of H-bonds retained in the pulp, and thus the BWPn-added handsheets had higher burst index values than those of the other samples. In accordance, Costa *et al.* (2022) reported that the burst index of 60 g/m² papersheets was 0.5 kPa·m²/g. The authors also noted that the addition of 5% and 8% NFC to the pulp suspensions increased the Schopper-Riegler degrees of the pulp to 26 and 37 °SR, respectively, and increased the burst index values to 1.5 and 1.8 kPa·m²/g (200% and 260%, respectively). In another study conducted by Tajik *et al.* (2018), the burst indices of 60 g/m² paper sheets made from semi-bleached soda bagasse pulp were found to be 23% higher with the addition of 2% NFC and 0.6% cationic starch, compared to control samples.

In contrast, Kasmani *et al.* (2021) found that the burst index values of paper sheets made from cotton fibers increased by 36.1% with the addition of 1% cationic starch and 5% NFC. However, adding NFC with 0.1% PAM instead of 1% cationic starch had no incremental effect on the burst index. As it can be seen from the SEM images of fabricated handsheets (Fig. 6), NFC successfully retained on the structure of paper and increased overall mechanical properties by increasing the bonding ratio. It can be concluded that the use of retention aid is inevitable to obtain desirable increase in mechanical properties NFC added papers. In addition, further studies should be conducted regarding the optimization of pretreatment conditions of deep eutectic solvent systems and different application parameters to obtain longer cellulose nanofibrils. Moreover, the addition of different high-mass-polyelectrolytes and retention aids to achieve optimum mechanical properties should be examined. Differences in the mean tensile and burst indices for all control, untreated and treated samples were statistically significant ($p < 0.001$).

CONCLUSIONS

1. Nanofibrillated cellulose (NFC) was successfully prepared from walnut pruning wastes and hydrated choline chloride-lactic acid deep eutectic solvent (DES) pretreatment facilitated the nanofibrillation process and led to obtain narrower and shorter nanofibrils.
2. Hydration of deep eutectic solvents protected cellulose chains from harsh hydrolysis even at 120 °C and degree of polymerization decreased from 997 to 895 after 5 h reaction time.
3. It is confirmed by Fourier-transform infrared (FT-IR) spectra analysis that cellulose fibrils successfully esterified by hydrated choline chloride-lactic acid DES during the pretreatment process and esterification degree of cellulose increased by increasing the pretreatment time.
4. The addition of untreated and DES-pretreated NFC to the bulk suspensions of kraft handsheets increased the tensile and burst indices up to 71.8% and 72.3%, respectively.
5. According to scanning electron microscopic (SEM) images of fabricated handsheets, using p-DADMAC as retention aid agent drastically improved the retention of isolated NFC to the paper substrate. Even at increasing concentrations, the retained amount of NFC increased, thus mechanical properties of handsheets increased.
6. Compared to other pretreatment processes, DES-pretreated NFCs have improved the mechanical properties of handsheets to a level that can compete with those achieved by oxidation and chemical pretreatments. On the other hand, because DES is non-toxic and inexpensive, it has been concluded that the DES pretreatment method could be an alternative to the toxic and costly chemical and oxidation pretreatments.
7. The NFC addition had a tremendous incremental effect on the freeness level of pulp (°SR). The addition of 8 wt% of untreated NFC to the pulp slurries increased °SR values up to 161.5% (from 13 °SR to 34 °SR). It can be concluded that desirable

freeness levels can be achieved by adding NFCs and cationic retention aids to the pulp during papermaking rather than through further refining, thus leading to a decrease in energy demand.

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