Cationized Dialdehyde Cellulose Synthesized with Deep Eutectic-like Solvents: Effects on Sheet Dewatering and Mechanical Properties When Used as Wet-End Additive

Mozhgan Hashemzehi,* and Björn Sjöstrand

The ability of cationized dialdehyde cellulose to improve the mechanical properties of paper was evaluated. The majority of cationized additives are synthesized by introducing cationic groups through chemical reactions. Here, cationized additives were produced in a more environmentally friendly manner by use of non-toxic and readily biodegradable deep eutectic-like solvent mixtures (DESs). The modified cellulose's properties were characterized by FTIR, polarized-light optical microscopy, charge titrations, and SEM/EDX. The cationized additives were investigated as strength additives for papermaking. Three different amounts of cationic additive (2%, 5%, and 10%) were added to the pulp, and the properties of handsheets were studied. Because increasing the additive content can affect dewatering of the process, the dewatering capabilities of the pulps with additives were evaluated by Schopper-Riegler (°SR) value, water retention value (WRV), and vacuum dewatering. Finally, the recyclability of the DES was assessed in terms of cationization reaction efficiency and their effect on paper mechanical properties.

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Keywords: Cationization of cellulose; Deep eutectic solvent; Mechanical strength; Dewatering; Recyclability of DES; Papermaking

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INTRODUCTION

The use of more sustainable materials becomes a necessity due to climate change and an increasing resource shortage of fossil-based materials. Less eco-friendly engineering materials must be substituted with high-performance bio-based alternatives (Tang *et al*. 2022). Sustainable products materials are being developed and advanced in a number of industries. On this subject, cellulosic materials are crucial for sustainable development. This is due to its abundance and biodegradability; it is both nontoxic and renewable (Calvino *et al*. 2020). Wood fibers have a hierarchical and complex structure, which means that different dimensional scales of the design can be achieved. Additionally, chemical modification can enhance their application (Osong *et al*. 2016).

Cationic polymers have been used for many different purposes in papermaking, including improving mechanical properties, fines retention, and water drainage (Tajik *et al.* 2018; Lourenço *et al.* 2020; Hashemzehi *et al.* 2022). Cationic polyelectrolytes can neutralize the fiber surface charges by introducing attractive forces, such as bridging, or diminishing electrostatic repulsion, thus increasing the influence of van der Waals forces (Salmi *et al*. 2007). The most commonly used cationic additive in paper manufacturing is

cationic starch (Sharma *et al*. 2020b). Recently, cationic cellulose has gained considerable attention because the D-glucose units of cellulose are β-linked D-monosaccharide units that tend to have a straight molecular chain. The functional reactive groups of straight polymer molecules are expected to interact more effectively with the cellulose molecules than those of polymer molecules in random configurations such as starch (Chi *et al*. 2007). To obtain cationic cellulose as a strength additive, the cellulose activator should swell the fibers, but not dissolve them (Aguado *et al.* 2019). Swelling and dissolving of cellulose are different processes. As a result of swelling, cellulose retains its gross structure despite changes in physical properties and an increase in volume. When cellulose dissolves, it transitions from a two-phase to a one-phase system (clear solution), in which the original supramolecular structure of cellulose is destroyed. Thus, cellulose solubility appears to react differently depending on the initial properties, operating conditions, and solvent type (Zhang *et al.* 2013).

Lin and Tsuchii (2022) classified solvents into four groups based on the cellulose solubility. In Type A, cellulose was dissolved in large amounts, whereas Type B dissolved just slightly and Type C swelled the cellulose, but could not dissolve it at all. Type D was not able to swell or dissolve cellulose (Lin and Tsuchii 2022). Solvents are widely recognized to be of great environmental concern. A major goal of green chemistry is to reduce their consumption as much as possible. Furthermore, selecting the appropriate solvent at the start of the chemical production process can greatly improve its sustainability (Anastas and Eghbali 2010; Welton 2015). Deep eutectic-like solvent mixtures (DESs) are a new generation of green solvents that fully agree with the 12 principles of green chemistry. A DES is a homogeneous mixture of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) with a lower melting point than the individual components (Tomé *et al.* 2018). DESs offer attractive options for the "green" swelling and dissolution of cellulose (Liu *et al.* 2017). In the case of cationic cellulose production, they can be used as reagents and media for adding functional cationic groups (Sirviö 2018; Jaekel *et al.* 2021). DES can be used for delignification of wood fibers as an alternative to conventional pulping (Pérez *et al.* 2021).

Cationic modification (or use of a cationic additive) can be particularly valuable when it comes to retaining the cellulose-based materials, *i.e.*, cellulose nanofibrils. The addition of cellulose nanofibrils to the wet-end of the papermaking process has been shown previously to increase the mechanical properties of the paper such as tensile strengths of the paper products (Ahola *et al.* 2008; Eriksen *et al.* 2008; Taipale *et al.* 2010; Lindqvist *et al.* 2011; Hii *et al.* 2012; González *et al.* 2013; Hellström *et a*l. 2014; Merayo *et al.* 2017; Sjöstrand *et al.* 2019). The proposed mechanisms of the increase in strength have been increase in fiber-fiber bonding, providing a stronger network of fibers (Taipale *et al.* 2010; Lindqvist *et al.* 2011; Sjöstrand *et al.* 2019). However, the cellulose nanofibrils are hard to retain during papermaking. But when the macroscopic fiber structure is kept, rather than forming nanocellulose, it is likely that the cationic charge is less essential, since the fibers will easily be retained on the forming fabric. In either case, cationic charge in the system can be beneficial for retention and drainage.

The use of such a cellulose-based additive synthesized by DESs is likely to lead more sustainable development in the paper industry, because it would allow the industry to use the most abundant biopolymer as a raw material. Furthermore, DESs have introduced as a class of sustainable reaction media owing to: i) negligible vapor pressure; ii) high-thermal stability; iii) nonflammability; and iv) easy recycling (Rodríguez *et al.* 2022). DES recycling has received a lot of attention in recent years. Chen *et al*. (2018) showed no

significant decrease in their efficiency after 4 cycles of using DES (Chen *et al* 2018). Kim *et al*. (2018) also reported that about 95% of DES was recovered after each cycle and recycle-DES remained effective after three cycles (Kim *et al* 2018). Therefore, this can contribute to their economic practicality, leading enhancement of their application in the synthesis and modification of a wide variety of materials (Liu *et al* 2022).

This study aims to produce cationized additives from commercial softwood kraft pulp using DES. The cationized additive was characterized by physicochemical methods such as Fourier transform infrared spectroscopy (FTIR), polarized-light optical microscopy, scanning electron microscopy, and elemental analysis (SEM-EDX), and their cationic demand was measured by polyelectrolyte titration. The cationized additives were used as dry strength additives in handsheets to investigate the effects on the tensile strength and sheet dewatering. Finally, the efficiency of recycled DES was evaluated in terms of cationization of cellulose and further on mechanical properties of the handsheets.

EXPERIMENTAL

Materials

Commercial, bleached, flash dried, unbeaten softwood kraft pulp was used as the starting material for the cellulose-based cationized additives and also for the handsheets; throughout this manuscript this is called reference pulp. Lithium chloride (99%) and sodium periodate (> 99%) was used for periodate oxidation of the pulp into dialdehyde cellulose (DAC). Ethanol (96%), ethylene glycol (97%), glycerol, and aminoguanidine hydrochloride (> 98%) were used for the cationization of DAC. Sodium polyethylene sulfonate (PES-Na) was used as a polyelectrolyte to determine the cationic charge. Deionized water and ethanol were used for washing. All reagents were supplied by VWR (Sweden).

Synthesis of Additive: Pretreatment-Periodate Reaction

Cationized dialdehyde cellulose (CDAC) was synthesized in a two-step procedure (Li *et al.* 2018). In the first step, DAC was synthesized by reacting the softwood kraft pulp in deionized water with sodium metaperiodate. Periodate reacts with crystalline and amorphous regions of cellulose without significantly degrading them. This reaction allows for further uniform distribution of the reaction throughout the fibers, making more modifications possible (Sabzalian *et al.* 2014). Periodate oxidation was carried out in the presence of sodium metaperiodate and LiCl for 3 h between 70 and 75 °C with continuous stirring. This initial reaction was performed in dark conditions due to the light sensitivity of $NaIO_4$. Finally, DAC fibers were washed with ethanol 96% and water.

Synthesis of DESs and Cationized Dialdehyde Cellulose Material

To make DESs, various HBDs, such as ammonium formate, betaine chloride, gunadine thiociayante, and guandine hydrochloride are used to swell dialdehyde cellulose (Parnica and Antalik 2014; Li *et al*. 2018; Hong *et al.* 2020; Jaekel *et al*. 2021). The combination of guandine hydrochloride and glycerol causes fibers to swell but not to dissolve, so it was chosen as hydrogen bond donor. Moreover, guandine hydrochloride is a form of salt of guanidine, which originates from both natural and synthetic sources and therefore has the potential to be compatible with natural processes. Previously, Li *et al*. (2018) synthesized cationic cellulose using DESs consisting of guanidine hydrochloride

and glycerol as hydrogen bond donor and acceptor. Cationization of dialdehydcellulose was carried out according to Li *et al*. (2018). They used only glycerol as the hydrogen bond acceptor, whereas this study used both glycerol and ethylene glycol to investigate the effects of the viscosity of the acceptor on the efficacy of DES. There are several factors controlling the ability of a DESs to dissolve a polyelectrolyte complex. Chen and Shull (2021) showed that dielectric constant and viscosity play important roles in polyelectrolyte dissolution. They studied acceptors with varying viscosities and dielectric constants and reported that a system consisting of ethylene glycol is particularly effective, perhaps because of its high dielectric constant and low viscosity for disrupting ionic complexes (Chen and Shull 2021). In this study, the hydrogen bond donor and hydrogen bond acceptor were mixed under 90 °C conditions for 30 min until a clear solvent was obtained. After that, 10 g of dialdehyde cellulose were added to the clear solvent at 75°C, and the reaction was stirred continuously with a magnetic stirrer for 30 minutes. Once the collected CDAC was washed thoroughly with ethanol, it was labelled as CDAC-EG and CDAC-G, which stand for cationized dialdehyde cellulose synthesized by DES in which ethylene glycol or glycerol served as the acceptor.

DES Recycling and Papermaking Applications

As a result of the modification of cellulose with DES, cationized dialdehyde cellulose was filtered; the filtrate, which contained both DES and ethanol, was kept to assess the sustainability of DES. The recycling of DES requires removing ethanol, and when ethanol was removed from the DES solution, a slight yellowing was observed, showing an unwanted reaction (Li *et al*. 2018). Recycle DESs were mixed with dialdehyde cellulose to cationize it and were labelled CDAC-Recycle DES. After cationizing DAC with recycle DES, the solvent was once again filtered and used to cationize DAC, and were labelled CDAC-Twice Recycle DES. As a final step, CDAC-Recycle DES and CDAC-Twice Recycle DES were added to the pulp as additives to make handsheets and to study their effects on drainage and paper properties.

Characterization of Additive

Fourier transform infrared spectroscopy (FTIR) analysis

FTIR analysis of the DAC and CDAC was performed using a Fourier Infrared Spectrometer (Cary 630 FTIR, Agilent Technologies, Palo Alto, CA, US). The spectrum region was recorded between 600 and 4,000 cm^{-1}.

Polarized-light optical microscopy

The reference pulp, DAC, and CDAC were observed using a polarized-light optical microscope (Olympus BX51, Tokyo, Japan). The microscope is equipped with two polarizers. One polarizer is placed in the light path, and a second is placed in the optical pathway between the objective and the observation tubes or camera. Polarized light can improve the detection of swollen fibers by improving contrast and the quality of the image. This may be due to the fact that polarized light is known to have effects on molecules when they are aligned, such as crystals. If the crystals themselves become swollen, less alignment of molecules would occur and therefore there would be less interaction with polarized light. Samples were observed at magnification 10X/0.25 under the microscope. The entire fiber swelling process was recorded on a video, using a camera attached to the microscope.

Morphology and elemental maps of the surface

The morphology of the samples and elemental analysis were determined by scanning electron microscopy/energy-dispersive X-ray (SEM/EDX). SEM measurements were conducted to evaluate their morphology (field emission JEOL 7900F (FE-SEM), Tokyo, Japan) at a voltage of 5.0 kV. Carbon tapes were used as supports for the samples, and a thin layer of Au was sputtered over the samples with a sputter coater. SEM instruments were equipped with an EDX device for analyzing elemental compositions (Oxford Instruments X-MaxN 20mm, Abingdon, UK, with Aztec as the processing software). Quantitative information about elements were derived by comparing the area of the peaks in the recorded spectra of maps. The EDX analysis was used to estimate the degree of modification of the fiber materials.

Cationic demand measurement

For determining the cationic charge in cellulose derivatives, titrations were carried out with a streaming current endpoint; such measurement are considered the most reliable method because they avoid complications related to impurities and side reactions (Vuoti *et al*. 2018). The cationic demand of the mixture with cationic cellulose was measured using a colloidal titration method with a Mutek PCD-03 PH. During the titration, the samples were diluted and then titrated with standard cationic polyelectrolyte [poly(diallyldimethyl-ammonium chloride) (poly-DADMAC)] and standard anionic polyelectrolyte [polyethene sodium sulfonate (PESNa)].

Papermaking and paper sheet analysis

The pulp was disintegrated in water with a disintegrator for 30,000 revolutions. More water was added to achieve the same consistency as the headbox of around 0.2%. Various amounts of cationized dialdehyde cellulose (2%, 5% and 10%) were added to the pulp under continuous stirring for 30 min. A standardized handsheet former was used to prepare handsheets with a basis weight of 60 g/m^2 according to TAPPI T205 sp-95 (1995)

Mechanical properties

The basis weight, thickness, and density of the sheets were measured. These data were used to determine the tensile index in accordance with ISO 1924-3 (2008) using a tensile tester (Zwick/Roell Z005, Ulm, Germany) (Sjöstrand and Brolinson 2022). Tensile test strips were 15 mm wide and 160 mm long, and there were no wrinkles on them.

Laboratory dewatering

Testing the dewatering ability of pulps was done by measuring their drainage resistance with the Shopper-Riegler method (ISO5267-4 1999). The water retention value (WRV) was also determined by centrifugation according to ISO 23714 (2014) (Sjöstrand *et al*. 2019). Finally, vacuum dewatering of pulps was tested in laboratory suction box (Karlstad University, Karlstad, Sweden). The sheets with a diameter of 18.4 cm were formed directly on the forming fabrics using a handsheet former for all tests. Sheets and fabrics were transferred manually to the sample frame of the suction box in the laboratory. All measurements were conducted at a vacuum level of 40 kPa and a vacuum dwell time of 20 ms. Consistency measurements according to ISO 638 (2008) were performed before and after the vacuum suction box dewatering (Sjöstrand *et al*. 2019).

RESULTS AND DISCUSSION

Additive Characterization

Physicochemical characterization

The effects of modification, periodate oxidation, and cationization on the hydrogen band in the structures of fibers can be seen in Fig. 1. All the spectra presented common characteristic peaks at 3332 cm^{-1} (stretching of C−H groups), 2899 cm^{-1} (C−H stretching of $-CH_2$ and C−H groups), 1428 cm^{-1} ($-CH_2$ symmetric bending vibration), 1368 cm^{-1} (C−H bending vibration), 1316 cm^{-1} (C−C and C−O skeletal vibrations), 1263 cm^{-1} (O−H in-plane bending), 1160 cm^{-1} (C−O antisymmetric bridge stretching), and 1031 cm^{-1} (C−O−C stretching vibration, ring deformation vibration), which are typical bands assigned to cellulose molecules (Huang *et al*. 2020).

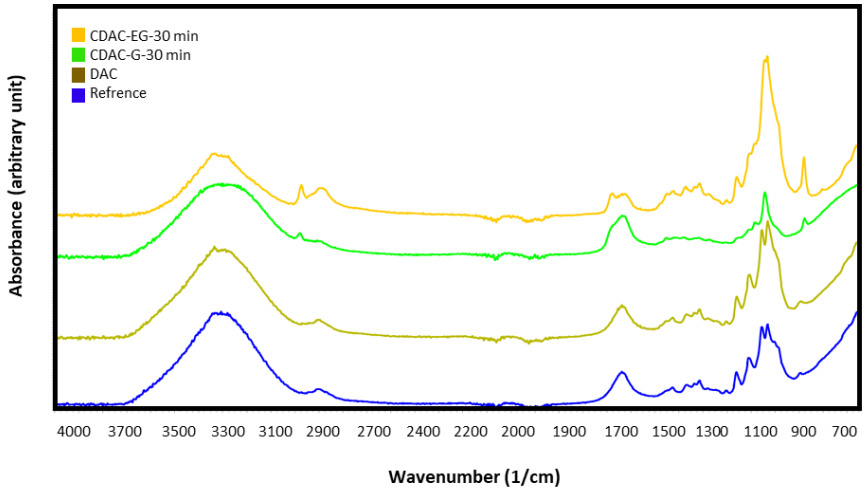

Fig. 1. FTIR spectra of Reference pulp, DAC, CDACG-30min, and CDAC-EG-30min

The spectra of DAC and CDAC samples showed several new peaks and changes in the peaks related to the reference pulp. To compare DAC and reference pulp, the intensity of the peaks at 1160 and 1031 cm^{-1} changed, which can be attributed to the C−O antisymmetric bridge stretching, and C−O−C stretching vibration, ring deformation vibration, respectively. In spectra of CDAC, the band at 1689 cm^{-1} was associated to the carbonyl group. The peak related to the imine bond formed on DAC was at 1559 cm^{-1}. Two peaks at 1480 and 1415 cm^{-1} are related to the methyl groups and carbon–nitrogen bond in the quaternary ammonium groups respectively (Yang and van de Ven 2016). A previous study noted that the imine band at 1610 cm^{-1} represents the stretching vibrations of C-N for the Schiff's base reaction of aldehyde and cationic additive which can be seen this new peak in the spectra related to the CDAC (Alam and Christopher 2017).

Cationic demand

The cationic demand of additives determines how much additive can attach to fiber surfaces. Charges on the cationized additive exchange with charges on the cellulose fibers, driven by the entropic gain obtained when counterions are released. The density of the charge determines whether electrons are constrained by the nucleus, which determines whether they can be polarized (Ninham and Nostro 2010). Figure 2 contains the cationic demand as a result of the 30-min reactions with DESs. The cationic demand increased more

when ethylene glycol was used as an acceptor. The cationic demand of CDAC-EG was 1.12 times higher than that of the CDAC-G, which shows that the DES-EG can disrupt ionic complexes more than DES-G.

The high-charge cationized additive, CDAC-EG-30min, was chosen for further characterization and application in papermaking. A higher charge density additive was assumed to attach more effectively to the negative fiber surface.

For sustainability reasons, recycled DES was used for modification of DAC and the charge density of CDAC-Recycle DES and CDAC-Twice Recycle DES were 1.76 and 1.26 *μ*eq/g respectively. A possible explanation for the reduction in charge density is that DES solvent efficiency decreases after each recycling cycle, but it still demonstrates its effectiveness and sustainability. Using CDAC Recycle or Twice Recycle in paper making may require a higher amount of these additives due to the fact that using a lower charge density additive in pulp results in a low saturation, requiring a higher amount of additives for compensation (Zhao *et al.* 2022). The CDAC-Fresh DES additive would also be more appealing since the high charge density additive competes with other ions for attachment to fibers/fines in the pulp (Taheri *et al.* 2022). In the final section of this paper, the effectiveness of CDAC with recycle DES was discussed in detail.

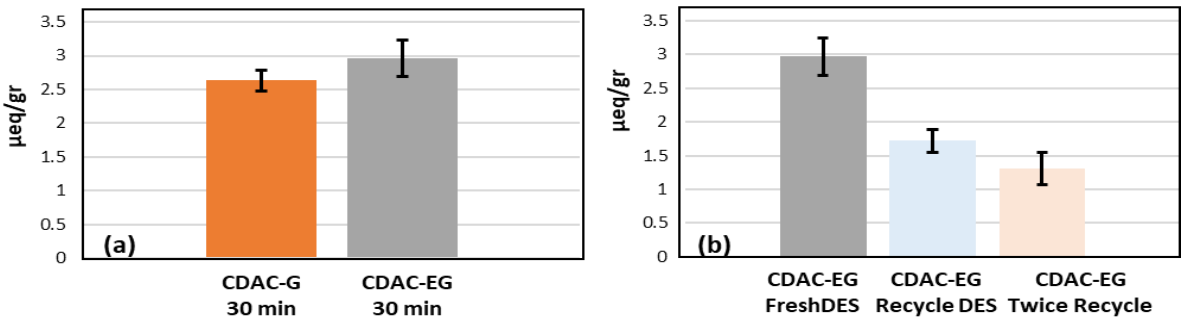

Fig. 2. Cationic demand of a) CDAC-G and CDAC-EG after 30 min b) Comparing the cationic demand of CDAC-Fresh DES, CDAC-Recycle DES and CDAC- Twice Recycle DES. Error bars indicate 95% confidence interval based on three measurements.

Polarized-light optical microscopy

Figure 3 shows the morphology and structure of the reference pulp, DAC, and CDAC-EG-30min. The reference pulp fibers were highly kinked and twisted, common to the flash dryer method. The DAC had thin walls and smoother surfaces and it seems that DAC had the same diameter as the reference pulp. Compared to DAC, CDAC diameters substantially increased after adding water. Microscopy images reveal swelling and volume change of additive, resulting in an increase in diameter of additive by around three times.

For this study, the solvent or reagent used for cationization was alkaline DES, which was synthesized by combining alkaline hydrogen bond donors and acceptors, since alkaline solvents are known to cause fiber swelling and dissolution pulp (Sirviö *et al.* 2020). Indeed, swelling occurs when the swelling agent travels through pores and channels, causing the breaking of some accessible hydrogen bonds, mostly in the amorphous areas of fibers (Cuissinat and Navard 2006). In this situation, the cellulose chains remain within the fiber structure, so solvent penetrates continuously, and osmotic pressure causes the expanding of the cell wall (You *et al.* 2021). Swelling progressed towards the center of the fiber until the whole fiber was swollen. Once the swelling process was complete, only the outer envelope of the fiber was visible (Chaudemanche and Navard 2011).

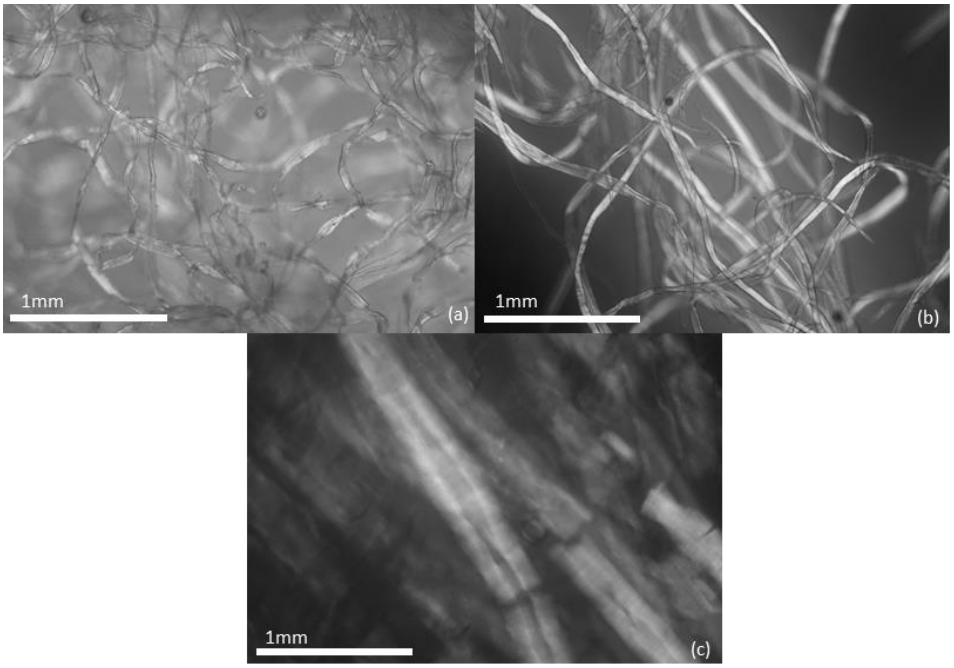

Fig. 3. Polarized-light optical microscopy of (a) reference pulp, (b) DAC and (c) CDAC

The swelling behavior of cellulose fibers was described in different modes by Cuissinat and Navard (2006): –Mode 1: Fast dissolution by disintegration. –Mode 2: Swelling by ballooning followed by dissolution. –Mode 3: Extensive swelling by ballooning, and partial dissolution of the fiber. –Mode 4: A homogenous swelling with no dissolution. –Mode 5: No swelling and no dissolution (Cuissinat and Navard 2006). According to Fig. 3c, CDAC showed homogeneous swelling throughout the fibers and no ballooning phenomenon can be observed. Furthermore, swelling type can be discussed in terms of an "irreversible swelling" or "reversible swelling". These types are described according to whether or not the cellulose fibrillar structure transformed from crystalline I to crystalline II (Cuissinat and Navard 2006). In the present experiment, there was reversible swelling as solvent penetrated the cell wall. This led to fiber volume expansion without allowing the cellulose chains to leave the cell and continuous penetrating of the solvent molecules increased the solvent concentration inside the cellulose. According to the study of Peng *et al.* (2017), the primary layer of natural cellulose is not easy to dissolve compared to the secondary wall, forming a semi-permeable membrane. The solution penetrates the secondary wall through osmotic pressure and integrates with the loose structural regions through interactions between the cellulose and solvent, despite the fact that the solvent penetrated into the polymer molecular chain cannot effectively break intermolecular forces, especially hydrogen bonds (Peng *et al.* 2017). In addition, it was easy to see if there was any dissolved cellulose present in the mixture by flushing water between the two glass plates, since any dissolved cellulose would precipitate, and it would appear as milky white traces (Chaudemanche and Navard 2011). In these experiments, no precipitated cellulose was observed around the fibers, indicating that very little or no cellulose was dissolved.

SEM and EDX

SEM was used to investigate the surface morphology of Reference pulp, DAC, and CDAC at 100 μm and 1 μm scale (Fig. 4). Figure 4a shows the fiber network of reference pulp (100 μm), and the organization of aggregated microfibrils on the fiber wall (1 μm). After pretreatment with periodate (DAC), its surface was fairly smooth and there were no noticeable changes in average diameter of the fiber (Fig. 4b). The fiber size of the CDAC pulp has increased relative to the reference pulp, as shown in Fig. 4c. The changes in the diameter of fiber may be ascribed to the swelling of amorphous structures. Most likely, this was due to the hindering of hydrogen bonds within the molecular chains of the cellulose, and the solvent molecules were embedded in the amorphous zone, which caused the fiber to expand (Liu *et al.* 2016). Figure 5 shows EDX attached to FE-SEM, providing a quantitative analysis of the elemental distribution. The spectrum of Fig. 5a shows that the reference pulp contained carbon and oxygen. Although cellulose is a carbohydrate composed of oxygen, carbon, and hydrogen, there are no hydrogen atoms here. This is because EDX cannot detect elements with low atomic number such as hydrogen. When the fibers were oxidized by periodate, the amount of oxygen elements increased in the sample. This observation confirmed that positions 2 and 3 of the AGU were oxidized to aldehyde groups by periodate oxidation, as shown in Fig. 5b. After treatment with DES, the uniform distribution of new elements, N and Cl, were observed in the sample. It is clear that a majority of O and some C have been substituted with N, showing that N was successfully introduced into the fibers and as a result of DES application. A peak associated with gold appears in Fig. 5 as a result of sputter coating the sample before analyzing it by SEM.

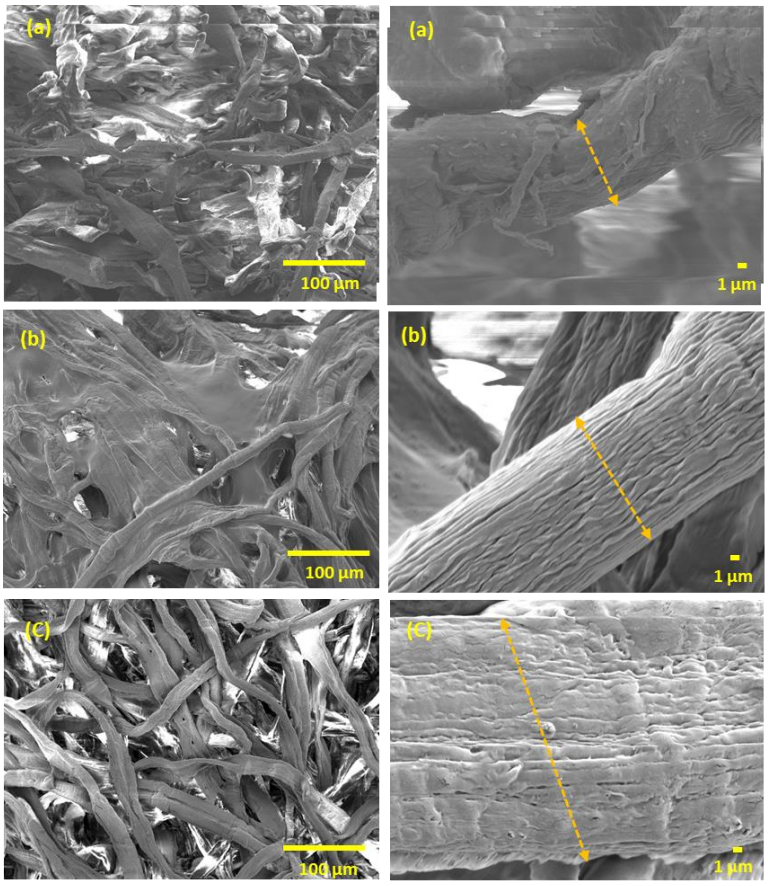

Fig. 4. Scanning electron microscopy of a) Reference pulp b) DAC and c) CDAC

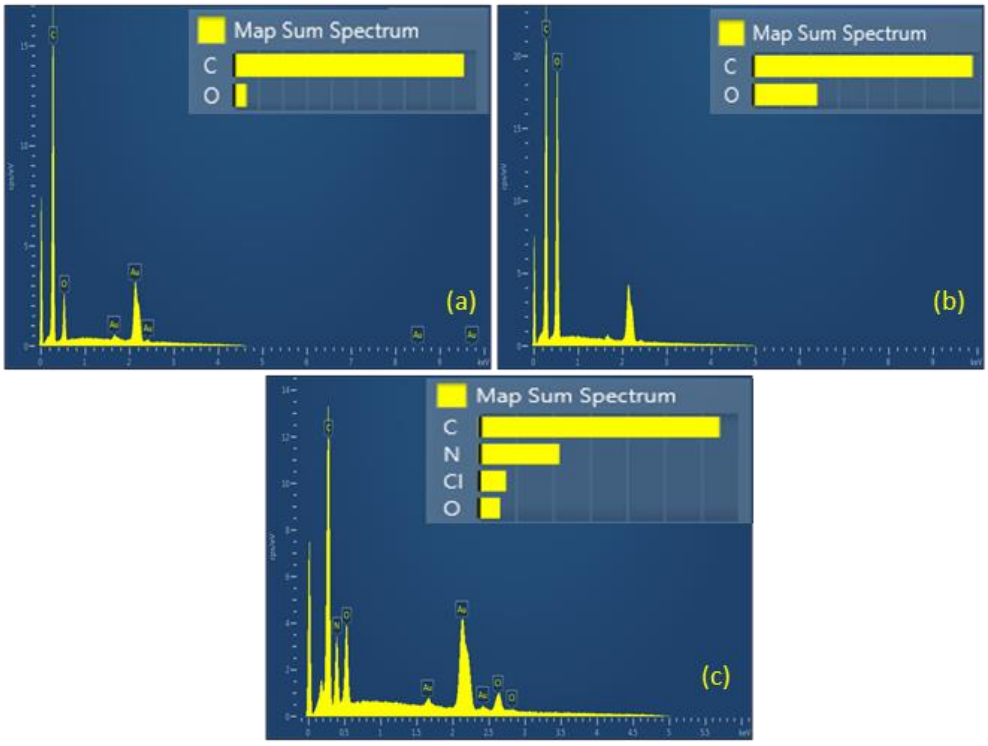

Fig. 5. EDX analysis of a) Reference pulp b) DAC and c) CDAC

Handsheet Characterization and Dewatering Analysis

Effect of modified cellulose on mechanical properties of Paper Sheets

The second set of experiments examined the effect of adding cationized additives synthesized by DESs, CDAC-EG-30 min, on papermaking. Various amounts of cationized additive were added to the disintegrated pulp, handsheets were formed, and their properties were analyzed. Figure 6a shows the tensile strength of handsheets in which different amounts of CDAC, 2%, 5%, and 10% were added as strength additive. This strength indicates how much tension a strip of paper can resist longitudinally before it breaks (Sharma *et al*. 2020a,b).

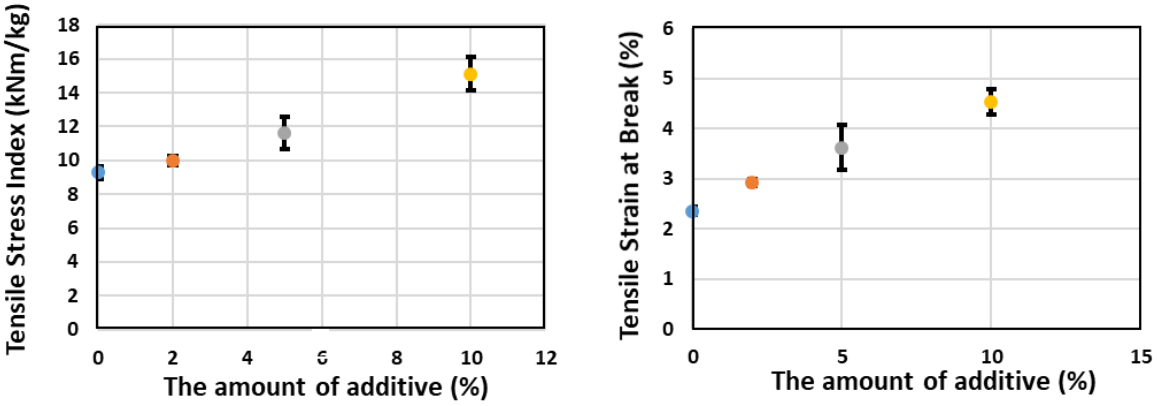

Fig. 6. a) Tensile Stress Index and b) Tensile Strain at Break of handsheets containing 0%, 2% CDAC, 5% CDAC, 10% CDAC. Error bars indicate 95% confidence interval based on four measurements

The different amounts of additive gave different strengths to the paper, and the more additive, the stronger the paper. The strain at break of paper was increased, as shown in Fig. 6b. For paper without any additive, tensile strength was around 9.2 kNm/kg, and strain at break was around 2.6%, while for paper made from 10% additive, tensile strength and strain at break were around 15 kNm/kg and 4.5% respectively.

The tensile strength of paper is generally determined by the properties of the fibers, such as fiber diameter and strength, and the bonding degree of fiber network bonding (Kajanto 1998; Gustafsson and Niskanen 2012). In this case, the addition of cationized polymer improved the inter-fiber bonding by strengthening the connection between the fibers and enhancing fiber-fines retention (Lu *et al.* 2020). Furthermore, the additive can result in a greater number of contact points between fibers, resulting in a stronger fibrous network (Marais and Wågberg 2012). The introduction of charge affected additive's swelling and therefore their flexibility, which in turn influenced conformability. A high level of conformability makes bonding easier because fiber surfaces can be close together, thus forming more bonds. Enhanced bonding results in high tensile strength and elastic modulus of sheets (Laine and Stenius 1997). The tensile energy absorption capacity of the handsheets with varying amounts of additive is shown in Fig. 7a, which illustrates behavior similar to tensile stress index. The tensile energy absorption of reference was about 157 J/kg and it grew gradually with increasing additive amounts until reaching 500 J/kg by 10%-CDAC additive. The tensile stiffness of handsheets is shown in Fig. 7b. It is clear that cationized additives attach onto fibers, increasing the sheet modulus, or stiffness of paper; however, compared to the tensile strength, their effect on tensile stiffness was limited.

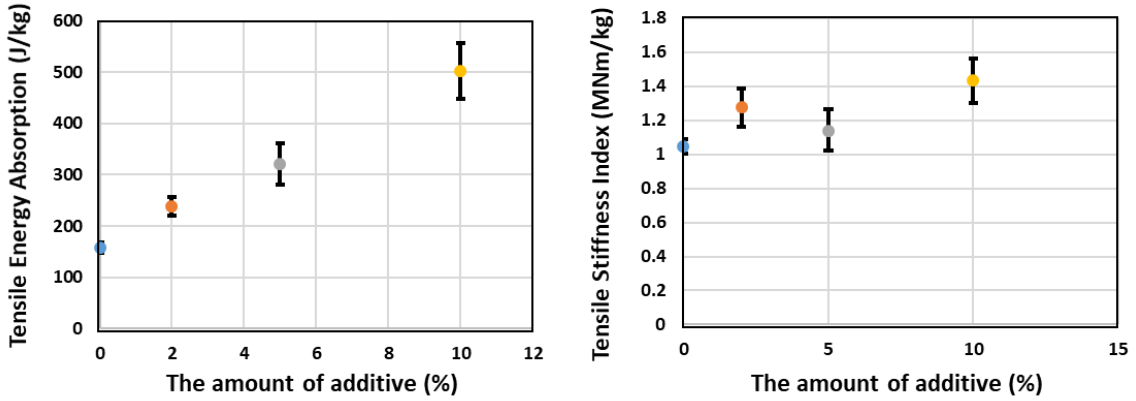

Fig. 7. a) Tensile energy absorption and b) Tensile stiffness index of handsheets containing 0%, 2% CDAC, 5% CDAC, 10% CDAC. Error bars indicate 95% confidence interval based on four measurements.

Dewatering properties

There is a direct correlation between the speed and energy consumption of a paper machine and dewatering process. The dewatering process becomes increasingly difficult along the paper machine, resulting in higher costs due to the fact that the water is placed within the sheet's structure in three different places: between fibers, within lumens, and, within cell walls (Chi *et al*. 2007; Sjöstrand *et al.* 2019; Sjöstrand *et al*. 2022). To evaluate pulp drainage behavior accurately, the dewatering study should cover the entire drainage process in the paper machine. The following methods were used in this study to simulate water removal from sheet structures: Schopper-Riegler (°SR), WRV, and vacuum dewatering.

Drainage

Cellulosic fibers and water interact significantly, affecting drainage rate, press solids, and drying energy (Park *et al*. 2006). The effect on drainage when using CDAC as strength agents was investigated on the pulps (Fig. 8). It is clear that drainage performance was not affected by the addition of CDAC additives. It was expected that drainage resistance would be higher when adding a swollen and flexible fiber additive. However, this time it seems to have adhered well to fibers, causing the effect on drainage to be minimal.

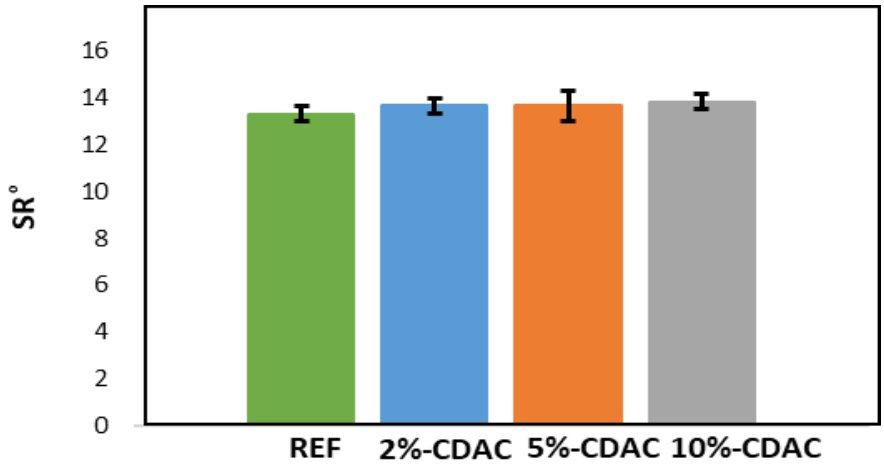

Fig. 8. Schopper-Riegler freeness of various pulp contain 2%CDAC, 5%CDAC and 10%CDAC. Error bars indicate 95% confidence interval based on four measurements.

Vacuum dewatering

The effect of cationized additive on the vacuum dewatering was studied by measuring moisture ratio before and after suction box, as shown in Fig. 9. The moisture ratio before vacuum dewatering depends on the amount of additive relative the reference, with relatively small differences (Fig. 9a). After vacuum dewatering, the moisture ratio has smaller differences still and it seems that the additive has only a small impact on the vacuum dewatering. This would be positive for the possibilities to use these additives in full-scale production of paper, even though many other aspects must also be taken into consideration before full-scale testing. The cationic nature of the additive can result in relatively efficient adhesion to fibers, which would be positive for early dewatering avoiding the clogging of drainage channels which could otherwise be very negative to dewatering rates (Hubbe and Heitmann 2007). The additives would mostly attach to the fibers due to their opposite charge, some of them moving in the bulk and makes to block in drainage channel in the fibers. The vacuum dewatering results indicate that the dewatering was efficient even with the additive present, in line with previous observations (Taipale *et al*. 2010; Lindqvist *et al.* 2011; Sjöstrand *et al.* 2019).

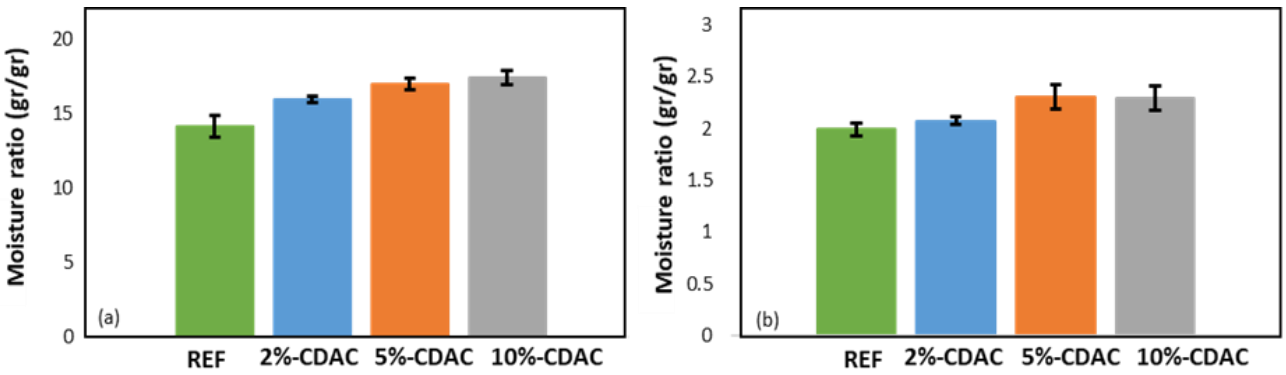

Fig. 9. a) Moisture ratio before and b) Moisture ratio after suction box for various pulp contain 2%CDAC, 5%CDAC and 10%CDAC. Error bars indicate 95% confidence interval based on three measurements.

Water retention value

In the next stage of dewatering analysis, water retention value is evaluated, which simulates some of what happens in the pressing section (Stenström and Nilsson 2015; Sjöstrand 2020). Indeed, the hydration of fibers must be understood from different perspectives. First, water absorbed by the cell wall of fibers due to charges and polarities within the fibers. Second, the capillary action within the lumens retains water. A third is inter-fiber water, which is trapped between the fibers in a pulp mat. All three types of water are included in the water retention value (Banavath *et al.* 2011). Previous studies have shown that highly charged cationic polymers with relatively high mass promoted dewatering and also decreased water retention values more efficiently. It is possible to use them as dewatering aids, where the most effective ones produced large patches of positive charge that aggregated fibrils (Hubbe and Heitmann 2007). However, adding modified additives led to increased water retention values, as shown in Fig. 10. Once the amount of cationized additive increased, the water retention values increased slightly. This may be due to swelling of CDACs, which keep more water in their structure, making sheet consolidation easier, but with a small impact on dewatering (Rahman *et al.* 2018).

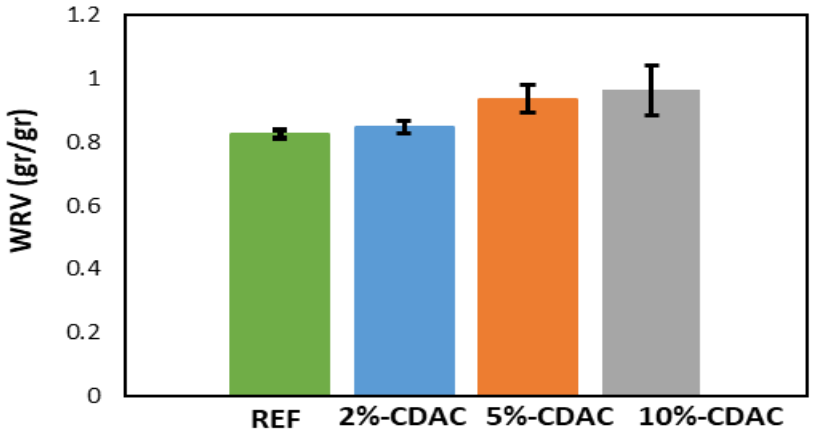

Fig. 10. Water retention values of various pulp containing REF, 2%CDAC, 5%CDAC, and 10%CDAC. Error bars indicate 95% confidence interval based on four measurements.

Recycling and Reuse of DES

To improve the environmental friendliness and efficiency of the process, solvent consumption should be reduced during processing, which would be achieved by using DES as it would be recyclable and sustainable, allowing waste emissions to be minimized (Sirviö *et al*. 2020). Thus, there is a need to study how much recycling of DES can be done before it is no longer productive. A decrease in efficiency of recovered DES was observed, which was attributed to an increase in impurities within the DES. In addition, the level of DES in the recovered solution gradually declined, resulting in a decrease in cellulose solubility because the Lewis acid in DES was lost as a result of complex formation with hemicellulose and lignin (Isli and Kaltschmitt 2022; Zhu *et al*. 2021)

Figure 11 shows how much solvent was efficient in swelling the fibers, and it is obvious that the diameter of swollen fiber decreased after each recycling run. Additionally, fresh solvent seems to penetrate deeper into the fiber region, resulting in a thicker translucent region, while the dark core, lumen, are thicker for twice recycle additive.

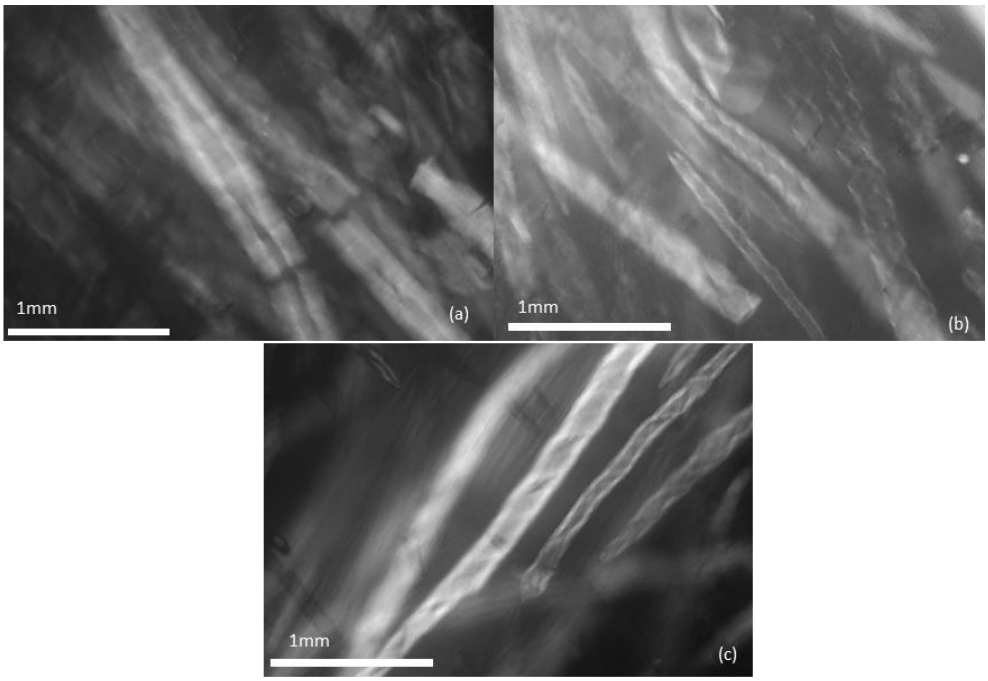

Fig. 11. A comparison of the swelling behavior (a) CDAC-Fresh DES, (b) CDAC-Recycle DES and (c) CDAC-Twice Recycle DES

A tensile strength study of handsheets made with CDAC-recycle DES was also conducted. There was a difference between the strength of handsheets made with CDAC-recycle DES and CDAC-fresh DES. The tensile index of handsheets made with 2% of CDAC-recycle was approximately 9.31 kNm/kg, approximately the same as that observed when no additive was added to the pulp. With the addition of 5% of CDAC-recycle DES, the tensile index was increased to 10.31 kNm/kg, whereas handsheets made with 5% of fresh CDAC DES had tensile strengths of 11.62 kNm/kg. The reason for this could be that after each cycle of recycling of DES, the cationization efficiency of dialdehyde cellulose decreased, which reduces swelling behavior and decreases the ability of fibers to form fiber-fiber bonds. To increase the mechanical properties of handsheets made with CDAC-Recycle DES, perhaps higher amounts of recycled additives may be required to enhance

bonding area between fibers. This is evident from the figure that when 2% of CDAC-Fresh DES was added to the pulp, the mechanical properties of the handsheets were similar to those obtained with 5% of CDAC-recycle DES. It is also important to consider that the additives' cationic demand affects saturation adsorption, but not always tensile index (Zhao *et al*. 2022). The dewatering study of pulp containing CDAC-Recycle DES and CDAC-Twice Recycle DES showed that the cationized additive caused no significant differences in moisture ratio and water retention value of the pulps when compared with pulp containing CDAC-fresh DES (Fig. 12).

Different methods have been proposed to improve the efficiency of recycling DES (anti-solvent addition, crystallization, membrane flotation, liquid–solid extraction, liquid–liquid extraction, short path distillation, supercritical liquid extraction, separation due to density, and viscosity differences). A common method of DESs purification is the addition of anti-solvents. In these cases water, ethanol, and acetone are more common because they are cheap and more environmentally friendly. By adding high concentrations of anti-solvents, there is a possibility to break hydrogen bonds between the impurity and DES causing precipitation of the solubilized solids. The anti-solvent will then be evaporated, as they are usually volatile compounds, and DES with higher purity can be reused more times (Asli and Kaltschmitt 2022).

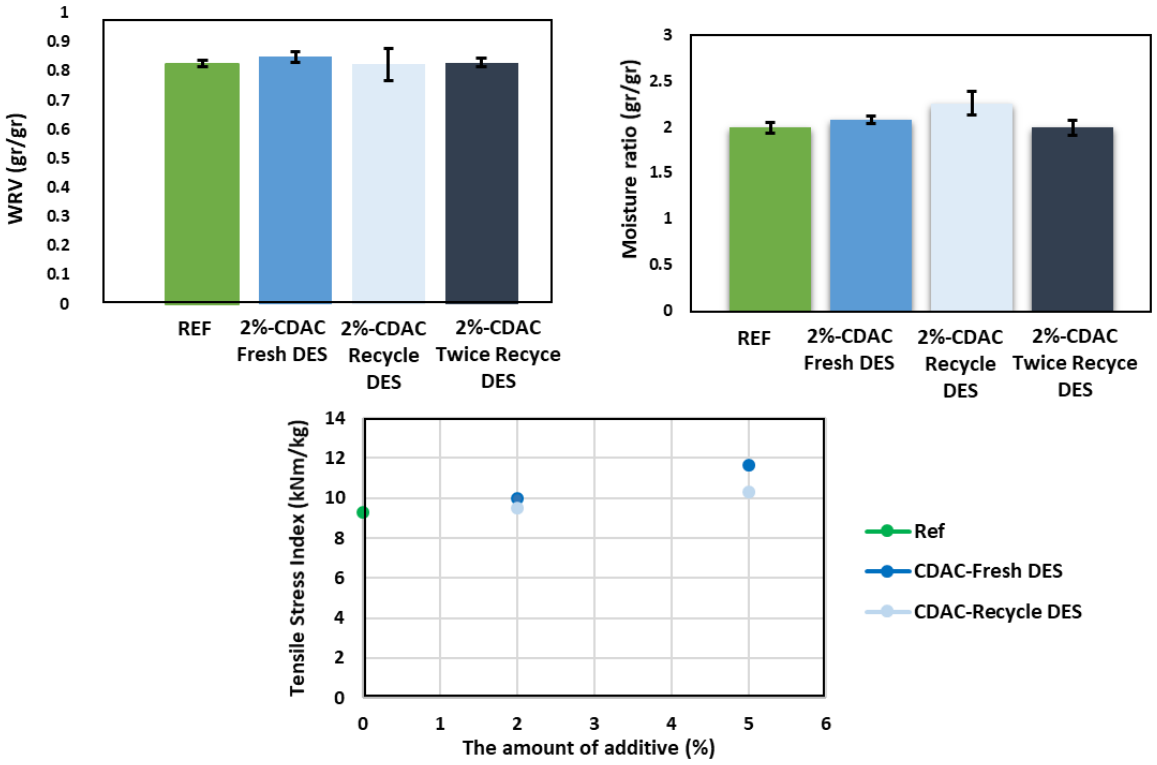

Fig. 12. A comparison of the moisture ratio, WRV, and tensile stress index between reference pulp and pulp with 2% CDAC, 2% CDAC-Recycle DES, and 2% CDAC-twice Recycle DES. Error bars indicate 95% confidence interval based on three and four measurement vacuum dewatering and WRV test, respectively.

CONCLUSIONS

1. Cationized dialdehyde cellulose enhanced the mechanical properties of handsheets. The tensile strength of handsheet of reference increased from 9.2 to 15 KN/kg with 10% cationic dialdehyde cellulose (CDAC) addition, and the corresponding energy absorption increase from 157 to 500 J/kg with 10%-CDAC.
2. Dewatering resistance was not increased as much as expected after CDAC application. Thus, the additive show potential to be used as an additive in full-scale paper production.
3. Even after two rounds of recycling, there was still swelling of the fibers and increasing of the fibers' cationic demand. By adding CDAC modified with recycled deep eutectic-like solvent (DES), the mechanical properties of handsheets also improved.
4. Thus, DES is a promising solvent system and reaction agent for modifying cellulose in an environmentally friendly way, and its recycling ability is also beneficial.

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REFERENCES CITED

Aguado, R., Lourenco, A. F., Ferreira, P. J. T., Moral, A., and Tijero, A. (2019). "The relevance of the pretreatment on the chemical modification of cellulosic fibers," *Cellulose* 26(10), 5925-5936. DOI: 10.1007/s10570-019-02517-7

Ahola, S., Österberg, M., and Laine, J. (2008). "Cellulose nanofibrils-adsorption with poly (amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive," *Cellulose* 15(2), 303-314. DOI: 10.1007/s10570-007-9167-3

Alam, M., and Christopher, L. P. (2017). "A novel, cost-effective and eco-friendly method for preparation of textile fibers from cellulosic pulps," *Carbohydrate Polymers* 173, 253-258. DOI: 10.1016/j.carbpol.2017.06.005

Anastas, P., and Eghbali, N. (2010). "Green chemistry: Principles and practice," *Chemical Society Reviews* 39(1), 301-312. DOI: 10.1039/B918763B

Banavath, H. N., Bhardwaj, N, K., and Ray, A. K. (2011). "A comparative study of the effect of refining on charge of various pulps," *Bioresource Technology* 102(6), 4544-4551. DOI: 10.1016/j.biortech.2010.12.109

Calvino, C., Macke, N., Kato, R., and Rowan, S. J. (2020). "Development, processing and applications of bio-sourced cellulose nanocrystal composites," *Progress in Polymer Science* 103, 101221. DOI: 10.1016/j.progpolymsci.2020.101221

Chaudemanche, C., and Navard, P. (2011). "Swelling and dissolution mechanisms of regenerated Lyocell cellulose fibers," *Cellulose* 18(1) 1-15. DOI: 10.1007/s10570-010-9460-4

Chen, Y.-L., and Shull, K. R. (2021). "Processing polyelectrolyte complexes with deep eutectic solvents," *ACS Macro Letters* 10(10), 1243-1247. DOI: 10.1021/acsmacrolett.1c00494

Chen, Z., Reznicek, W. D., and Wan, C. (2018). "Deep eutectic solvent pretreatment enabling full utilization of switchgrass," *Bioresource technology* 263, 40-48. DOI: 10.1016/j.biortech.2018.04.058

Chi, H., Li, H.-B., Liu, W.-H., and Zhan, H.-Y. (2007). "The retention- and drainage-aid behavior of quaternary chitosan in papermaking system," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 297(1), 147-153. DOI: 10.1016/j.colsurfa.2006.10.039

Cuissinat, C., and Navard, P. (2006). "Swelling and dissolution of cellulose. Part 1: Free floating cotton and wood fibres in N-methylmorpholine-N-oxide–water mixtures," in: *Macromolecular symposia* 244(1), 1-18. DOI: 10.1002/masy.200651201

Eriksen, Ø., Syverud, K., and Gregersen, Ø. (2008). "The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper," *Nordic Pulp & Paper Research Journal* 23(3) 299-304. DOI: 10.3183/npprj-2008-23-03-p299-304

González, I., Vilaseca, F., Alcalá, M., Pèlach, M. A., Boufi, S., and Mutjé, P. (2013). "Effect of the combination of biobeating and NFC on the physico-mechanical properties of paper," *Cellulose* 20(3), 1425-1435. DOI: 10.1007/s10570-013-9927-1

Gustafsson, P-J., and Niskanen, K. (2012). "Paper as an engineering material," in: *Mechanics of Paper Products*, K. Niskanen (ed.), Walter de Gruyter, Germany.

Hashemzehi, M., Mesic, B., Sjöstrand. B., and Naqvi, M. (2022). "A comprehensive review of nanocellulose modification and applications in papermaking and packaging: Challenges, technical solutions, and perspectives," *BioResources* 17(2), 3718-3780. DOI: 10.15376/biores.17.2.Hashemzehi

Hellström, P., Heijnesson-Hultén, A., Paulsson, M., Håkansson, H., and Germgår, U. (2014). "Fenton pre-treated microfibrillated cellulose evaluated as a strength enhancer in the middle ply of paperboard," *Nordic Pulp & Paper Research Journal* 29(4), 732-740. DOI: 10.3183/npprj-2014-29-04-p732-740

Hii, C., Gregersen, Ø. W., Chinga-Carrasco, G., and Eriksen, Ø. (2012). "The effect of MFC on the pressability and paper properties of TMP and GCC based sheets," *Nordic Pulp & Paper Research Journal* 27(2), 388-96. DOI: 10.3183/npprj-2012-27-02-p388-396

Hong, S., Yang, Y, Li, P., Zhang, K., Lian, H., and Liimatainen, H. (2020). "Enhancement of the nanofibrillation of birch cellulose pretreated with natural deep eutectic solvent," *Industrial Crops and Products* 154, article 112677. DOI: 10.1016/j.indcrop.2020.112677

Huang, X.-Y., Dognani, G., Hadi, P., Yang, M., Job, A. E., and Hsiao, B. S. (2020). "Cationic dialdehyde nanocellulose from sugarcane bagasse for efficient chromium (VI) removal," *ACS Sustainable Chemistry & Engineering* 8(12), 4734-4744. DOI: 10.1021/acssuschemeng.9b06683

Hubbe, M. A., and Heitmann, J. A. (2007). "Review of factors affecting the release of water from cellulosic fibers during paper manufacture," *BioResources* 2(3), 500-533.

Isli, A., and Kaltschmitt, M. (2022). "Recovery and recycling of deep eutectic solvents in biomass conversions: A review," *Biomass Conversion and Biorefinery* 12, 197-226.

DOI: 10.1007/s13399-021-01860-9

Jaekel, E. E., Sirviö, J. A., Antonietti, M., and Filonenko, S. (2021). "One-step method for the preparation of cationic nanocellulose in reactive eutectic media," *Green Chemistry* 23(6), 2317-2323. DOI: 10.1039/D0GC04282J

Kajanto, I. (1998). "Structural mechanics of paper and board," in: *Paper Physics*, K. Niskanen (ed.), Fapet Oy, Helsinki.

Kim, K. H., Dutta, T., Sun, J., Simmons, B., and Singh, S. (2018). "Biomass pretreatment using deep eutectic solvents from lignin derived phenols," *Green Chem*. 20, 809-815. DOI:10.1039/C7GC03029K.

Laine, J., and Stenius, P. (1997). "Effect of charge on the fibre and paper properties of bleached industrial kraft pulps," *Paperi ja Puu/Paper and Timber* 79(4), 257-266.

Li, P., Sirviö, J. A., Asante, B., and Liimatainen, H. (2018). "Recyclable deep eutectic solvent for the production of cationic nanocelluloses," *Carbohydrate Polymers* 199, 219-227. DOI: 10.1016/j.carbpol.2018.07.024

Lin, L., and Tsuchii. K. (2022). "Dissolution behavior of cellulose in a novel cellulose solvent," *Carbohydrate Research* 511, article 108490. DOI: 10.1016/j.carres.2021.108490.

Lindqvist, H., Salminen, K., Kataja-Aho, J., Retulainen, L., Fardim, P., and Sundberg, A. (2011). "The effect of fines on dewatering, wet and dry web properties," in: *Paper Conference*, Cincinnati, USA.

Liu, Y., Shi, Z., Gao, Y., An, W., Cao, Z., and Liu, J. (2016). "Biomass-swelling assisted synthesis of hierarchical porous carbon fibers for supercapacitor electrodes," *ACS Applied Materials & Interfaces* 8(42), 28283-28290. DOI: 10.1021/acsami.5b11558

Liu, Y., Chen, W., Xia, Q., Guo, B., Wang, Q., Liu, S., Liu, Y., Li, J., and Yu, H. (2017). "Efficient cleavage of lignin–carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent," *ChemSusChem* 10(8), 1692. DOI: 10.1002/cssc.201601795

Liu, J., Li, X., and Row, K. H. (2022). "Development of deep eutectic solvents for sustainable chemistry," *Journal of Molecular Liquids* 362, article 119654. DOI: 10.1016/j.molliq.2022.119654

Lourenço, A. F., Gamelas, J. A., Sarmento, P., and Ferreira. P. J. (2020). "A comprehensive study on nanocelluloses in papermaking: The influence of common additives on filler retention and paper strength," *Cellulose* 27(9) 5297-5309. DOI: 10.1007/s10570-020-03105-w

Lu, Z., An, X., Zhang, H., Liu, L., Dai, H., Cao, H., Lu, B., and Liu, H. (2020). "Cationic cellulose nano-fibers (CCNF) as versatile flocculants of wood pulp for high wet web performance," *Carbohydrate Polymers* 229, article 115434. DOI: 10.1016/j.carbpol.2019.115434

Marais, A., and Wågberg, L. (2012). "The use of polymeric amines to enhance the mechanical properties of lignocellulosic fibrous networks," *Cellulose* 19(4) 1437-1447. DOI: 10.1007/s10570-012-9712-6

Merayo, N., Balea, A., De la Fuente, E., Blanco, Á, and Negro, C. (2017). "Synergies between cellulose nanofibers and retention additives to improve recycled paper properties and the drainage process," *Cellulose* 24(7) 2987-3000. DOI: 10.1007/s10570-017-1302-1

Ninham, B. W., and Nostro, P. L. (2010). "Molecular forces and self assembly," in: *Colloid, Nano Sciences, and Biology*, Cambridge University Press. DOI: 10.1063/1.3554316

Osong, S. H., Norgren, S., and Engstrand, P. (2016). "Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: A review," *Cellulose* 23(1), 93-123. DOI: 10.1007/s10570-015-0798-5

Park, S., Venditti, R. A., Jameel, H., and Pawlak, J. J. (2006). "Hard to remove water in cellulose fibers characterized by high resolution thermogravimetric analysis-methods development," *Cellulose* 13(1), 23-30. DOI: 10.1007/s10570-005-9009-0

Parnica, J., and Antalik, M. (2014). "Urea and guanidine salts as novel components for deep eutectic solvents," *Journal of Molecular Liquids* 197, 23-26. DOI: 10.1016/j.molliq.2014.04.016

Peng, H., Dai, G., Wang, S., and Xu, H. (2017). "The evolution behavior and dissolution mechanism of cellulose in aqueous solvent," *Journal of Molecular Liquids* 24, 959-966. DOI: 10.1016/j.molliq.2017.06.103

Pérez, A. D., Fiskari, J., and Schuur, B. (2021). "Delignification of low-energy mechanical pulp (asplund fibers) in a deep eutectic solvent system of choline chloride and lactic acid," *Frontiers in chemistry* 9, 688291. DOI: 10.3389/fchem.2021.688291

Rahman, H., Engstrand, P., Sandström, P., and Sjöstrand, B. (2018). "Dewatering properties of low grammage handsheets of softwood kraft pulps modified to minimize the need for refining," *Nordic Pulp & Paper Research Journal* 33(3), 397-403. DOI: 10.1515/npprj-2018-3037

Rodríguez-Álvarez, M. J., García-Garrido, S. E., Perrone, S., García-Álvarez, J., and Capriati, V. (2022). "Deep eutectic solvents and heterogeneous catalysis with metallic nanoparticles: A powerful partnership in sustainable synthesis," *Current Opinion in Green and Sustainable Chemistry*, article 100723. DOI: 10.1016/j.cogsc.2022.100723

Sabzalian, Z., Alam, M. N., and van de Ven, T. G. (2014). "Hydrophobization and characterization of internally crosslink-reinforced cellulose fibers," *Cellulose* 21(3), 1381-1393. DOI: 10.1007/s10570-014-0178-6

Salmi, J., Österberg, M., Stenius, P., and Laine, J. (2007). "Surface forces between cellulose surfaces in cationic polyelectrolyte solutions: The effect of polymer molecular weight and charge density," *Nordic Pulp & Paper Research Journal* 22(2) 249-257. DOI:10.3183/npprj-2007-22-02-p249-257

Sharma, D., Kumar, V., and Sharma, P. (2020a). "Application, synthesis, and characterization of cationic galactomannan from ruderal species as a wet strength additive and flocculating agent," *ACS Omega* 5(39), 25240-25252. DOI: 10.1021/acsomega.0c03408

Sharma, M., Aguado, R., Murtinho, D., Valente, A. J., De Sousa, A. P. M., and Ferreira, P. J. (2020b). "A review on cationic starch and nanocellulose as paper coating components," *International Journal of Biological Macromolecules* 162, 578-598. DOI: 10.1016/j.ijbiomac.2020.06.131

Sirviö, J. A. (2018). "Cationization of lignocellulosic fibers with betaine in deep eutectic solvent: Facile route to charge stabilized cellulose and wood nanofibers," *Carbohydrate Polymers* 198, 34-40. DOI: 10.1016/j.carbpol.2018.06.051

Sirviö, J. A., Hyypiö, K., Asaadi, S., Junka, K., and Liimatainen, H. (2020). "High-strength cellulose nanofibers produced via swelling pretreatment based on a choline chloride–imidazole deep eutectic solvent," *Green Chemistry* 22(5) 1763-1775. DOI: 10.1039/C9GC04119B

Sjöstrand, B. (2020). *Vacuum Dewatering of Cellulosic Materials: New Insights into Transport Phenomena in the Papermaking Process*, Ph.D. Dissertation, Karlstad University, Karlstad, Sweden.

Sjöstrand, B., Barbier, C., Ullsten. H., and Nilsson, L. (2019). "Dewatering of softwood kraft pulp with additives of microfibrillated cellulose and dialcohol cellulose," *BioResources* 14(3), 6370-6383. DOI: 10.15376/biores.14.3.6370-6383

Sjöstrand, B., and Brolinson, A. (2022). "Addition of polyvinylamine in chemi-thermomechanical pulp and kraft pulp and the effects on dewatering, strength, and air permeance," *BioResources* 17(3), 4098-4115. DOI: 10.15376/biores.17.3.4098-4115

Stenström, S., and Nilsson, L. (2015). "Predicting water removal during vacuum dewatering from fundamental fibre property data," *Nordic Pulp & Paper Research Journal* 30(2) 265-71. DOI: 10.3183/npprj-2015-30-02-p265-271

Taheri, A., Rahmaninia, M., and Khosravani, A. (2022). "Interaction of the electrical conductivity of recycled pulp colloidal suspension with chitosan and bentonite as a papermaking additive system," *BioResources* 17, 1805-1817. DOI: 10.15376/biores.17.1.1805-1817

Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., and Laine, J. (2010). "Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength," *Cellulose* 17(5) 1005-20. DOI: 10.1007/s10570-010-9431-9

Tajik, M., Jalali Torshizi, H., Resalati, H., and Hamzeh, Y. (2018). "Effects of cationic starch in the presence of cellulose nanofibrils on structural, optical and strength properties of paper from soda bagasse pulp," *Carbohydrate Polymers* 194, 1-8. DOI: 10.1016/j.carbpol.2018.04.026

Tang, Y., Yang, H., and Vignolini, S. (2022). "Recent progress in production methods for cellulose nanocrystals: Leading to more sustainable processes," *Advanced Sustainable Systems* 6(3), article 2100100. DOI:10.1002/adsu.202100100

Tomé, L. I., Baião. V, da Silva, W., and Brett, C. M. (2018). "Deep eutectic solvents for the production and application of new materials," *Applied Materials Today* 10, 30-50. DOI: 10.1016/j.apmt.2017.11.005

TAPPI T205 sp-95 (1995). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA, USA.

Vuoti, S., Narasimha, K., and Reinikainen, K. (2018). "Green wastewater treatment flocculants and fixatives prepared from cellulose using high-consistency processing and deep eutectic solvents," *Journal of Water Process Engineering* 26, 83-91. DOI: 10.1016/j.jwpe.2018.09.003

Welton, T. (2015). "Solvents and sustainable chemistry," *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 471, article 20150502. DOI:10.1098/rspa.2015.0502

Yang, H., and Van de Ven, T. G. (2016). "Preparation of hairy cationic nanocrystalline cellulose," *Cellulose* 23(3) 1791-801. DOI: 10.1007/s10570-016-0902-5

You, X., Chen, F., Ma, Y., Roselli, A., Enqvist, E., and Hassi, H. (2021). "Single fiber swelling behavior for natural and man-made cellulose fibers under alkaline treatment," *Cellulose* 28(18) 11287-98. DOI: 10.1007/s10570-021-04280-0.]

Zhang, S., Wang, W. C., Li, F. X., and Yu, J. Y. (2013). "Swelling and dissolution of cellulose in NaOH aqueous solvent systems," *Cellulose Chemistry and Technology* 47(9-10), 671-79.

Zhao, M., Robertsén, L., Wågberg, L., and Pettersson. T. (2022). "Adsorption of paper strength additives to hardwood fibres with different surface charges and their effect on paper strength," *Cellulose* 29(4) 2617-2632. DOI: 10.1007/s10570-022-04447-3

Zhu, Y., Qi, B., Liang, X., Luo, J., Wan, Y. (2021). "Comparison of corn stover pretreatments with Lewis acid catalyzed choline chloride, glycerol and choline chloride-glycerol deep eutectic solvent," *Polymers* 13, article 1170. DOI: 10.3390/polym13071170

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