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Cellulose nanocrystal/amino-aldehyde biocomposite films

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Abstract

From the suspensions of cellulose nanocrystals (CNCs) derived from cotton and flax by acidic hydrolysis, transparent and smooth films were produced with different plasticizers and an amino-aldehyde based cross-linking agent in a wide composition range by a simultaneous casting and wet cross-linking process. The effect of cross-linker concentration on the optical and tensile properties and on the morphology of CNC films was investigated by various measurements. The interaction of films with liquid water and water vapour was also characterized by water sorption and water contact angle as well as performing a sinking test. Cross-linking improved the transparency, reduced the porosity and surface free energy, and prevented the delamination of CNC films in water at a concentration of 10 % or higher. The surface of CNC films is basic in character and has an electron donor property. The CNC/amino-aldehyde films had a high tensile strength (45 MPa) and modulus (11 GPa).

1. Introduction

Nanocrystalline cellulose, which can be extracted from cellulose-based materials by an acidic hydrolysis, consists of rod-like nano-sized crystals of cellulose and possesses several attractive properties, such as versatile fibre morphology, easy surface modification, large surface area and high aspect ratio (Klemm et al., 2011; Tang, Sisler, Grishkewich, & Tam, 2017). Cellulose nanocrystals (CNCs) have been used for various applications, such as antimicrobial/antiviral systems, tissue engineering, drug/gene delivery, biosensors, adsorbents in wastewater treatment, super-capacitors, conductive films, electronic sensors, Pickering emulsifier, drilling fluid, antioxidant or food additive/packaging. In recent years, there has been an increasing interest in the production of transparent thin films of CNCs with special properties and the number of research papers published in this field has been growing exponentially (Lagerwall et al., 2014; Majoinen, Kontturi, Ikkala, & Gray, 2012; Sun et al., 2018; Tang et al., 2017).

CNC films are highly hydrophilic and this property can limit their applications in certain areas. Water sorption of CNC films was found to be similar to that of MFC films (around 25-30 % mass gain), and the water contact angle was around 45° (Belbekhouche et al., 2011). The thickness of CNC ultrathin films changed proportional to the changes in relative humidity. At the point of hydration, each individual CNC in the film became enveloped by a 1 nm thick layer of adsorbed water vapour (Niinivaara, Faustini, Tammelin, & Kontturi, 2015).

To improve the properties of films and to modify their interaction with water, the cellulose in CNC films is usually cross-linked during or after casting. In chemical cross-linking, polymer chains are interconnected by permanent covalent bonds, which results in a brittle product (Peng, Zhai, She, & Gao, 2015; Yang, Zhao, Xu, & Sun, 2013). Chemical cross-linking of cellulose is a well-known reaction in the field of textile finishing and can be carried out in a heterogeneous system with various aldehydes. However, only formaldehyde, glutaraldehyde and gyloxal cross-link successfully the cellulose, resulting in wrinkle recovery cellulosic textiles (Frick & Harper, 1982; Kim & Csiszár, 2005). Commonly used cross-linking agents are amino-aldehyde compounds (such as urea-formaldehyde and melamine formaldehyde) which are widely applied to improve the wearing and easy-care properties of cellulosic textiles.

The cross-linking can be carried out in fully swollen or partially swollen fibres (both are called as wet cross-linking), or in dry state (so-called dry cross-linking). Depending on the accessibility and reactivity of the different cellulose areas, conversion of cellulosic fibres can progress to various degrees. Three different situations are possible in the reactions: (1) formation of one covalent bond between the cross-linker and a cellulose chain; (2) formation of at least two covalent bonds between the cross-linker and a cellulose chain (intra-chain linkage); (3) formation of at least two covalent bonds between the cross-linker and two cellulose chains (cross-linking). All of these reactions affect the properties of cellulosic substrates in a greater or lesser degree. Cross-linking has the most significant and distinctive effects (Krässig, 1993; Rouette, 2002). In optimal conditions, the amino-aldehyde based pre-polymers mixed with cellulose lead to composite formation (Devallencourt, Saiter, & Capitaine, 2000).

Aldehyde-aided cross-linking was also used in the preparation of nanocellulose films with advanced properties. Nanocomposite films of microfibrillated cellulose (MFC) and melamine formaldehyde (MF) were semi-transparent, stiff and brittle, and their density increased with increasing MF content (Henriksson & Berglund, 2007). Moisture sorption of the MFC/MF films was lower than that of the neat MFC films, due to the interaction between the resin and the hydroxyl groups of the cellulose surface, which left fewer hydroxyl groups accessible for water molecules. The maximum of Young-modulus, 19.3 GPa was measured for the MFC/MF nanocomposite films. Besides cross-linking, only the introduction of a cross-linker to nanocellulose can also enhance the water repellence of nanocellulose films by filling the pores in it and reducing polarity. Improvements in the mechanical properties of films were also achieved by increasing the water repellence, since water itself acts as a plasticizer in nanocellulose films (Henriksson & Berglund, 2007).

Extensive work has been done on using cross-linking agents different from aldehydes. Thermo-responsive and water-responsive shape-memory polymer nanocomposites were developed by chemically cross-linking cellulose nanocrystals with polycaprolactone (PCL) and polyethylene glycol (Liu, Li, Yang, Zheng, & Zhou, 2015). Since PCL is hydrophobic, it may be used to develop water repellent CNC composites. As the ratio of nanocellulose to PCL decreased, the water repellence of PCL-nanocellulose nanocomposites increased (Si, Cui, Wang, Liu, & Liu, 2016). Poly(acrylic acid) was used as a cross-linking agent in a poly(vinyl alcohol)/CNC nanocomposite. The formation of ester linkages between poly(vinyl alcohol) and CNC resulted in a highly networked structure and improved mechanical properties (Pakzad, Simonsen, & Yassar, 2012). Cross-linking of nanocellulose with citric acid has also been studied (Quellmalz & Mihranyan, 2015). For other biopolymers such as polyhydroxyalkanoates, cross-linking was also beneficial and a significant improvement in the mechanical properties and water resistance of composites was achieved (Raza, Riaz, & Banat, 2017).

In spite of the fact that amino-aldehyde based compounds are the most frequently used cross-linking agents of cellulose and they are widely applied in the field of finishing of cellulosic textiles, very little is known about their use in cross-linking of nanocrystalline cellulose. Thus the goal of our study was to prepare cellulose nanocrystal/amino-aldehyde (CNC/AA) nanocomposite films, to demonstrate the effect of wet cross-linking of cellulose on the structure and properties of nanocrystalline cellulose-based thin films, and to evaluate the interaction of films with water as a function of cross-linking. Cellulose nanocrystals were extracted from bleached cotton and flax fibres by sulphuric acid hydrolysis. Two plasticizers (sorbitol and glycerol) were used for casting a series of films with an amino-aldehyde (AA) based cross-linking agent applied in a wide range of concentrations. The results proved that the properties of CNC films can be enhanced and tuned by the amino-aldehyde based cross-linking of cellulose.

2. Experimental

2.1 Preparation of cellulose nanocrystals

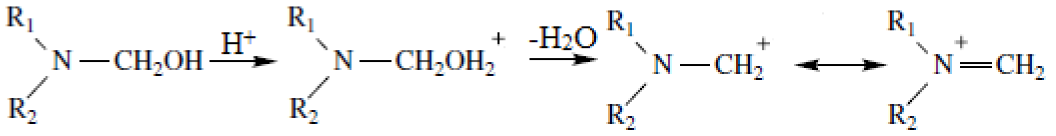
CNCs were prepared from bleached cotton and flax plain-weave fabrics (110 g/m^2 and 165 g/m^2, respectively) provided by Pannon-Flax Linen Weaving Co. (Hungary) and used without any further wet treatment. The nanocrystals were denoted as cotton-CNC and flax-CNC, depending on the source of cellulose. The fabrics were ground using a ball mill (Mixer Mill MM400, Retsch GmbH, Germany), then 10.0 g of the fine powders were hydrolyzed with 64 wt % sulphuric acid (acid to fibre ratio: 8.75 ml/g) at 45 °C for 25 min (Hamad & Hu, 2010). Subsequent to the post-treatments (washing, centrifugation and dialysis), the total volume of the stock suspensions was subjected to ultrasonication for 10 min using an ultrasonic horn type reactor (Vibra-Cell VCX500, Sonics & Materials, Inc. CT, USA) at 60 % amplitude with a driving frequency of 20 kHz (Csiszar, Kalic, Kobol, & Ferreira, 2016). The dry solid content of the suspension was determined by drying (at 80 °C) and weighing 2 ml of the suspension. Yield of CNC calculated as a percentage of the initial weight of the bleached fibres was in the range of 41-43 %. The final aqueous suspensions contained 2-3 weight % of CNCs.

2.2 Preparation of films from the CNC suspensions

Rectangular films were cast from the aqueous suspension of CNCs on the surface of a polypropylene plastic sheet, and their water content was allowed to evaporate at room temperature for about 2 days. In order to overcome the brittle nature of the CNC films, two different plasticizers, namely sorbitol and glycerol were added in 20 % concentration (Csiszár & Nagy, 2017). These polyhydroxy compounds were already successfully applied as plasticizers for thermoplastic starch films (Mathew & Dufresne, 2002).

For the cross-linking of cellulose nanocrystals, an amino-aldehyde based, water soluble cross-linking agent (dimethylol-dihydroxy-ethylene-urea) with an acidic catalyst (trade names: Reaknitt B-FV and Reaknitt Catalyst FV, respectively, received from Bezema AG, Switzerland), recommended for wet cross-linking of cellulosic textiles, were added in different percentages (0, 2.5, 5, 10, 20, 30, 50 % and 0, 0.75, 1.5, 3.3, 6.6, 10, 16.7 %, respectively) on a dry CNC basis to the CNC suspensions before casting. Both the cross-linking agent and the catalyst were commercialized in water as solvent medium. The cross-linking reaction of cellulose took place in the presence of the applied catalyst for about 2 days at room temperature. The thickness of films was in the range of 31-44 μm and slightly increased with increasing the concentration of the cross-linking agent.

The chemical reaction between the amino-aldehyde based cross-linking agents and the hydroxyl groups of cellulose usually takes place with addition of acidic catalyst, which acts as a reaction trigger and accelerator. Acidic catalyst breaks the carbon-oxygen linkage in the N-methylol group of the AA-based cross-linker with discharging of water (equation 1) and then catalyses the reaction with a hydroxyl group of cellulose (equation 2) (Rouette, 2002).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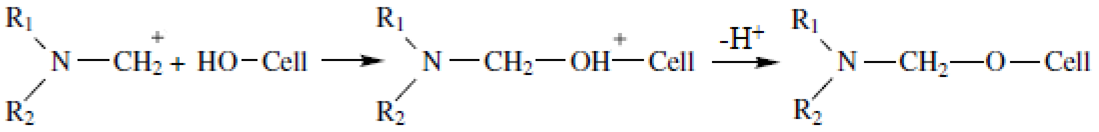
(2)

Conditioning and determining the physical and mechanical properties of the detached films were carried out in a test laboratory where the temperature and humidity were controlled to 23 °C and 55 %, respectively. Since cotton-CNC and flax-CNC films containing either sorbitol or glycerol plasticizers and an amino-aldehyde based cross-linking agent were produced in a relatively wide composition range, films with selected compositions were only investigated in some of the experiments. Furthermore, the films prepared with 50 % cross-linking agent content were characterized exclusively by tensile properties in order to find out whether the tensile strength was a maximum or not at a cross-linking agent concentration of 30 %.

2.3 Characterization of CNC films

From the suspensions, transparent and smooth thin films were cast. Transparency was characterized by the transmittance values measured at 600 nm using a Unicam UV 500 (USA) spectrophotometer. For measuring the haze, films were tested by a Color Quest XE (HunterLab, Reston, USA) spectrophotometer. Haze specifies the percentage of transmitted light that while passing through the specimen, deviates from the incident beam by more than 2.5 ° (Wang, Kamal, & Rey, 2001).

Morphology of the films was characterized by scanning electron microscopy (SEM) using a JEOL JSM 6380 LA equipment. SEM micrographs were taken of the fracture surface of films which were frozen in liquid nitrogen and subsequently broken. For determining the density of films, the weight of 13 specimens from each of the films in different series as well as their area and thickness were measured. Then, for the determination of film porosity the theoretical pore-free density of films was calculated from the density of film components weighted by their mass fraction. Density values of 1.57, 1.49, 1.26 and 1.4 g/cm^3 were used for the CNCs, sorbitol, glycerol and the amino-aldehyde based cross-linker, respectively. In the calculation, the density of air was neglected (Henriksson & Berglund, 2007). The following formula was used for the calculation of porosity:

$$\text{Porosity (\%)} = (\text{theoretical density} - \text{measured density})/(\text{theoretical density})\times 100 \qquad (3)$$

Density and porosity data were used for statistical analysis, where the univariate analysis of variance (ANOVA) was applied. Parameters of the fitted trend-lines were calculated by regression analysis. Details of the statistical tests are included in the Supporting Information.

Contact angles were measured at 23 °C and 55 % relative humidity using a Rame-Hart contact angle goniometer (USA) with a camera and a drop image standard software of DT-Acquire. Liquid drops of 20 μl were deposited on each film and the image of drops was captured immediately by the camera. The values reported are the average of contact angles of at least 5 drops for each sample. To calculate the surface energy of the CNC films, contact angle measurement was carried out with two liquid probes: distilled water and diiodomethane (Sigma Aldrich, 99%); and from the equilibrium contact angle data the surface free energy was calculated by the Owens-Wendt formula (Owens & Wendt, 1969):

$$\gamma_{LV}(cos\theta + 1) = 2\left(\gamma_{LV}^{d}\gamma_{SV}^{d}\right)^{1/2} + 2\left(\gamma_{LV}^{p}\gamma_{SV}^{p}\right)^{1/2} \qquad (4)$$

where γ_{LV}, $\gamma_{LV}{}^{d}$ and $\gamma_{LV}{}^{p}$ are the surface tension of the liquid and that of its dispersion and polar components, respectively, used in the measurements. The values of γ_{LV}, $\gamma_{LV}{}^{d}$ and $\gamma_{LV}{}^{p}$ used for the calculations are 72.8, 21.8 and 51.0 mJ/m^2 for distilled water, and 51.0, 51.0 and 0 mJ/m^2 for diiodomethane. $\gamma_{SV}{}^{d}$ and $\gamma_{SV}{}^{p}$ are the dispersion and polar components of the surface free energy of films, respectively. The total surface free energy of the films was calculated by the following equation:

$$\gamma_{S}^{total} = \gamma_{SV}^{d} + \gamma_{SV}^{p} \qquad (5)$$

Moisture regain (based on the dry weight of films) at 55 % relative humidity was determined using a Denver Instrument IR-35 (USA) moisture analyzer. Two sinking tests were developed for characterising the swelling behaviour of CNC films in liquid water. (1) In the dynamic sinking test, a film sample (1×1 cm) was laid gently onto the surface of distilled water (50 ml) under orbital shaking at 100 rpm (Boeco OS 20, Germany) at room temperature, and the elapsed time for the complete immersion of the film (if any) was recorded. (2) In the static sinking test the measurement introduced above was carried out but without shaking and for 24 hours. The extent of swelling was characterized by measuring the water uptake of films. After floating or immersion for 24 hours, the excess water was removed from the surface of samples and the mass was measured. Water uptake as a percentage of dry weight (weight of water/initial dry weight of the film) was calculated. Furthermore, each of the films from the static sinking test was dried and the percentage weight loss of the initial dry weight of films was also calculated in order to characterize the delamination of nanocrystals and/or dissolution of components in the nanocomposite films (if any) occurring during the 24-hour test.

The crystalline structure of cellulose in films plasticized with both plasticizers and prepared with or without 10 or 30 % cross-linking agent content was characterized by X-ray diffraction (XRD) using a Philips PW 1710/PW 1820 diffractometer at 2θ=4-40°. To define the crystallinity index (CrI), the following equation was used:

$$\mathrm{CrI}\ (\%) = (1 - I_{AM}/I_{200}) \times 100 \qquad (6)$$

where I_{AM} denotes the intensity of diffraction at 2θ=18°, and I_{200} represents the maximum intensity of the *200* lattice diffractions at 2θ=22.7° (Segal, Creely, Martin, & Conrad, 1959).

Mechanical properties were examined using an Instron 5566 tensile tester (USA) equipped with a 500 N load cell. At least ten specimens with the size of 7×50 mm were cut from each of the films in different series. They were tested at 10 mm/min cross-head speed and with 20 mm span length. Linear trend lines were fitted to the initial steep sections of typical stress strain curves of films, in order to determine the Young's modulus of films (He et al., 2016).

3. Results

3.1 Transparency and haziness

Smooth and transparent films with a thickness of c.a. 40 μm were cast from the aqueous suspensions of cellulose nanocrystals, and then the water content was evaporated. Besides plasticizers (i.e. glycerol and sorbitol), different amount of an amino-aldehyde cross-linker was added to the suspension in order to investigate the effect of wet cross-linking on the structure and properties of the cotton-CNC and flax-CNC films. UV-vis spectra proved that none of the films has significant absorbance in the wavelength range of visible light (Table 1), and they are transparent and colourless. However, there are some differences in the transparency of films. The flax-CNC films and the films plasticized with glycerol are less transparent than the cotton-CNC and the sorbitol plasticized films, respectively. Also, when adding cross-linking agent, the transmittance values at 600 nm are slightly increasing.

Table 1

Transmittance and crystallinity index of cotton-CNC and flax-CNC films plasticized with sorbitol or glycerol and prepared with different amount of amino-aldehyde based cross-linking agent.

Characteristics	Source of cellulose	Type of plasticizer	Concentration of cross-linking agent (%)					
			0	2.5	5	10	20	30
Transmittance (%)[a]	Cotton	Sorbitol	73	80	82	83	83	83
		Glycerol	74	79	82	81	78	80
	Flax	Sorbitol	72	75	77	79	79	80
		Glycerol	70	72	73	78	75	74
Crystallinity index (%)[b,c]	Cotton	Sorbitol	93.6	-[d]	-	93.3	-	91.7
		Glycerol	93.3	-	-	88.0	-	87.3
	Flax	Sorbitol	89.7	-	-	85.4	-	85.2
		Glycerol	88.4	-	-	83.6	-	83.5

[a] At 600 nm

[b] Determined by XRD.

[c] Crystallinity of the cellulose sources, namely the ground bleached cotton and flax: 75.9 % and 64.8 %, respectively (Csiszár & Nagy, 2017).

[d] - Not determined.

Haze-index data correlate well with the transmittance values and reveal in general that cotton-CNC films are less hazy (Fig. 1a) than the flax-CNC films (Fig. 1b), and the haze-indices are in the range of 8-20 % and 14-27 %, respectively. Moreover, films plasticized with sorbitol show lower haze-index (8-23 %) than those plasticized with glycerol (12-27 %).

Thus, the flax-CNC films plasticized by glycerol show the highest values of haze-index. However, they are still transparent.

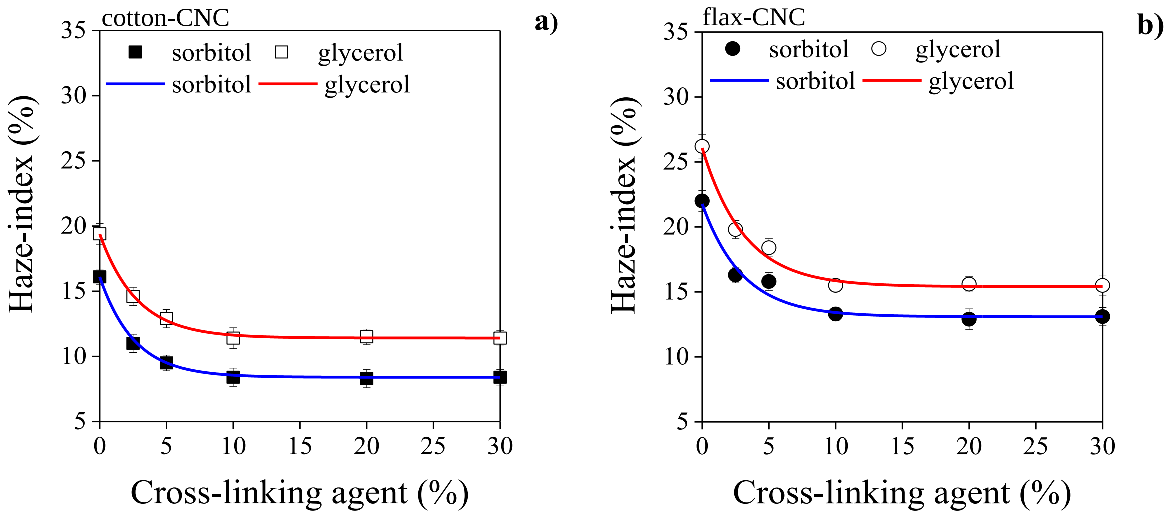

Fig. 1. Haze-index of cotton-CNC (a) and flax-CNC (b) films, plasticized with sorbitol or glycerol, as a function of amino-aldehyde based cross-linker concentration.

Concerning the effect of cross-linking agent on the haziness of films, it is obvious that when the AA cross-linking agent concentration increases, the haze-index first decreases and then levels off at 10 % cross-linking agent content (Fig. 1). The tendency and shape of curves are similar for each series of films, however, the minimum values are different for each. The lowest haze-index is around 8 and 12 % for cotton-CNC films and 13 and 16 % for flax-CNC films plasticized with sorbitol and glycerol, respectively. Furthermore, the addition of cross-linking agent leads to formation of films with very smooth surface compared to the structure of other surfaces. This can also influence haziness, since a rougher surface deflects more light than a smoother one (Roy Choudhury, 2014).

3.2 Morphology

Scanning electron micrographs were taken to characterize the morphology of CNC films by examining the surfaces fractured at the boiling point of liquid nitrogen. The effects of cellulose source (cotton, flax), type of plasticizer (sorbitol, glycerol) and the amount of amino-aldehyde cross-linking agent were examined. The scanning electron micrographs of plasticized films from different sources confirmed our earlier observations that neither the source of cellulose nor the type of plasticizer affect significantly the inner morphology and structure of CNC films (Csiszár & Nagy, 2017). Adding 30 % cross-linking agent to the CNC suspension before film casting, however, leads to a slightly rougher fractured surface, as it is demonstrated for flax-CNC films in Fig. 2. Consequently, films with cross-linking agent have a slightly tougher structure, which presumably occurs because of cross-linked nanocrystals. Researchers examined SEM images of CNC dry film cross sections and found that cellulose nanocrystals exhibit a self-assembled, closely packed layer-by-layer arrangement in dry films (Abraham et al., 2016; Csiszár & Nagy, 2017), which can be seen also in the SEM images of Fig. 2. This phenomenon was explained by the liquid crystalline properties and anti-parallel crystalline arrangement of cellulose Iβ structure, which was proven by ^{13}C-NMR spectroscopy (Larsson, Hult, Wickholm, Pettersson, & Iversen, 1999).

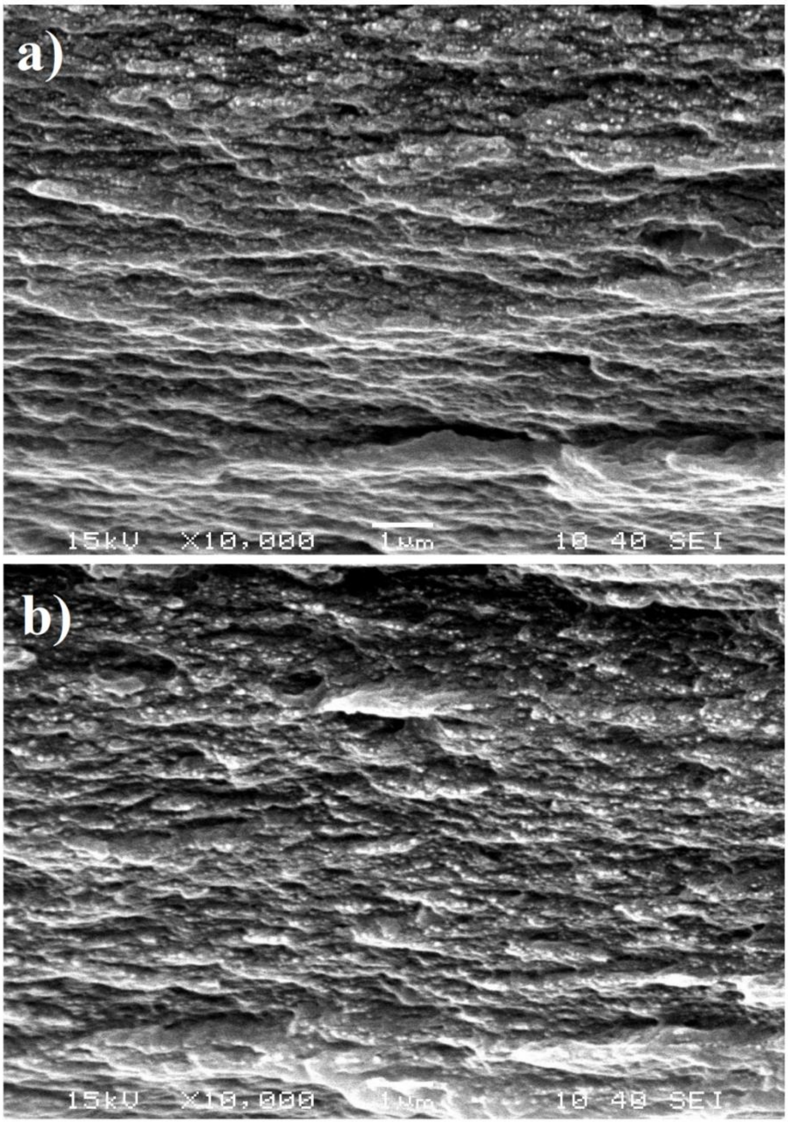

Fig. 2. Scanning electron photomicrographs of the fractured surface of flax-CNC films: (a) plasticized with 20 % glycerol; (b) plasticized with 20 % glycerol and cross-linked with 30 % amino-aldehyde based cross-linking agent.

Changes in morphology of CNC-nanocomposite films were further characterized by measuring density and porosity values. Density data of the sorbitol plasticized cotton-CNC films (Fig. 3a) reveal that by increasing the concentration of cross-linking agent to 20 %, density grows from 1.30 ± 0.04 to 1.36 ± 0.03 g/cm^3, as AA fills the pores between nanocrystals. By further increasing the cross-linking agent content from 20 to 30 %, the density values slightly decrease after passing the maximum reached at about 20 %. This is accounted for the lower density of cross-linking agent (1.4 g/cm^3) compared to that of cellulose nanocrystals (1.57 g/cm^3). Films plasticized by glycerol and made from flax-CNC follow similar trends, but differences are observed mainly between the values of cotton-CNC and flax CNC films (Figs. 3a and b). Density of MFC films (around 1.34 g/cm^3) (Henriksson & Berglund, 2007) was found to be similar to that of CNC films.

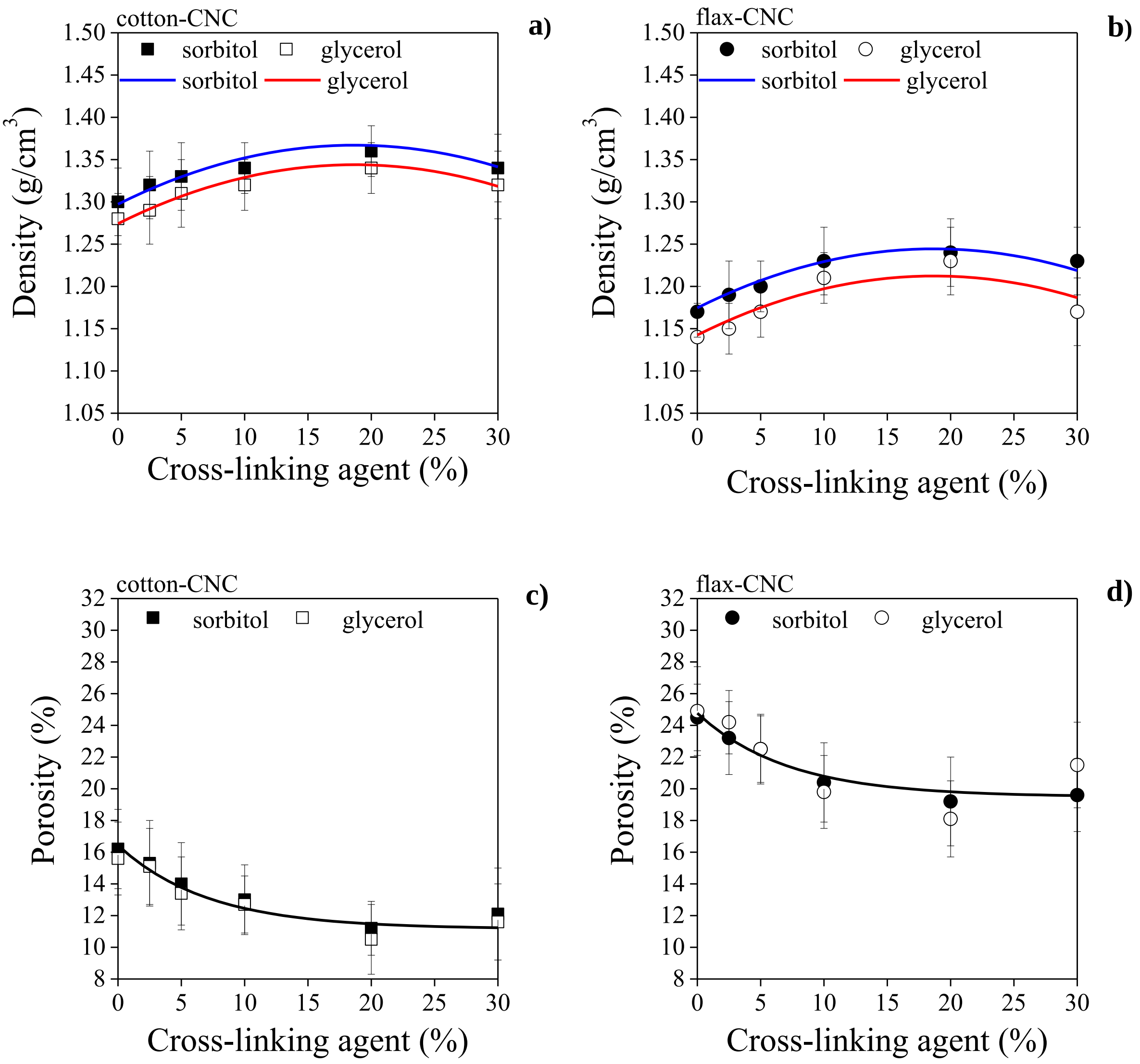

Fig. 3. Density (a, b) and porosity (c, d) of CNC films from cotton (a, c) and flax (b, c), plasticized with sorbitol or glycerol, as a function of amino-aldehyde based cross-linker concentration.

Sorbitol plasticized films show higher density than glycerol plasticized ones. Moreover, cotton-CNC films are denser than flax-CNC films (Figs. 3a and b). Results fit with an earlier study on plasticized CNC films (Csiszár & Nagy, 2017). It should be mentioned that the standard deviation of each sample is notable. However, statistical analysis showed that cellulose source, plasticizer type and also the amount of cross-linking agent significantly affects the density values of films ($p<0.05$). An empirically selected quadratic polynomial correlation was fitted in the graph of density versus the amount of cross-linking agent, and maximum density is reached at approximately 20 % cross-linking agent content. Analysis of variance indicated that there is no significant difference between the shapes of the fitted curves (Table S1 and S2, Supplementary Material).

Porosity of films was also defined (Henriksson & Berglund, 2007). The difference between porosity of cotton- and flax-CNC films could be explained by the higher chance of aggregation for flax-CNC films, which was proven earlier (Csiszár & Nagy, 2017). Thus, cotton-CNC films are denser and less porous than flax-CNC films, containing more aggregated regions. Statistical analysis showed that cellulose source significantly affects the porosity of films ($p<0.05$). However, the effect of plasticizer type is not significant. An empirically selected exponentially decaying trend line was fitted in the graph of porosity versus the amount of cross-linking agent. Fitted curves for sorbitol and glycerol plasticized cotton- or flax-CNC results are joint, because of the insignificant effect of plasticizer type on film porosity. Analysis of variance showed that there is no significant difference between the shape of the fitted curves (Table S3 and S4 in Supplementary Material). In a previous study, similar results were presented concerning the effect of cellulose source and plasticizer on the porosity of CNC films (Csiszár & Nagy, 2017). When increasing the amount of cross-linking agent, porosity values decrease: from around 16 to 12, and from 25 to 21 % for cotton- and flax-CNC films, respectively (Figs. 3c and d). This is caused by the cross-linking agent that fills the porous parts of CNC films. Minimum porosity is reached at c.a. 20 % cross-linking agent content, in all four groups. Thus, porosity can be adjusted by setting the cross-linker amount. Less porous structure adsorbs less water, which phenomenon was examined henceforward.

The crystallinity of cellulose in some compositions of CNC films (prepared with both plasticizers at 0, 10 and 30 % AA content) was also characterized by XRD (Table 1). While in the original cotton and flax ground fibres the crystallinity of cellulose was 75.9 % and 64.8 %, respectively, the crystallinity in CNC films is significantly higher, since the acidic hydrolysis removed the non-crystalline constituents from the fibres. The values range from 83.5 % to 93.6 % and depend slightly on both the cellulose source and the type of plasticizers. This means that the crystallinity of flax CNC-films and films plasticized with glycerol is slightly smaller compared to the cotton CNC-films and films plasticized with sorbitol, respectively. Furthermore, the crystallinity slightly decreases with the increasing cross-linking agent content of films. The lower crystallinity can be explained by the smaller lateral dimension of the fibrillar units in nanocrystals, which was created by interfibrillar swelling (Krässig, 1993). Swelling can disrupt the naturally existing aggregations of nanocrystals and increases the accessible surface of particles. The greater the reactive surface is, the smaller the lateral dimensions of the nanocrystals are. Consequently, the smaller lateral dimensions involve an increased interaction with the cross-linking agent and result in a more diffuse equatorial X-ray diffraction. Since flax-CNC has a higher aggregation ability, and glycerol is a better plasticizer than sorbitol (Csiszár & Nagy, 2017), the decrease in crystallinity is more pronounced in the cross-linked flax-CNC films plasticized with glycerol. More significant decrease in crystallinity of polyhydroxybutyrate (PHB) was observed due to the presence of residual amorphous PVA used as an emulsifier in the formation of PHB nanospheres (Abid, Raza, & Rehman, 2016).

3.3 Interaction with water

In the next experiments the interaction of CNC films with liquid water and water vapour was investigated. First, the surface energetics of films was characterized and the dispersion (γ_{SV}^{d}) and polar (γ_{SV}^{p}) components of surface free energy were determined by contact angle measurements against water and diiodomethane. All cotton- and flax-CNC neat films display small water contact angles of about 16 °, indicating good wetting property and high hydrophilicity. Water contact angles of the neat cotton and flax films increase significantly from about 16 to 70 °, while the contact angles against diiodomethane decreases only by about 30-40 %, with the increasing amount of cross-linking agent in the range of 0-30 % (Table 2). Based on the contact angle data, the surface free energy of CNC films was calculated. Results prove that the total surface free energy values decrease from 74-76 to 53-54 mJ/m^2 when increasing the amount of cross-linking agent (Table 2). However, the total surface free energy values hardly differ for the films derived from different cellulose sources and cast with different plasticizers. For neat CNC films prepared by spin-coating, the equilibrium water and diiodomethane contact of angles of 23.7 and 27.8 °, respectively, were measured, and a slightly lower surface free energy (58 mJ/m^2) was calculated (Aulin et al., 2009).

Changes in the dispersion (γ_{SV}^{d}) and polar (γ_{SV}^{p}) components of surface free energy as a function of concentration of cross-linking agent are presented in Figs. 4 a and b for cotton-CNC and flax-CNC films, respectively. The shape of the relevant curves appears to be roughly the same for all films, indicating that only the amount of cross-linking agent affects the surface energetic. By increasing the concentration of cross-linking agent, the dispersion component of the surface free energy (γ_{SV}^{d}) increases slightly (from about 42 to 47 mJ/m^2), while the polar component (γ_{SV}^{p}) decreases drastically (from about 33 to 5 mJ/m^2). Since the γ_{SV}^{d} values of the surface free energy are larger than the γ_{SV}^{p} ones for both the neat and composite films, the surface of CNC films is basic in character and has an electron donor property.

Table 2

Contact angles against water and diiodomethane, and surface free energy of cotton-CNC and flax-CNC films, plasticized with sorbitol or glycerol and prepared with different amount of amino-aldehyde based cross-linking agent.

Characteristics	Source of cellulose	Type of plasticizer	Concentration of cross-linking agent (%)					
			0	2.5	5	10	20	30
Water contact angle (°)	Cotton	Sorbitol	17 ± 2	20 ± 3	25 ± 3	33 ± 2	37 ± 1	70 ± 4
		Glycerol	16 ± 4	18 ± 1	23 ± 2	31 ± 3	33 ± 3	66 ± 2
	Flax	Sorbitol	16 ± 3	21 ± 4	28 ± 3	31 ± 4	36 ± 5	70 ± 1
		Glycerol	17 ± 2	18 ± 2	29 ± 1	32 ± 3	35 ± 2	68 ± 2
Diiodomethane contact angle (°)	Cotton	Sorbitol	39 ± 3	34 ± 3	32 ± 2	28 ± 2	26 ± 2	22 ± 1
		Glycerol	31 ± 2	30 ± 3	26 ± 2	25 ± 2	24 ± 2	22 ± 3
	Flax	Sorbitol	33 ± 3	28 ± 1	26 ± 3	25 ± 3	24 ± 3	22 ± 2
		Glycerol	29 ± 2	28 ± 2	24 ± 2	24 ± 3	23 ± 2	21 ± 3
Surface free energy (mJ/m^2)	Cotton	Sorbitol	74	74	73	70	68	53
		Glycerol	76	76	74	71	71	54
	Flax	Sorbitol	76	75	73	71	69	53
		Glycerol	76	76	72	71	70	54

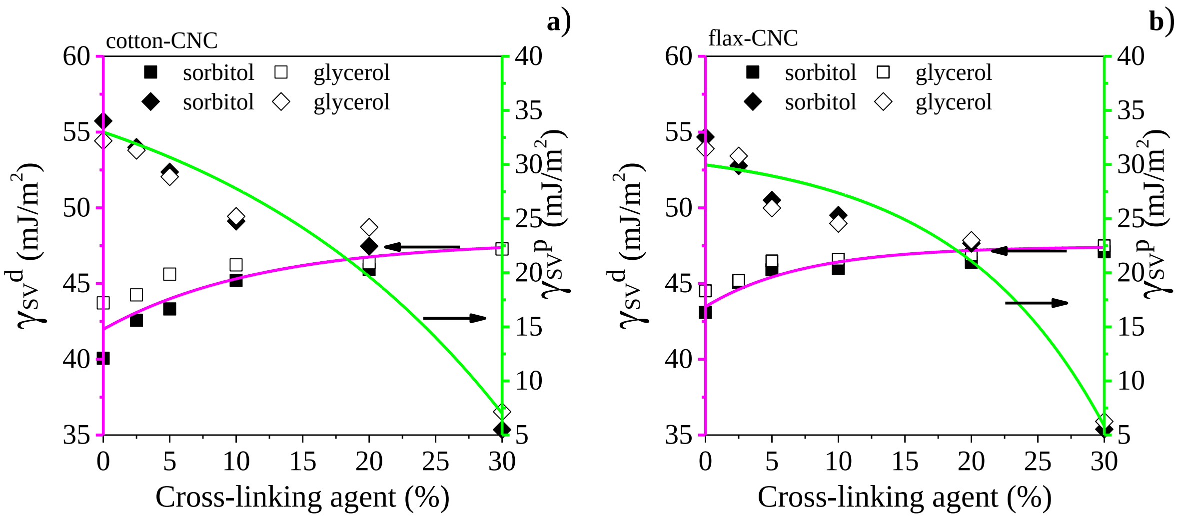

Fig. 4. Dispersion ($\gamma_{SV}{}^{d}$) and polar components ($\gamma_{SV}{}^{p}$) of surface free energy of cotton-CNC (a) and flax-CNC (b) films, plasticized with sorbitol or glycerol, as a function of amino-aldehyde based cross-linker concentration.

Moisture regain is related to the accessible internal surface in the conditioned cotton fibre (Bertoniere & King, 1992; Krässig, 1993). Moisture regain at 55 % relative humidity reveals that CNC films with more cross-linking agent absorb less water. Data in Figs. 5a and b decrease gradually from about 4 to 2 %. The deposition of cross-linking agent on the surface of cellulose nanocrystals and between the nanocrystals decreases the porosity of films (Figs. 3c and d) and also the available internal cellulose surfaces for water vapour sorption, resulting in a lower amount of absorbed water (Figs. 5a and b). There is no difference in moisture regain of cotton-CNC and flax-CNC films, thus the source of cellulose and the type of plasticizer do not affect the moisture regain values, whereas their dependence on the concentration of AA cross-linker is obvious. The shape of curves in Figs 5a and b is similar, indicating that each film with the same cross-linking agent content absorbs water vapour at approximately the same rate. Due to the cross-linking reaction at higher concentrations, the amount of accessible hydroxyl groups on the surface of nanocrystals decreases and, as a result, the interaction of cellulose with water is hindered. Thus, cross-linking suppresses the water sorption of CNC films, and the moisture regain data suggest a decrease in the internal surface in the conditioned CNC films.

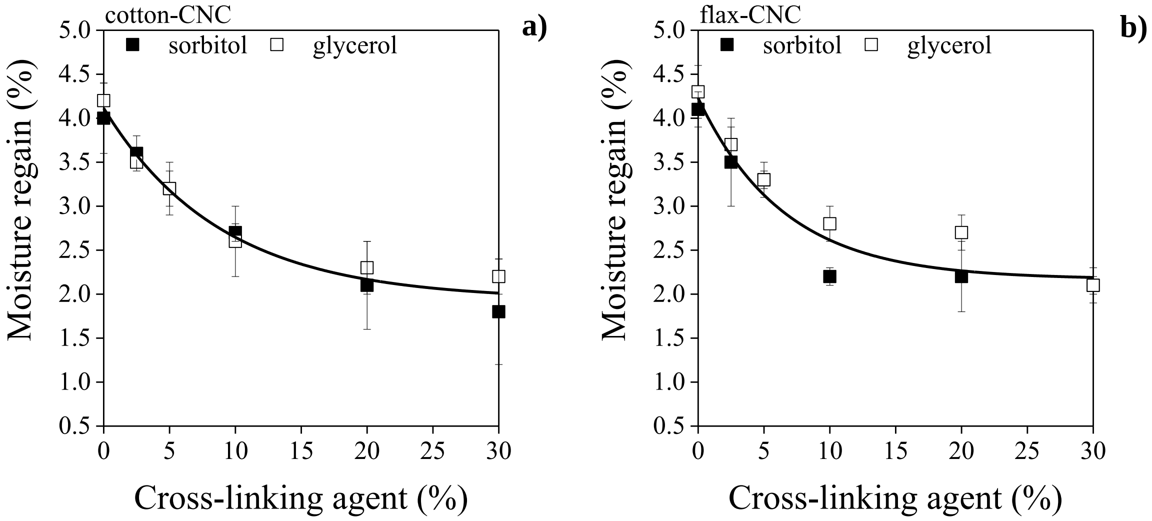

Fig. 5. Moisture regain of cotton-CNC (a) and flax-CNC films (b), plasticized with sorbitol or glycerol, as a function of amino-aldehyde based cross-linker concentration.

Results of dynamic sinking test (Fig. 6a) reveal that progressive cross-linking causes an increase in sinking time. Immersion of films laid onto the surface of distilled water depends largely on the surface energetic and morphology of films. All changes in these parameters that occurred during cross-linking affect the sinking behaviour of films. Sinking time as a function of the amount of cross-linker shows a general growing trend, which is evident from the data of all four series of films (Fig. 6a). Sinking time data were higher for cotton-CNC films (11-30 min) than for flax-CNC films (4-17 min), which can be attributed to the higher porosity of the flax-CNC films (Fig. 3 d). Sorbitol plasticized films show higher values (6-30 min) than films made with glycerol (4-22 min). The highest sinking time (30 min) was measured for the sorbitol plasticized cotton-CNC film with 20 % cross-linking agent content. It has to be mentioned that Fig. 6a does not show the data of films with 30 % cross-linking agent, since they do not immerse at all during the 2-hour dynamic test.

Furthermore, it was also observed that the treatment in water under orbital shaking disintegrates the films at lower concentrations of cross-linking agent (0, 2, 5 and 10 %) into cellulose nanocrystals and their aggregates during the course of two hours. However, cross-linking agent with a concentration of 20 % or more prevents delamination and preserves the original shape of films. At higher concentrations of a cross-linker, besides the filling of pores, another process, i.e. cross-linking also occurs (Frick & Harper, 1982) resulting in a water resistant CNC film. For spin-coated films, a heat-treatment at 90 °C for 4 hours was applied to avoid delamination upon exposure to an aqueous solution (Aulin et al., 2009).

To investigate further the interaction of films with water, we developed a method to measure the water uptake of films. For textiles and fibres, the method of water of imbibition provides similar (but not identical) information on water holding capacity and reflects the internal volume of the fibres in the water-swollen state (Bertoniere, Martin, Florine, & Rowland, 1972). For films, the values of water uptake derived from the static sinking test can be related to the internal volume of cellulose in the swollen state and can also be used for characterizing the rate of swelling. From the results of water uptake plotted in Fig. 6b it appears that maximum swelling occurs at 10 % cross-linking agent concentration, the values are higher for the flax-CNC films (160 and 130 %) than for the cotton-CNC ones (150 and 100 %) and also higher for the glycerol plasticized films than for the sorbitol plasticized ones (160 and 150 % vs. 130 and 100 %, respectively). Results also reveal that with increasing the concentration of cross-linking agent from 10 to 20 % the water uptake decreases abruptly. Then the water uptake levels off at about 20 % cross-linking agent content. This correlates well with the tendencies of film porosity in Figs. 3c and d, since both porosity and water uptake decrease with increasing cross-linking agent content and the minimum values in both are reached at 20 % cross-linking agent content. In addition, the films with 20 and 30 % cross-linker content display similar swelling behaviour, their water uptake is under 10 %, indicating a compact and tightly bound structure.

It is also obvious that when the time of sinking or the water uptake are plotted against cross-linking agent concentration in Figs 6a and b, respectively, the differences between the films tested become much more apparent than in the relationships obtained in the preceding experiments. It means that the extent of properties mentioned here depends not only on the concentration of cross-linking agent, but also on the source of cellulose and the type of plasticizers.

It was observed that films with lower cross-linking agent content (0, 2.5 and 5 %) have ‘disappeared’ during the course of treatment, which may result from the delamination of nanocrystals by a progressive and infinite swelling of films. However, films with a cross-linking agent concentration of 10 % or more retain their shape and besides the water uptake, the dried weight can also be determined. The results in Fig. 6c reveal the weight loss of films at equal cross-linking agent content that occurred over the course of 24 hours is very similar, indicating that neither the source of cellulose nor the type of plasticizer affects the data. Thus, the extent of weight loss depends only on the concentration of cross linking agent. The most water resistant films contain 30 % of cross-linking agent and their weight decreases only by about 5 %. At 10 % of cross-linking agent, however, about the 20 weight % of films is released, which may be attributed to the removal of plasticizer and/or the disruption of the edges of films. Information from swelling experiments gives further evidence about the wet-curing of nanocrystals with an amino-aldehyde based compound.

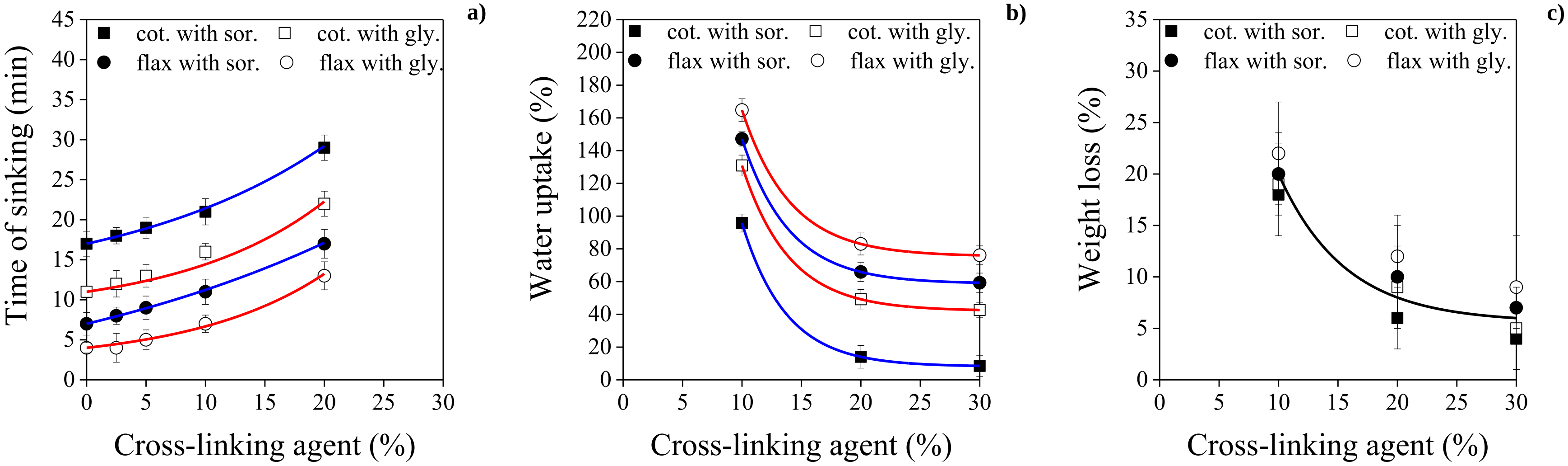

Fig. 6. Results of sinking tests of cotton-CNC and flax-CNC films plasticized with sorbitol or glycerol, as a function of the amount of amino-aldehyde based cross-linking agent. Dynamic sinking test: (a) sinking time as a function of cross-linking agent content (0, 2.5, 5, 10 and 20 %). Static sinking test at 10, 20 and 30 % cross-linking agent content: (b) water uptake as a percentage of dry weight of CNC film by swelling over the course of 24-hours; c) weight loss of CNC films caused by sinking test over the course of 24-hours. Calculation of values (%) in Figs. b and c was based on the initial dry weight of films.

3.4 Mechanical properties of the CNC nanocomposite films

Tensile properties of CNC films were also tested but in a slightly wider concentration range of the cross-linker (0-50 %). Results in Figs 7a and b reveal that the tensile strength of neat films (0 %) increases from about 18-32 MPa to around 40 MPa and then decreases with increasing cross-linking agent concentration. The maximum tensile strength values can be reached at 30 % cross-linker content for all the films tested. The elongation-at-break values also show a maximum (2.5-4 %) at a cross-linking agent concentration of 2.5 % and then decrease sharply. It can be assumed that a small amount of cross-linking agent works also as a plasticizer for nanocellulose (Henriksson & Berglund, 2007). Results in the former chapters proved that a concentration of 2.5-5 % is not enough for building a cross-linked structure between the cellulose nanocrystals. Nevertheless, by penetrating into the connection points between the nanocrystals during the course of a simultaneous casting-wet curing and covalent bonding to the accessible hydroxyl groups of cellulose surfaces, the cross-linking agent can prevent the development of a hydrogen bonding network in CNC films. Since this hydrogen bonded structure is responsible for the stiffness of films, cross-linking agent at low concentrations contributes to slipping of nanocrystals on each other. However, at higher concentrations the stiffness of films is higher and the elongation-at-break values decrease to 0.3-1.2 %. This proves that at higher cross-linking agent concentration (> 5 %) cellulose nanocrystals are cross-linked in CNC films.

The modulus of films was determined from the initial slope of typical stress-strain curves (Table 3). It was found that modulus increases (from 3-6 GPa to 9-11 GPa) with the increasing amount of cross-linking agent in films. The maximum modulus value achieved was higher for cotton-CNC (c.a. 11 GPa) then for flax-CNC (c.a. 9 GPa). The type of plasticizer does not especially affect the values, however, at lower cross-linking agent concentrations, some diversity with respect to modulus can be observed.

Furthermore, the moduli in Table 3 show correlations with the crystallinity indices in Table 1 since films with higher extent of crystallinity tend to have higher modulus. The correlation coefficients were found to be 0.5943, 0.3527 and 0.6489 for the films prepared with 0, 10 and 30 % cross-linking agent, respectively.

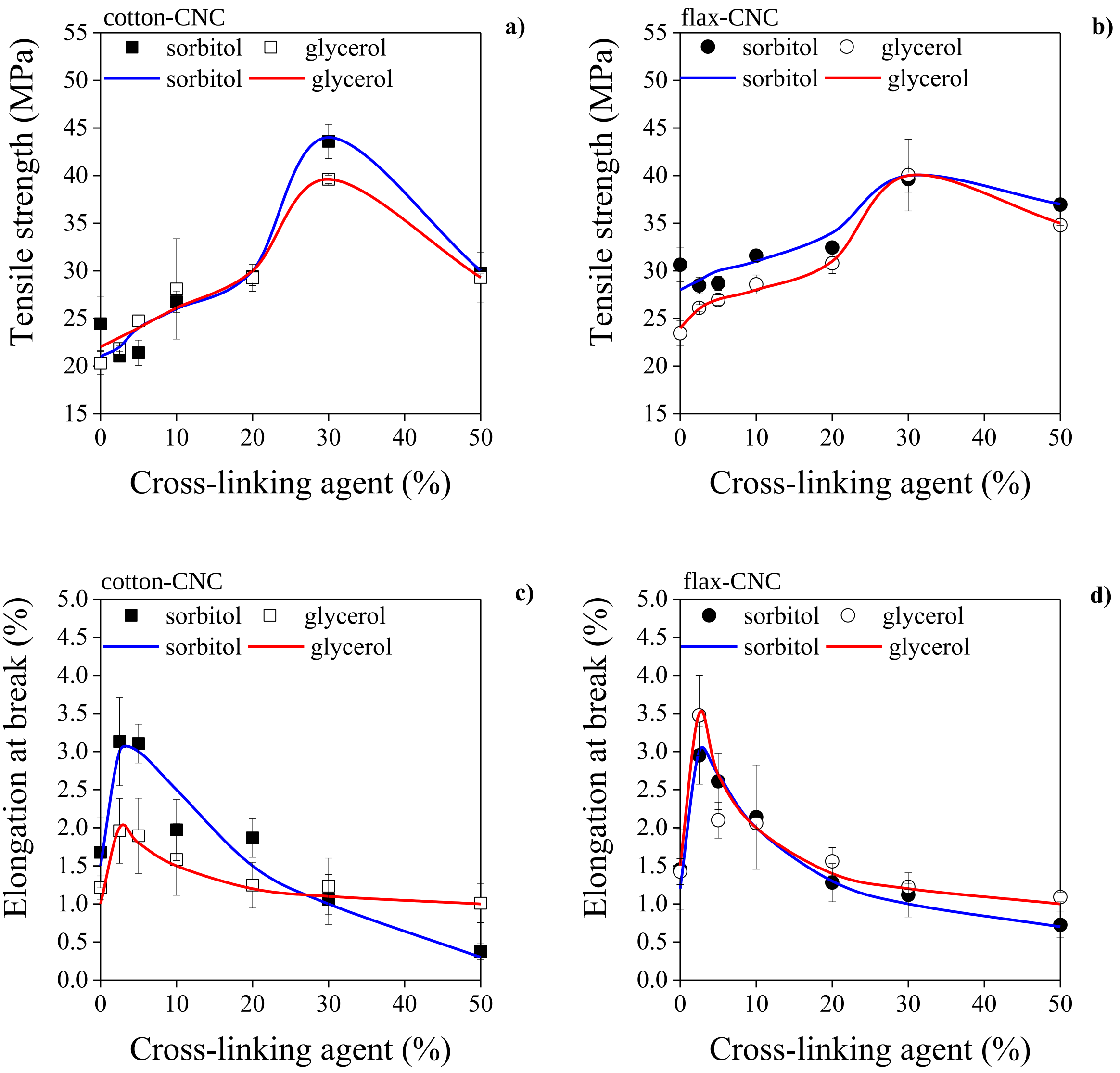

Fig. 7. Tensile strength (a, b) and elongation at break (c, d) of CNC films from cotton (a, c) and flax (b, d), plasticized with sorbitol or glycerol, made with different amount of cross-linker. The uncertainty of data is represented by a 95 % confidence interval.

Table 3

Young's modulus (GPa) of cotton-CNC and flax-CNC films plasticized with sorbitol or glycerol and prepared with different amount of amino-aldehyde based cross-linking agent.

Concentration of cross-linking agent (%)	Source of cellulose			
	Cotton		Flax	
	Type of plasticizer			
	Sorbitol	Glycerol	Sorbitol	Glycerol
0	5.56 ± 0.53	4.19 ± 0.61	5.01 ± 0.45	3.21 ± 0.32
2.5	2.76 ± 0.74	2.23 ± 0.71	3.12 ± 0.39	2.12 ± 0.81
5	3.53 ± 0.55	2.61 ± 0.58	4.03 ± 0.58	2.53 ± 0.74
10	4.89 ± 0.81	4.07 ± 0.72	5.47 ± 0.61	3.51 ± 0.81
20	8.37 ± 0.32	5.61 ± 0.39	6.41 ± 0.76	5.27 ± 0.32
30	9.91 ± 0.81	6.83 ± 0.76	8.72 ± 0.72	7.39 ± 0.55
50	11.22 ± 0.32	10.57 ± 0.45	9.03 ± 0.71	8.52 ± 0.53

The effect of cross-linking of nanocellulose with different reagents was also reported in the scientific literature. When nanopaper was cross-linked by first soaking it in 16 wt % citric acid solution in the presence of 1 wt % sodium hypophosphate (pH 2) overnight and then curing at 160 °C for 10 min in a hot-press, its mechanical properties were not improved in dry state, but the modulus was increased from 5.3 to 8.5 GPa. Furthermore, the wet strength of the cross-linked nanopaper improved significantly and an almost ten-fold increase in the stress to failure value was detected (Quellmalz & Mihranyan, 2015).

4. Discussion

Transparent and smooth nanocomposite films were prepared from cellulose nanocrystals extracted from cotton and flax fibres, with different plasticizers (sorbitol, glycerol) and an amino-aldehyde based cross-linking agent in a wide composition range (0-30 wt %), during the course of a simultaneous casting and wet curing. The effect of cross-linker concentration on the morphology, optical and tensile properties of films was investigated, and the interaction of films with liquid water and water vapour was also characterized by various measurements. Results showed that properties of films were substantially affected by the concentration of cross-linking agent, but were only slightly influenced by the source of cellulose and type of plasticizers.

While the transparency of films was unaffected, the haze-index decreased significantly with the increasing concentration of cross-linker. SEM micrographs revealed that the fractured surface of the cross-liked films became slightly rougher comparing to the neat counterparts. Density increased and porosity decreased when cross-linking occurred, and a maximum density and a minimum porosity were reached at an amino-aldehyde concentration of 20 %. Furthermore, the crystallinity of cellulose in the composite films slightly decreased with the increasing concentration of cross-linking agent. Besides the cross-linking agent content, the source of cellulose and the type of plasticizer had also an effect on the crystallinity.

All cotton- and flax-CNC neat films displayed small water contact angles of about 16 °, indicating good wetting property and high hydrophilicity. Significantly higher water contact angles were measured for the cross linked films (66-70 ° at 30 % cross-linker concentration) and simultaneously a drastic decrease (from about 33 to 5 mJ/m^2) in the polar component (γ_{SV}^p) of surface free energy was calculated. The surface of CNC films is basic in character and has an electron donor property. Cross-liked films with a less porous structure absorbed less water. Moisture regain decreased with the increasing amount of the cross-linking agent, indicating a decrease in the internal surface in the conditioned CNC films. Furthermore, cross-linking suppressed the swelling determined by water uptake, and prevented the delamination of CNC films at a cross-linker concentration of 10 % or higher.

The tensile strength of CNC films first increased from about 18-32 MPa to around 40 MPa and then decreased with increasing cross-linking agent concentration. The maximum tensile strength was measured at 30 % cross-linker content. Elongation-at-break values also reached a maximum (2.5-4 %) at a cross-linking agent concentration of 2.5 %, suggesting that the small amount of cross-linking agent worked as a plasticizer for nanocellulose. All the presented results demonstrated that the structure and properties of CNC films can be modified and tuned by cross-linking with and amino-aldehyde based compound.

5. Conclusions

In the frame of this study, cellulose nanocrystal/amino-aldehyde biocomposite films were prepared and characterized. In the simultaneous casting and wet cross-linking process the nanocellulose particles had enough time for self-ordering and forming a compact three-dimensional layered structure. The cross-linking agent made the interactions of CNC particles stronger and modified the optical and tensile properties as well as the morphology of films. Furthermore, a significant improvement in water resistance was achieved. The effect of the cross-linking agent in the applied concentration range was more significant than that of the cellulose source (cotton or flax) or the type of plasticizers (sorbitol or glycerol).

6. References

Abid, S., Raza, Z. A., & Rehman, A. (2016). Synthesis of poly(3-hydroxybutyrate) nanospheres and deposition thereof into porous thin film. *Materials Research Express*, *3*(10). https://doi.org/10.1088/2053-1591/3/10/105042

Abraham, E., Kam, D., Nevo, Y., Slattegard, R., Rivkin, A., Lapidot, S., & Shoseyov, O. (2016). Highly Modified Cellulose Nanocrystals and Formation of Epoxy-Nanocrystalline Cellulose (CNC) Nanocomposites. *ACS Applied Materials and Interfaces*, *8*(41), 28086–28095. https://doi.org/10.1021/acsami.6b09852

Aulin, C., Ahok, S., Josefsson, P., Nishino, T., Hirose, Y., Österberg, M., & Wågberg, L. (2009). Nanoscale cellulose films with different crystallinities and mesostructures - Their surface properties and interaction with water. *Langmuir*, *25*(13), 7675–7685. https://doi.org/10.1021/la900323n

Belbekhouche, S., Bras, J., Siqueira, G., Chappey, C., Lebrun, L., Khelifi, B., … Dufresne, A. (2011). Water sorption behavior and gas barrier properties of cellulose whiskers and microfibrils films. *Carbohydrate Polymers*, *83*(4), 1740–1748. https://doi.org/10.1016/j.carbpol.2010.10.036

Bertoniere, N. R., & King, W. D. (1992). Pore Structure of Cotton Fabrics Crosslinked with Formaldehyde-Free Reagents. *Textile Research Journal*, *62*(6), 349–356. https://doi.org/10.1177/004051759206200607

Bertoniere, N. R., Martin, L. F., Florine, A. B., & Rowland, S. P. (1972). Alteration of the pore structure of cotton by the wet-fixation durable-press process. *Textile Research Journal*, *42*(12), 734–740.

Csiszar, E., Kalic, P., Kobol, A., & Ferreira, E. D. P. (2016). The effect of low frequency ultrasound on the production and properties of nanocrystalline cellulose suspensions and films. *Ultrasonics Sonochemistry*, *31*, 473–480. https://doi.org/10.1016/j.ultsonch.2016.01.028

Csiszár, E., & Nagy, S. (2017). A comparative study on cellulose nanocrystals extracted from bleached cotton and flax and used for casting films with glycerol and sorbitol plasticisers.

Carbohydrate Polymers, *174*, 740–749. https://doi.org/10.1016/j.carbpol.2017.06.103

Devallencourt, C., Saiter, J. M., & Capitaine, D. (2000). Reactions between melamine formaldehyde resin and cellulose: Influence of pH. *Journal of Applied Polymer Science*, *78*(11), 1884–1896. https://doi.org/10.1002/1097-4628(20001209)78:11<1884::AID-APP60>3.0.CO;2-2

Frick, J. G., & Harper, R. J. (1982). Crosslinking cotton cellulose with aldehydes. *Journal of Applied Polymer Science*. https://doi.org/10.1002/app.1982.070270317

Hamad, W. Y., & Hu, T. Q. (2010). Structure-process-yield interrelations in nanocrystalline cellulose extraction. *Canadian Journal of Chemical Engineering*, *88*(3), 392–402. https://doi.org/10.1002/cjce.20298

He, W., Goudeau, P., Le Bourhis, E., Renault, P. O., Dupré, J. C., Doumalin, P., & Wang, S. (2016). Study on Young's modulus of thin films on Kapton by microtensile testing combined with dual DIC system. *Surface and Coatings Technology*, *308*, 273–279. https://doi.org/10.1016/j.surfcoat.2016.07.114

Henriksson, M., & Berglund, L. A. (2007). Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *Journal of Applied Polymer Science*, *106*(4). https://doi.org/10.1002/app.26946

Kim, E., & Csiszár, E. (2005). Chemical Finishing of Linen and Ramie Fabrics. *Journal of Natural Fibers*, (2:3), 39–52. https://doi.org/10.1300/J395v02n03

Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., & Dorris, A. (2011). Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie - International Edition*, *50*(24), 5438–5466. https://doi.org/10.1002/anie.201001273

Krässig, H. A. (1993). *Cellulose: Structure, accessibility and reactivity*. Gordon and Breach

Science Publishers, Switzerland.

Lagerwall, J. P. F., Schütz, C., Salajkova, M., Noh, J., Hyun Park, J., Scalia, G., & Bergström, L. (2014). Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. *NPG Asia Materials*, *6*(1), 1–12. https://doi.org/10.1038/am.2013.69

Larsson, P. T., Hult, E., Wickholm, K., Pettersson, E., & Iversen, T. (1999). CPrMAS 13 C-NMR spectroscopy applied to structure and interaction studies on cellulose I. *Solid State Nuclear Magnetic Resonance*, *15*, 31–40. https://doi.org/10.1016/S0926-2040(99)00044-2

Liu, Y., Li, Y., Yang, G., Zheng, X., & Zhou, S. (2015). Multi-stimulus-responsive shape-memory polymer nanocomposite network cross-linked by cellulose nanocrystals. *ACS Applied Materials and Interfaces*, *7*(7), 4118–4126. https://doi.org/10.1021/am5081056

Majoinen, J., Kontturi, E., Ikkala, O., & Gray, D. G. (2012). SEM imaging of chiral nematic films cast from cellulose nanocrystal suspensions. *Cellulose*, *19*(5), 1599–1605. https://doi.org/10.1007/s10570-012-9733-1

Mathew, A. P., & Dufresne, A. (2002). Plasticized waxy maize starch: Effect of polyols and relative humidity on material properties. *Biomacromolecules*, *3*(5), 1101–1108. https://doi.org/10.1021/bm020065p

Niinivaara, E., Faustini, M., Tammelin, T., & Kontturi, E. (2015). Water vapor uptake of ultrathin films of biologically derived nanocrystals: Quantitative assessment with quartz crystal microbalance and spectroscopic ellipsometry. *Langmuir*, *31*(44), 12170–12176. https://doi.org/10.1021/acs.langmuir.5b01763

Owens, D. K., & Wendt, R. C. (1969). Estimation of the surface free energy of polymers.

Journal of Applied Polymer Science, *13*(8), 1741–1747. https://doi.org/10.1002/app.1969.070130815

Pakzad, A., Simonsen, J., & Yassar, R. S. (2012). Gradient of nanomechanical properties in the interphase of cellulose nanocrystal composites. *Composites Science and Technology*, *72*(2), 314–319. https://doi.org/10.1016/j.compscitech.2011.11.020

Peng, P., Zhai, M., She, D., & Gao, Y. (2015). Synthesis and characterization of carboxymethyl xylan-g-poly(propylene oxide) and its application in films. *Carbohydrate Polymers*, *133*, 117–125. https://doi.org/10.1016/j.carbpol.2015.07.009

Quellmalz, A., & Mihranyan, A. (2015). Citric Acid Cross-Linked Nanocellulose-Based Paper for Size-Exclusion Nanofiltration. *ACS Biomaterials Science and Engineering*, *1*(4), 271–276. https://doi.org/10.1021/ab500161x

Raza, Z. A., Riaz, S., & Banat, I. M. (2017). Polyhydroxyalkanoates: Properties and chemical modification approaches for their functionalization. *Biotechnology Progress*. https://doi.org/10.1002/btpr.2565

Rouette, H. K. (2002). *Encyclopedia of textile finishing*. Springer, Berlin, Heidelberg.

Roy Choudhury, A. K. (2014). *Principles of Colour and Appearance Measurement*. *Principles of Colour and Appearance Measurement* (Vol. 2). https://doi.org/10.1016/C2014-0-01832-1

Segal, L., Creely, J. J., Martin, A. E., & Conrad, C. M. (1959). An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Textile Research Journal*, *29*(10), 786–794. https://doi.org/10.1177/004051755902901003

Si, J., Cui, Z., Wang, Q., Liu, Q., & Liu, C. (2016). Biomimetic composite scaffolds based on mineralization of hydroxyapatite on electrospun poly(Ɛ-caprolactone)/nanocellulose fibers. *Carbohydrate Polymers, 143,* 270–278. https://doi.org/10.1016/j.carbpol.2016.02.015

Sun, Q., Zhao, X., Wang, D., Dong, J., She, D., & Peng, P. (2018). Preparation and characterization of nanocrystalline cellulose/Eucommia ulmoides gum nanocomposite film. *Carbohydrate Polymers, 181,* 825–832. https://doi.org/10.1016/j.carbpol.2017.11.070

Tang, J., Sisler, J., Grishkewich, N., & Tam, K. C. (2017). Functionalization of cellulose nanocrystals for advanced applications. *Journal of Colloid and Interface Science, 494,* 397–409. https://doi.org/10.1016/j.jcis.2017.01.077

Wang, L. E. I., Kamal, M. R., & Rey, A. D. (2001). Light Transmission and Haze of polyethylene blown thin films. *Polymer Engineering & Science*, *41*(2), 358–372.

Yang, J., Zhao, J. J., Xu, F., & Sun, R. C. (2013). Revealing strong nanocomposite hydrogels reinforced by cellulose nanocrystals: Insight into morphologies and interactions. *ACS Applied Materials and Interfaces,* *5*(24), 12960–12967. https://doi.org/10.1021/am403669n