Heat-induced changes in cellulose nanocrystal/amino-aldehyde biocomposite systems

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Abstract

Cellulose nanocrystals (CNCs) were extracted from natural cellulosic fibres such as bleached cotton and flax with a controlled multi-step sulphuric acid hydrolysis. From the aqueous suspensions of CNCs, the biocomposite films were prepared by casting and evaporation, with an amino-aldehyde (AA) compound in a wide concentration range from 0 to 30%. The AA compound (dimethylol dihydroxy ethylene urea) was considered both as a cross-linker of the CNC and as a matrix polymer for the CNC-reinforced composite system. Two series of films were prepared using different polyols such as sorbitol and glycerol as plasticizers to improve tractability. Heat treatment of the films was performed at elevated temperatures ranging from 140 to 200 °C for 10 min. Results clearly proved that besides temperature, the factors affecting the response of CNC-based nanocomposites to heat treatment were the source of cellulose, the type of plasticizer and the amount of cross-linking agent. Films based on flax–CNC and plasticized with glycerol showed a higher increase in yellowness and a more significant decrease in haze than those derived from cotton–CNC and plasticized with sorbitol, respectively. The cross-linking agent (AA) had a moderating effect on the heat-induced changes of properties. Furthermore, thermal gravimetric analysis (TG) of films revealed that thermal stability of the CNC films improved considerably when AA was added and cross-linking occurred. The increase in $T_{\max}$ was more significant for the flax–CNC films (from about 230 to 290 °C) than for the cotton–CNC ones (from about 250 to 280 °C).

Keywords Cellulose nanocrystals · Nanocomposites · Thermal degradation · Discolouration · Plasticizers · Cross-linking

Introduction

Today's complex composites industry requires sustainable and value-added products that are environmentally efficient. Among the various composite materials, natural fibre-reinforced polymer composites have found great interest. Cellulose is the most important natural polymer, which

is available in a large quantity and represents a renewable resource for different industrial applications. Recently, cellulosic nanomaterials have received much attention in an effort to improve their production, as well as the application especially in green composites including packaging and coating materials. Nanocelluloses are novel forms of cellulose, and each type (i.e. nanofibrillated, nanocrystalline and bacterial) has special properties, including nanoscale dimension, high surface area and crystallinity, high specific strength and modulus, unique appearance and optical properties. These attractive characteristics can be exploited to make new nanocellulose-based or nanocellulose-reinforced composites with improved mechanical and barrier properties [1, 2].

Cellulose nanocrystals (CNCs) can be prepared from different cellulosic materials (like lignocellulose-based biomass, wood, cellulosic fibres, etc.) by removing the amorphous, less ordered cellulose phase with acid hydrolysis. For the efficient extraction of CNCs, a controlled sulphuric acid hydrolysis is the most frequently used method, but other types of hydrolysis reactions like hydrochloric acid, formic, phosphoric, etc.,

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are also effective [3]. It was proven that certain properties of the cellulose nanocrystals and their water-based suspension as well as the yield depend not only on the cellulose source, but also the conditions of sulphuric acid hydrolysis and the subsequently applied sonication [4, 5]. During sulphuric acid extraction, sulphate ester groups ($-\text{OSO}_3^-$) are introduced onto the surface of cellulose nanocrystals in a minor amount (e.g. 66 and 54 mmol/kg for CNCs extracted from bleached cotton and flax, respectively) [6]. Owing to these negatively charged groups, the aqueous suspensions of CNCs are highly stable. In addition, the sulphate ester groups can form sulphuric acid upon heating which catalyses the hydrolytic degradation of glycosidic bonds in cellulose chains [7]. Thus, these bulky groups can accelerate the thermal degradation of cellulose [8, 9].

A disadvantage of CNCs is the poor thermal stability, which inhibits their industrial application in certain areas. Recently, many studies have been conducted to investigate and to improve the thermal properties of CNCs prepared by sulphuric acid hydrolysis and those of their products [10]. Good thermal stability of CNCs is an important prerequisite for their processing with common industrial processing methods [11]. For CNC films, it was proven that thermal degradation started at 150 °C and a sharp decomposition peak at 320 °C was observed in the DTG curves [12]. Additionally, thermal degradation of cotton- and flax-origin CNCs was compared with that of the original cotton and flax fibres, respectively. Results revealed that while the degradation temperature values (T_{onset}) of the bleached cotton and flax fibres were 372 and 364 °C, respectively, those of the CNC films were significantly lower ranging from 223 to 245 °C [6]. The influence of several factors, including surface functionalization [12] and grafting [13] of CNC, the presence of additives such as plasticizers [6], metallic nanoparticles [14], the methods of drying [15], etc., on the thermal properties was investigated. Thermal behaviour of composites filled with cellulose nanocrystals [16] or nanofibres [17] was also widely tested. Additionally, incorporation of amino-aldehyde compounds such as melamine-formaldehyde [18] and urea-formaldehyde (e.g. dimethylol dihydroxy ethylene urea, DMDHEU) [19] into the nanocellulose-based thin films was reported.

In the textile technology, N-methylol compounds are classical cellulose cross-linking reagents with the ability to cross-link with hydroxyl groups of the adjacent cellulose chains (Cell-OH) via dual N-linked methylol ($\text{N}-\text{CH}_2\text{OH}$) groups (Eq. 1) [20]. Although this reaction is the most preferably reaction, the N-methylol groups may also react with themselves.

N-methylol compounds such as DMDHEU affect the thermal behaviour of cellulose, and as a finishing agent of cellulosic textiles it can improve the thermal stability of

cotton fabric [21, 22]. Additionally, DMDHEU is largely used as a constituent of coatings for woody materials to increase their durability [23]. Recently, for improving the mechanical, water barrier and thermal expansion characteristics, nanocomposite coating was developed with CNCs as fillers in a photocurable system for wood protection [24]. Cellulose nanocrystals–DMDHEU-based films—comparable to wood coating systems—possessed excellent characteristics, like high tensile strength (up to 45 MPa) and modulus (9–11 GPa), high density (ca. 1.35 g cm⁻³) and low water sorption [19]. Since AA compounds as finishing agents can improve the thermal stability of cotton fabric, we assumed them to have a similar effect in improving the thermal stability of CNC-based films by cross-linking.

Our current project was designed to conduct short-term heating studies in the temperature range of 140–200 °C on cellulose nanocrystals–amino-aldehyde (AA) nanocomposite systems (films) of various compositions. The concept behind the present research was to explore how the cellulose source and the addition of cross-linker and its concentration affect the heat-induced perceptible, chemical and physical characteristics of CNC-based composites. In this study, bleached cotton and flax served as cellulose sources for the sulphuric acid extraction of CNCs. Model films were cast with different plasticizers (sorbitol and glycerol) and with a DMDHEU-based cross-linking agent in a wide composition range. The heat-induced discolouration and changes in haziness of the neat films (without a cross-linker) and the polymer composites were investigated by spectrophotometry in reflectance and total transmittance modes, respectively. Furthermore, thermal degradation of the CNC-based films as a function of chemical composition was also studied by thermal gravimetric analysis (TG).

Experimental

Materials

Bleached cotton and flax plain-weave fabrics with a mass per unit area of 110 g m⁻² and 165 g m⁻², respectively, served as cellulose sources for the CNCs production. The fabrics were kindly provided by Pannon-Flax Linen Weaving Co. (Hungary) and used without any further wet treatment. The large-scale pretreatment technology of the cotton fabric consisted of the following processes: an amylase enzymatic desizing, a scouring with sodium hydroxide solution and a bleaching with hydrogen peroxide solution. The flax fabric was scoured with a solution of sodium hydroxide/sodium carbonate and bleached with hydrogen peroxide. The holocellulose content of bleached flax was determined by the Wise's chlorite method [25]

using sodium chlorite in acidic medium at 80 °C for 1 h. The process was repeated three times.

For cross-linking of cellulose in CNC films, an amino-aldehyde-based (DMDHEU) water-soluble cross-linking agent was used with an acidic catalyst (Reaknitt B-FV and Reaknitt Catalyst FV, respectively, from Bezema AG, Switzerland). The AA compound together with the acidic catalyst (CAT) shows high reactivity at room temperature and is recommended for wet cross-linking of cellulose-based textiles. All other chemicals (concentrated sulphuric acid, glycerol and sorbitol) used in the experiments were analytical grade, were purchased from Sigma-Aldrich and were used as received.

Preparation of cellulose nanocrystals

Cellulose nanocrystals were prepared from bleached cotton and flax powder obtained by ball-milling of the fabrics with a Mixer Mill MM400 (Retsch GmbH, Germany) at a frequency of 30 s^{-1} for 2.5 min. The particles with length between 200 and 315 μm were collected by sieving and used in the research. Cellulose nanocrystals were isolated by acid hydrolysis with 64% w/w sulphuric acid at 45 °C for 25 min under constant stirring [26]. The hydrolysis was stopped by diluting the acidic cellulose suspension with cold, deionized distilled water. The white milky suspension was washed with cold deionized water and centrifuged at 5 °C with a refrigerated high-speed Hermle Z326 K centrifuge (Labnet, USA) at 13,000 rpm for 10 min. Thenceforth, the white suspension was dialysed against tap water for 5 days using a dialysis tube (MWCO 12–14 kD, Spectra/Por®, Spectrum Laboratories, Inc, USA). A more detailed description of the multi-step process was widely introduced elsewhere [5]. The CNC suspensions (with an average dry solid content of 4%) were subjected to ultrasonication for 10 min by using an ultrasonic horn-type reactor (Sonics & Materials, Model: Vibra-Cell VC505) with a driving frequency of 20 kHz at 60% amplitude. The nanocrystals were denoted as cotton–CNC and flax–CNC. Their yield was around 40% as a percentage of the initial mass of bleached fibres (10 g). TEM images of the diluted CNC suspensions (0.05 w/v %) were obtained with a Morgagni 268D TEM (100 kV; W filament, top-entry; point-resolution = 0.5 nm, line resolution = 0.3 nm; Megaview III CCD camera /1376_1032 pixels/).

Preparation of films from the CNC suspensions

From the aqueous CNC suspensions, rectangular films were cast on the surface of a polypropylene plastic sheet. To overcome brittleness of the films, either sorbitol (Sor) or glycerol (Gly) as plasticizer was added. Their amount was always 20% related to the quantity of CNC. For improving and modifying the properties of films, the amino-aldehyde compound

and the catalyst were added in different concentrations on a dry CNC basis (AA: 0, 2.5, 5, 10, 20, 30% and CAT: 0, 0.75, 1.4, 3.3, 6.6, 10%, respectively) to the CNC suspension before casting (Table 1). The water content of CNC suspension was allowed to evaporate at room temperature for about 48 h. The curing of amino-aldehyde occurred simultaneously with the evaporation of water [6]. The detached films with an average thickness of about 40 μm were conditioned for 1 day at 23 °C and 55% relative humidity before testing. In some of the experiments, only selected compositions of CNC films were investigated because of the wide composition range studied in the research.

Furthermore, films containing only the amino-aldehyde and the catalyst with 0, 15 or 30% sorbitol or glycerol, but without CNC (denoted as AA films) were also prepared and some of their thermal characteristics were also investigated in order to determine the contribution of additives (i.e. cross-linker and plasticizer) to the properties of films.

Heating experiments and sample analysis

To investigate the heat-induced changes in colour and haziness, we first conducted controlled heating experiments on CNC-based films with different compositions (such as 0, 10 and 30% AA content). We applied only a 10-min long heat treatment in the temperature range of 140–200 °C that the CNC-based biocomposites are likely to encounter during their processing and application, e.g. as packaging or coating material. For the treatment, a drying oven (Venti-Line, VWR International Ltd.) was used (Table 1). Then, the films were cooled down to ambient temperature and reconditioned. A HunterLab Color QUEST XE spectrophotometer was used for both testing the colour in reflectance mode ($D_{65}/10^\circ$) and for measuring the haze in total transmittance mode. For reflected colour measurement, each of the transparent films was backed with the standard white tile of equipment which provided a constant background. Colour evaluation was done according to the CIELab colour space. The yellowness (E313) values were determined and the data are the average of 3 readings. Haze is defined as the percentage of transmitted light that while passing through a specimen,

Table 1 A summary of the composition of CNC-based nanocomposite films and the experimental design

Source of cellulose	Bleached cotton, bleached flax
Plasticizer ^a	Glycerol, sorbitol
Concentration of AA/CAT/% ^b	0/0; 2.5/0.75; 5/1.4; 10/3.3; 20/6.6; 30/10
Heating/°C ^c	140; 160; 180; 200

^a20%, related to the amount of CNC

^bBased on the amount of CNC

^cFor 10 min

deviates from the incident beam by more than 2.5° from the normal incident beam [27]. The values were determined in triplicate. A schematic representation of the multi-step process carried out in the research is shown in Fig. 1.

Thermal analysis of CNC/AA nanocomposite films

Thermal decomposition of the CNC films was examined by TG, with a PerkinElmer TGA6 equipment (USA) at a heating rate of $10^\circ\text{C min}^{-1}$. The experiments were completed under nitrogen atmosphere with a flow rate of 20 mL min^{-1} , from 30 to 700°C temperature. For comparison, TG curves of the original bleached cotton and bleached flax both in fibrous and ground forms and also the AA films were detected. For determination of the maximum pyrolysis temperature of samples, derivative of TG curves with respect to temperature (DTG; dm/dT) was calculated [9, 24]. Global minimum of DTG curve was used to define the maximum pyrolysis temperature (T_{max}). The residual mass (RM) of samples at the end of measurement (at 700°C) was also

Fig. 1 Schematic representation of the main research processes for CNC films derived from bleached flax

detected and expressed in percentage of initial mass.

Results and discussion

Heat-induced discolouration

In this research, cellulose nanocrystals were obtained from cellulosic fibres, such as bleached cotton and flax with a controlled sulphuric acid hydrolysis. The time-consuming multi-step process resulted in aqueous suspensions of CNCs. Data published previously revealed that flax–CNCs are slightly smaller than cotton–CNCs. For flax–CNCs, the averaged length and width values are $57 \pm 5\text{ nm}$ and $6\text{ nm} \pm 0$, respectively, while these values are $68 \pm 5\text{ nm}$ and $8\text{ nm} \pm 0$, respectively, for cotton–CNCs [6]. The rod-like cellulose nanocrystals in water create aggregates with ordered deposition of the individual whiskers (Fig. 2a, b). TEM images of the suspensions prove our previous observation that the flax–CNC particles have a more pronounced aggregation ability than the cotton–CNCs [6]. Furthermore, as the tiny light spots in Fig. 2b reveal, the flax–CNC suspension contains accompanying materials, which most likely came from the non-cellulosic ingredients of flax fibres.

Transparent and smooth CNC/amino-aldehyde composite films with a thickness of ca. $40\text{ }\mu\text{m}$ were obtained from the aqueous CNC suspensions by casting and evaporation. The yellowness indices of films cast with sorbitol or glycerol plasticizer (20%) and with an AA content of 0, 10 and 30% are very low, indicating that the untreated (both neat /without AA/ and composite /with AA/) films are colourless (Table 2). The values are in the range of 4.8–7.5 and 7.2–10.2 for cotton–CNC and flax–CNC films, respectively. Thus, the difference between cotton–CNC and flax–CNC films is detectable. However, there is no perceptible difference in colour of films belonging to the two groups mentioned above. The slightly higher yellowness values of flax–CNC films can be explained by the presence of non-cellulosic matters, mostly lignin, in the

Fig. 2 Transmission electron micrographs of cellulose nanocrystals (left: cotton–CNC; right: flax–CNC). Concentration: (0.05 w/v%); magnification: 20,000×

Table 2 Yellowness indices of CNC films from bleached cotton and flax plasticized with glycerol or sorbitol (20%) as a function of amino-aldehyde-based cross-linker concentration^{a,b}

Source of cellulose	Plasticizer	Amino-aldehyde concentration/% ^a		
		0	10	30
Cotton	Glycerol	7.5	6.3	5.5
	Sorbitol	5.2	5.1	4.8
Flax	Glycerol	10.2	9.8	8.4
	Sorbitol	8.9	7.4	7.2

^aYI E313 (D65/10)^bBased on the amount of CNC

flax–CNC suspension (Fig. 2b). Lignin—present probably as structural lignin (discussed later) surviving the sulphuric acid hydrolysis during the CNC production—has a brownish colour and affects considerably the colour of CNC-based composites [2].

Data also reveal that all films plasticized with glycerol show higher yellowness values than the sorbitol plasticized ones. Obviously, the yellowness slightly decreases with an increase in the AA content. This could be attributed to the presence of colourless cross-linking agent in films.

Thermal treatment in an air circulating oven at various temperatures (from 140 to 200 °C) for 10 min caused perceptible changes in colour from the initial beige to beige to brownish as the temperature increased. Discoloration of films indicated the appearance of chromophore groups with conjugated unsaturated molecular structures brought about by heat-induced oxidation [28]. Tables 3 and 4 contain representative photos from the flax–CNC series. Changes in yellowness indices of the plasticized CNC/AA films for cotton–CNC and flax–CNC occurred during thermal exposure are presented in Figs. 3 and 4, respectively.

Heating at 140 °C for 10 min did not cause visible discoloration of cotton–CNC films (Fig. 3a, b) and flax–CNC–Sor films (Fig. 4b) and all these films with various compositions have roughly the same yellowness values, varying in the range of 5–10 (symbols on the Y-axis). However, even at

Table 3 Heat-induced discolouration of bleached flax–CNC films plasticized with glycerol (20%). Effect of temperature and the AA cross-linker used in a concentration of 0 and 10%

AA/%	140/°C	160/°C	180/°C	200/°C
0	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
10	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY
	C_GLY	BF_CNC_GLY	BF_CNC_GLY	BF_CNC_GLY

Table 4 Heat-induced discolouration of bleached flax–CNC films plasticized with sorbitol (20%). Effect of temperature and the AA cross-linker used in concentration of 0 and 10%

AA/%	140/°C	160/°C	180/°C	200/°C
0	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
10	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR
	C_SOR	BF_CNC_SOR	BF_CNC_SOR	BF_CNC_SOR

Fig. 3 Effect of the temperature of heat treatment (140–200 °C) and the amino-aldehyde-based cross-linker concentration (0, 10 and 30%) on the yellowness of cotton–CNC films plasticized with glycerol (a) and sorbitol (b)

Fig. 4 Effect of the temperature of heat treatment (140–200 °C) and the amino-aldehyde-based cross-linker concentration (0, 10 and 30%) on the yellowness of flax–CNC films plasticized with glycerol (a) and sorbitol (b)

140 °C a slight yellowing of the neat flax–CNC–Gly film (Fig. 4a) was observed, showing the heat sensitivity of the bleached flax-origin CNC films plasticized with glycerol that can be characterized by an increase in yellowness value (from 10 to 20 units). Discolouration of all films intensified significantly above this temperature. The values increased with increasing temperature and ranged from 6 to 37 and from 9 to 73 for cotton–CNC (Fig. 3) and flax–CNC (Fig. 4) films, respectively. Obviously, the films based on flax–CNC have a higher yellowness than those derived from cotton–CNC. Additionally, the yellowness of films plasticized with glycerol is significantly higher than that of the sorbitol plasticized ones. The figures clearly show that the neat films (AA: 0%) have the highest yellowness values and the cross-linking agent (AA) has a decreasing effect on heat-induced discolouration. In summary, results proved that besides temperature, the factors affecting the rate of discolouration of CNC-based films are (including but not limited to) the source of cellulose, the amount of cross-linking agent and the type of plasticizer. For films of CNC, cellulose nanofibril

(CNF) and cellophane, the influence of surface groups (sulphate ester, carboxyl and hydroxyl, respectively) of building blocks on thermal stability and the heat-induced changes in colour was more pronounced than that of the size of building blocks and crystalline structure [29].

It is obvious that AA has a reducing effect on discolouration of CNC films. The rate of process depends not only on the AA concentration, but surprisingly on the type of plasticizer. It was proven that at low concentration (10%), AA acts “only” as a plasticizer [19], softening the films, as well as filling in the voids within the aggregates of CNCs. At a concentration of 30%, however, AA can wrap the CNC nanocrystals like an envelope and improve their interaction by chemical cross-linking. The presence of cross-linking in CNC films was proven indirectly by several methods. One of them revealed that water can disintegrate the composite films at lower cross-linker concentration (10%), whereas at higher AA content the films retained their original film structure [19]. Similarly, the fact that CNC-based films retained their structural integrity in water provided evidence

for the presence of cross-linking between the CNC whiskers [30].

For CNC–glycerol films (Figs. 3a, 4a), discolouration of the films with a lower AA content (10%) is more pronounced than that of the films with an AA content of 30%. The reason can be explained by the elimination of glycerol from the pores of film together with the moisture content, starting even at about 140 °C and increasing the accessible surface of cellulose. This may contribute to an increased thermal degradation and a more pronounced discolouration. Thus, the glycerol-plasticized CNC films with a lower AA content are more sensitive to heat treatment than the films cross-linked with a higher AA concentration. By using sorbitol as a plasticizer, the difference in heat-induced discolouration of films prepared with various AA contents is less pronounced (Figs. 3b, 4b), since elimination of sorbitol can be neglected during the thermal treatment.

It has to be highlighted that desulphation of CNCs takes place even at low temperature heating above 40–50 °C for some hours [31]. The sulphuric acid released from the sulphate ester groups upon thermal treatment highly accelerates the thermo-oxidative processes of CNC [32]. The chemical structure of the nanocomposite films has not been investigated, but it is known that in the presence of oxygen, aldehyde and carboxyl groups are formed in oxidative and hydrolytic processes, reducing the polymerization degree of cellulose molecules and leading to discolouration of the cellulosic sample [33]. A significant increase in reducing sugars was observed by heating of cotton above 140 °C [34], and reducing sugars, especially hexoses show a yellowing similar to the aldehyde-containing celluloses [35]. Thermal treatment at 140 °C for 20 min decreased the degree of polymerization of cotton cellulose by about 13% [36], resulting in terminal aldehyde groups. It was proved that the contribution to yellowing of these aldehydes at C1 position is higher by

70% than that of the aldehyde groups at other positions of the cellulose chain [35].

It was also found previously [6] that the porosity of flax–CNC films and the water content of glycerol-plasticized films were higher than those of their counterparts (i.e. cotton–CNC films and sorbitol-plasticized films, respectively). The higher porosity and most likely the higher surface area can accelerate the thermal degradation of flax–CNC films. Furthermore, evaporation of the water content and elimination of glycerol can also contribute to an additional increase in porosity and as a result, to a more pronounced degradation of the glycerol-plasticized films. Furthermore, the cross-linking agent can fill in the porous part of CNC films, decreasing the porosity [19]. Thus, the conclusion is that the heat-induced yellowing of the CNC-based films with higher porosity was more favourable than those with a denser and less porous structure.

Heat-induced changes in haziness

The neat CNC films are transparent, but their discolouration by thermal exposure modified the transparency and altered the haze (Fig. 5, for films plasticized with glycerol). A similar decrease in transparency was reported on neat cellulose nanocrystal films as browning occurred with a low temperature heating at 85 °C for 24 h [37]. Haze indicates changes in optical properties of CNC-based films more sensitively than transparency. Aggregates of cellulose nanocrystals and internal volumes among CNC aggregates can be large enough to interfere with visible light and this interference results in considerable haze of CNC-based films. Concerning the cellulose source, the flax–CNC films are hazier than the cotton–CNC ones. This can be explained by the higher aggregation ability of CNCs derived from flax and the lower homogeneity of

Fig. 5 Effect of the amino-aldehyde-based cross-linker concentration (0, 10 and 30%) and the temperature of heat treatment (140–200 °C) on the haze of CNC films derived from cotton (a) and flax (b) and plasticized with glycerol

CNC–flax films in general and also by the retaining accompanying substances in flax cellulose [6]. It was proven that the non-cellulose content of cellulosic materials used for CNC production has a significant effect on the purity of CNC. Sulphuric acid hydrolysis of the pretreated (alkaline and bleaching) recycled newsprint with a non-cellulose (hemicelluloses, lignin and ash) content of 12% resulted in CNC with a purity of 93.3% [38]. Since the holocellulose (cellulose and hemicelluloses) content of the alkaline scoured and bleached flax is $97.5 \pm 0.1\%$ and it contains structural lignin [6], it is likely that the CNC suspension contains the residues of non-cellulosic matters (Fig. 2b) that affect the haziness of CNC films. Additionally, the films plasticized with glycerol are slightly hazier (Fig. 5) than those plasticized with sorbitol (data not shown).

Addition of a cross-linking agent to CNC decreased the haze indices of the untreated films to about 12% from 16% and from 23% (for neat cotton–CNC and flax–CNC, respectively), and the haziness did not alter significantly by the AA content (symbol ▼; Fig. 5a, b). The decrease in haze by AA can be explained by various processes occurred during the formation of composite films. First, the low haze is attributable to the smooth surface of films, since a smoother surface deflects less light than a rougher one [28]. Second, AA surrounding the cellulose nanoparticles can separate them during evaporation in the film casting process, preventing the formation of large aggregates by strong hydrogen bonding [39], and resulting in a more homogeneous distribution of nanoparticles with reduced light scattering. Furthermore, the voids within the aggregates of CNCs can also scatter the light and AA—together with the plasticizer—can fill in these volumes. Thus, by eliminating pores and cavities, the structure of CNC/AA films shows less light scattering.

Results also reveal that the haziness of neat films (symbols at 0% AA in Fig. 5) increased with an increase in the temperature and reached the maximum values (for cotton–CNC: 37%; for flax–CNC: 51%) at the highest temperature (200 °C). Thus, the effects associated with heating were more pronounced on the flax–CNC films than on the cotton–CNC ones. The increase in haziness by heat treatment can be a close correlation with evaporation of glycerol plasticizer at elevated temperature. The new structure has partially empty pores and cavities that scatter light. This leads to a higher haziness of films aged at high temperature. Furthermore, the haziness was always lower for the films having AA content, because DMDHEU can reduce accessible internal volume [39]. Thus, cross-linking can moderate the light scattering reducing the haziness of CNC-based films.

Thermal degradation

It is well known that cellulose nanocrystals produced by sulphuric acid hydrolysis are sensitive to heat, since introduction of the bulky sulphate ester groups onto some of the surface hydroxyl groups decreases their thermal stability. In order to use CNC as a nanofiller for developing for example new and promising coatings and packaging materials, the heat sensitivity of CNC has to be characterized and reduced for example by cross-linking. Figure 6a, b shows the mass loss (TG) curves of cotton–CNC films cross-linked with different amounts of AA (from 0 to 30%) and plasticized with either sorbitol or glycerol, respectively. To precisely determine the maximum pyrolysis temperature, their respective derivatives were also generated, and the DTG curves are presented in Fig. 6c, d. The maximum pyrolysis temperature data determined from DTG and not only for cotton–CNC but also for flax–CNC films are collected in Table 5. In order to evaluate and interpret the results of composite films, thermal degradation of the cellulose sources (cotton, flax and their ground counterparts) as well as the plasticized AA films was also characterized similarly (Fig. 7a, c and b, d, respectively).

Results reveal that the films showed a fast decline in mass at the maximum pyrolysis temperature. The TG curves of CNC films were comparable, and there were noticeable differences in onset temperature neither between the cotton– and flax–CNC films, nor between the sorbitol- or glycerol-plasticized films. However, the $T_{\max}$ of flax–CNC films changed in a greater extent (from about 230 to 290 °C) than that of cotton–CNC films (from 250 to 280 °C), which difference may be caused by traces of lignin-like and other accompanying substances present in flax cellulose nanocrystals and their water-based suspension. Although the sulphuric acid hydrolysis used for separation of CNC destroyed almost all of the non-cellulosic substances in bleached flax, a little ratio of lignin remained in the crystalline cellulose fibrils [40] and was detected previously in the aqueous suspension of CNC by UV spectroscopy [6]. This so-called structural lignin is likely to cross-link adjacent cellulose and this association of cellulose and lignin in flax is strong, surviving harsh chemical treatment (like sulphuric acid hydrolysis) and it is resistant to ageing [41].

Furthermore, the $T_{\max}$ of CNC films increased proportionally with increasing AA content. A similar increase in the $T_{\max}$ of linen with the cross-linker concentration was also reported for dimethylol–urea cross-linking agent [42]. The thermal stability of CNC films improved with a 30–55 °C increase of maximum pyrolysis temperature when amino-aldehyde was added and cross-linking occurred. This indicates that the cross-linking reaction

Fig. 6 TG (a, b) and the respective DTG (c, d) curves of the CNC films prepared from bleached cotton with sorbitol (a, c) and glycerol (b, d) at various amino-aldehyde contents (0–30%)

Table 5 Maximum pyrolysis temperature of CNC/AA films prepared with sorbitol or glycerol (20%) as a function of amino-aldehyde content^{a,b}

AA/%	Maximum pyrolysis temperature/°C			
	Cotton–CNC		Flax–CNC	
	With sorbitol	With glycerol	With sorbitol	With glycerol
0	252	253	229	247
2.5	254	276	243	265
5	260	279	267	269
10	262	279	269	271
20	279	279	269	274
30	281	281	276	287

^aMaximum pyrolysis temperatures (°C): cotton fibre: 378, ground cotton: 373; flax fibre: 372, ground flax: 366

^bMaximum pyrolysis temperature (°C) of AA film: 366; AA with 15 and 30% sorbitol: 366 and 363, respectively; AA with 15 and 30% glycerol: 381 and 377, respectively

between cellulose and the AA compound took place and the combustion of cross-linked cellulose occurred at higher temperature than that of cellulose without

cross-linking [42]. Another possible explanation for the increasing $T_{\max}$ can be that AA with a higher maximum pyrolysis temperature (near 374 °C, Fig. 7d) envelopes cellulose nanocrystals, protecting them from heat. This correlates with porosity data of these films determined in an earlier study [19]. It was found that porosity of cellulose nanocrystal films decreased with an increase in the amount of AA incorporated in the films.

However, the AA films (without CNC) have also another DTG peak near 150–200 °C (Fig. 7d), but it was not detectable on TG curves of CNC/AA films. In the AA films, a certain ratio of the AA compound is likely to be in an unbound state after wet fixation at room temperature. During TG the heating exposure can act as a post curing step, and self-condensation of the AA reagent residues can occur near 160 °C, which is accompanied by formaldehyde release. That can be the explanation of mass loss detected in the TG curves. In the CNC/AA films, however, the irreversible cross-linking reaction with cellulose is preferred and at the 0–30% application level of AA, formaldehyde cannot be released at high temperature during the course of TG [39, 43]. At low AA content (0–10%), CNC films with glycerol showed a bit higher $T_{\max}$ values and in some cases the difference

Fig. 7 TG (a, b) and DTG (c, d) curves of the bleached cotton and flax fibres and their ground forms (a, c) and the amino-aldehyde films (b, d) prepared with different amounts of sorbitol and glycerol (15 and 30%)

reached 25 °C. However, at higher AA contents, differences were unnoticeable.

Moreover, the cellulosic fibres have higher maximum pyrolysis temperatures (ca. 375 °C; Fig. 7a,c) than CNC/AA films, as expected [6, 10], since the surface sulphate ester groups accelerate the thermal degradation of CNCs, as mentioned above [8]. Interestingly, a second peak for CNC films (around 380 °C) can be observed in the DTG curves, which is close to the $T_{\max}$ of fibres. This peak can be associated with the degradation and breakdown of the crystalline fraction, which has not been attacked by sulphuric acid during the extraction of nanocrystals [44]. Meanwhile, the first peak of DTG curves of CNC films is probably due to thermal decomposition of nanocellulose and disintegration of interunit linkages [45]. Another explanation is that the first peak corresponds to primary pyrolysis of CNC catalysed by sulphate ester groups, and the process at higher temperature is assigned to a slow charring of solid residue [9].

Considering the residual mass (Table 6) at the end of heating procedure (at 700 °C), only a slight difference

Table 6 Residual mass of cotton–CNC/AA and flax–CNC/AA films prepared with sorbitol or glycerol (20%) as a function of amino-aldehyde concentration^{a,b}

AA/%	Residual mass/%			
	Cotton–CNC		Flax–CNC	
	With sorbitol	With glycerol	With sorbitol	With glycerol
0	19.7	20.3	15.9	19.0
2.5	23.8	21.7	19.4	20.6
5	24.1	22	20.2	21.1
10	24.1	22.5	23	21.4
20	25.1	23.9	23.3	22.1
30	27.1	26.7	25.3	25.4

^aResidual mass at 700 °C (%): Cotton fibre: 6.7, ground cotton: 2.6; Flax fibre: 8.9, ground flax 3.3

^bResidual mass of AA film at 700 °C (%): 20.3; with 15 and 30% sorbitol: 16.7 and 17.7, respectively; with 15 and 30% glycerol: 18.4 and 20.0, respectively

between CNC films was observed. Residual mass increased with increasing cross-linking concentration from ca 16–20% (neat films) to about 25–27% (at 30% AA content). It seems that the amino-aldehyde-based cross-linking protects the cellulose nanocrystals by enveloping them and repressing degradation and vaporization of cellulose. The amino-aldehyde-aided interaction between nanocrystals leads to a cross-linked network and that makes films more stable at high temperature [19, 46]. This structure induces char formation protecting the nanocrystals from mass loss during thermal decomposition. It was also stated that only textile finishes (e.g. DMDHEU) that cross-link with cotton cellulose exhibited any progressive reduction in maximum rate of mass loss in thermal treatment [47]. Thus, the cross-linked cotton had a better thermal stability than non-cross-linked one that can be attributed to the interpenetrating nature of cross-linking molecules and the high residue percentage [48].

The effect of AA on charring of thermal stable fractions of cotton–CNC and flax–CNC films was similar. However, the combustion residues were slightly lower for most of the films plasticized with glycerol, which could be explained by the partial evaporation of glycerol mentioned above. The peak near 200 °C in DTG curve of AA with 30% of glycerol (Fig. 7d) is probably associated with the boiling off process of glycerol. Furthermore, it is obvious that cellulosic fibres (both fibrous and ground) had lower residue (2.6–8.9%) than CNC films at the end of the heating procedure, due to lower crystallinity and higher low molecular mass content of fibres [6, 22].

Conclusions

Cellulose nanocrystals were released from bleached cotton and flax as cellulose sources by sulphuric acid hydrolysis. From the aqueous suspensions of CNCs, thin and transparent films were prepared via solution casting and evaporation by addition of sorbitol or glycerol as plasticizers and an amino-aldehyde-based cross-linker (DMDHEU) in various concentrations. Heat treatment of films was performed in a temperature range of 140–200 °C for 10 min. The effect of thermal exposure on the properties was investigated and evaluated.

CNC-based nanocomposites can be exposed to temperatures up to 200 °C when they are processed or applied. The behaviour of CNC-based films and coatings at elevated temperature is becoming an important issue because of the increased use of CNCs and their products in medical or packaging areas. Under the conditions used in this study, the heat-induced changes in properties were depending not only on the temperature but also on the source of cellulose (bleached cotton or bleached flax), the type of plasticizer (glycerol or sorbitol) and the amount of cross-linking agent (0, 10 and 30%).

Heating caused visible discolouration, indicating formation of chromophore groups during thermal degradation of cellulose. Discolouration of the neat films (AA: 0%) started at 140 °C and its rate intensified significantly above this temperature. Yellowing of the flax–CNC films with a higher porosity and internal surfaces was more remarkable than that of the cotton–CNC films with a denser structure. Furthermore, the yellowish appearance of films plasticized with glycerol was more significant than that of the sorbitol plasticized ones, and addition of cross-linking agent had a significant moderating effect on the discolouration of CNCs.

It was also apparent from the results that treatment at elevated temperature increased the haziness of CNC films, revealing the formation or emergence of regions (with voids, pores, cavities) inside the films, large enough to scatter of the light. The haziness of neat films prepared without a cross-linker increased with an increase in the temperature. Changes in haze were more pronounced on the flax–CNC films than on the cotton–CNC ones. However, the haze decreased with increasing AA content.

The results listed above seem to be directly related to the morphology of films, which changed during thermal exposure. It is likely that the volatilization of glycerol and moisture from the internal volume can increase the accessible internal surface of CNC films, resulting in a cellulose structure with moderate heat sensitivity, and it can also lead to partially empty pores and cavities that scatter light. However, AA can reduce the accessible internal volume [39] by filling in the pores and cavities. Thus, AA has a significant effect on both heat sensitivity and haziness of films: both of them decreased with an increase in the AA content.

TG analysis clearly showed that thermal stability of CNC films improved with a 30–55 °C increase of maximum pyrolysis temperature when amino-aldehyde was added and cross-linking occurred. However, the maximum pyrolysis temperature of CNC/AA films was still lower than that of the cellulosic fibres, serving as sources for CNC production.

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