PREPARATION AND PROPERTIES OF BIONANOCOMPOSITE FILMS REINFORCED WITH NANOCELLULOSE ISOLATED FROM MOROCCAN ALFA FIBRES

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Abstract:

Nanocellulose (NC) were extracted from the Moroccan Alfa plant (*Stipa tenacissima* L.) and characterised. These Alfa cellulosic nanoparticles were used as reinforcing phase to prepare bionanocomposite films using carboxymethyl cellulose as matrix. These films were obtained by the casting/evaporation method. The crystallinity of NC was analysed by X-ray diffraction, the dimension of NC by atomic force microscopy, molecular interactions due to incorporation of NC in carboxymethyl cellulose (CMC) matrix were supported by Fourier transforms infrared (FTIR) spectroscopy. The properties of the ensuing bionanocomposite films were investigated using tensile tests, water vapour permeability (WVP) study and thermogravimetric analysis. With the progress of purification treatment of cellulose, the crystallinity is improved compared to the untreated fibres; this can be explained by the disappearance of the amorphous areas in cellulose chain of the plant. Consequently, the tensile modulus and tensile strength of CMC film increased by 60 and 47%, respectively, in the bionanocomposite films with 10 wt% of NC, and decrease by 8.6% for WVP with the same content of NC. The NC obtained from the Moroccan Alfa fibres can be used as a reinforcing agent for the preparation of bionanocomposites, and they have a high potential for the development of completely biodegradable food packaging materials.

Keywords:

Alfa fibres, nanocellulose, carboxymethyl cellulose, bionanocomposite film, characterisation.

1. Introduction

In recent years, more attention has been paid to natural polymers for sustainable development and environmental preservation [1–3]. There has been spectacular development and rapidly growing interest in renewable biopolymers derived, especially from natural resources for a wide range of applications (biodegradable packaging materials, automotive industries, agriculture, pharmaceuticals...) [4–7].

In this context, Alfa grasses have been used in various composite applications [8, 9]. The main components of these fibres are cellulose, hemicellulose and lignin. These fibres are characterised by their interesting physical and mechanical properties that favour its exploitation to produce biodegradable composites [8–9]. In North Africa, Alfa is a name of the plant *Stipa tenacissima* L. Species belongs to the grass family typically Mediterranean localised, especially in the western part of the Mediterranean region. It covers a large area estimated to about 3,186,000 ha in Morocco, 4,000,000 ha in Algeria, 400,000 ha in Tunisia and 350,000 ha in Libya [10–12].

Cellulose is the most abundant natural polymer in the biosphere. It has been extensively studied in both theory

and experimentation. Carboxymethyl cellulose (CMC) is a derivative of cellulose and can be produced from annual plant pulps, cotton cellulose and wood. It is produced by introducing -CH₂COOH groups into cellulose molecular chain. According to unique physicochemical properties such as non-toxic, viscosity, transparency, hydrophilicity and biodegradability [13, 14], CMC can be employed for several applications such as medicine constituents, viscosity controllers, paper industry, detergents, food and textile printing among others [15–17].

Nanocellulose (NC) is also a cellulose derivative composed of a nanosized fibre network, which determines the product properties and its functionality. It has generated much attention and interest during these few last decades because of their value-added applications in science and technology, for example, (1) in pharmaceutical formulations, as a potential direct compression excipient, especially in the design and development of tablets of poorly compressible and soluble drug [18–20]; (2) in food industry, as stabiliser, emulsifier, thickener and gelling agents in several dairy [21, 22]; (3) in nanocomposite materials with improved mechanical properties and good tensile strength [23]. NC fibres' quality depends on the cellulose raw materials, its pretreatment, and more crucially on the disintegrating process itself. Several processes of

extraction have been described from various cellulose sources such as mechanical treatments [24], chemical treatments [25], and biological treatments [26]. However, chemical methods, for example, acid hydrolysis, are the conventional method of choice for manufacturing NC having a great crystallinity [25]. NC are very interesting nanomaterials for production of cheap, lightweight and very strong nanocomposites (Young's modulus of the cellulose crystal is as high as 134 GPa). A considerable amount of research has been done on the isolation of these nanofibres from plants for use as fillers in the next generation of biodegradable materials. To improve properties of CMC, different nanoparticles have been incorporated into CMC matrix, such as graphene oxide [27], silver nanoparticles [28, 29], ferrite nanoparticles [30], cellulose nanocrystal [31], hydroxyapatite [32], calcium carbonate [33], ZnS [34] and copper complexes [35].

In this study, we evaluate the effect of incorporation of NC on the mechanical, thermal and water vapour barrier properties of CMC bionanocomposite films. The NC/CMC bionanocomposite films have been prepared by casting NC/CMC aqueous solution. The microstructure, mechanical, thermal and water vapour permeability of NC/CMC bionanocomposite films were examined as function of NC content by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), water vapour permeability (WVP) and mechanical tests. The NC content in the bionanocomposite films ranged from 0 to 10 wt%. The crystallinity of NC was analysed by X-ray diffraction (XRD) and atomic force microscopy (AFM).

2. Experimental

2.1. Raw material

Alfa fibres were collected from the Oujda area, in Morocco, during the period of April–May 2012. The CMC, with a nominal molecular weight of 700.000 g.mol⁻¹, used in the present work was supplied by Sigma–Aldrich. Preliminary tests showed that the preparation of CMC solutions requires a minimum time to fully dissolve the CMC powder. This time depends on the polymer concentration and the temperature. Consequently, aqueous solutions of CMC were prepared by dissolving the appropriate amount of CMC in distilled water at room temperature. All commercial reagents were purchased from Aldrich Chemical Co.

2.2. Pulping and bleaching

The Alfa plant was milled with a laboratory milling device (POLYMIX_ PX-MFC 90 D) to obtain fine particulate substance. The Alfa fibres were extracted in a 4 wt% aqueous NaOH solution at room temperature under mechanical stirring during 2 h. This treatment was done two times to purify cellulose by removing other constituents present in the fibres. After each treatment, fibres were filtered and washed with distilled water until the alkali was completely eliminated. To bleach the fibres, the residue was treated with solution of equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water), and distilled water at 80°C under mechanical stirring during 2 h and was repeated

two times. After this treatment, the cellulose pulp was washed with distilled water until pH of 7 was reached. At last, the residue obtained was dried for 24 h at 60°C.

2.3. Nanocellulose preparation

The dry cellulose Alfa fibre was hydrolysed with preheated H₂SO₄ (64 wt%) with fibre to solution ratio of 1:12 (g/ml) for 30 min at 45°C under strong agitation. The reaction was quenched by adding an excess of distilled water to the reaction mixture and the resulting mixture was then cooled to the room temperature. Then, the suspension was centrifuged at 9000 rpm at 20°C for 15 min in a bench-top centrifuge (Hettich Universal 320) repeatedly and the supernatant was discarded until it became turbid. Subsequently, the fractions were washed with bi-distilled water by centrifugation. Under this condition, the pH of the suspension was above 5. Then the suspension was subjected to dialysis with bi-distilled water until neutrality was attained. After this, the NC of the Alfa fibre obtained after freeze drying was snow white in appearance.

2.4. Preparation of films

The NC/CMC films with a NC content of 3, 5 and 10% (w/w), respectively, were prepared by solution casting from water. The CMC was first dissolved in water at a concentration of 1 wt% by stirring at room temperature for 8 h. NC/water dispersions of a concentration of 1 mg/ml were prepared by mixing the components in the appropriate ratio and sonicated at 40% amplitude (BRANSON Analog Sonicator, 200W S-250 CE). Aliquots of the NC dispersions and CMC/water solution were combined, stirred for 15 min, and cast into plastic dishes. The water was evaporated at ambient temperature over a period of at least 3 days and the obtained films were dried for 4 h at 40°C for evaporating the residual water. Neat CMC film was also prepared according to the processing method mentioned above, without the addition of the NC for properties comparison.

2.5. Characterisation

2.5.1. FTIR spectroscopy

FTIR spectra of samples were measured on a Nicolet iS10 spectrometer. The spectra were recorded in transmittance band mode in the range of 4000–600 cm⁻¹. Spectra were achieved from 32 accumulated scans at 4 cm⁻¹ were co-added in order to achieve an acceptable signal-to-noise ratio.

2.5.2. XRD analysis

XRD patterns of the samples were obtained at room temperature on a Bruker AXS D-8 diffractometer using Cu-K α radiation in Bragg–Brentano geometry (θ – 2θ). The diffraction patterns were obtained at diffraction angles between 5 and 50° with a scanning rate 0.02°/min at room temperature. The crystallinity index (CrI%) of different cellulose samples was determined following the method of Segal *et al.* [36] (Eq. 1).

$$\text{CrI\%} = \left[\frac{I_{200} - I_{\text{am}}}{I_{200}} \right] \times 100$$

Where I_{200} and I_{am} were the intensity of the 200 peak (at $2\theta = 22^\circ$) and of the peak at $2\theta = 18^\circ$, respectively. The d-spacings were calculated using the Bragg's equation.

2.5.3. Atomic force microscopy

AFM measurement was carried out using a Veeco Dimension ICON. The samples used for AFM characterisations were deposited on mica sheets. [37]

2.5.4. Thermogravimetric analysis

TGA and derivative thermograms (DTGA) were conducted under nitrogen in Versa Therm apparatus (Thermofisher) with a $20^\circ\text{C}/\text{min}$ ramp between 25 and 1000°C .

2.5.5. Water vapour permeability

WVP test of films was conducted using a method described by Vargas-Torres *et al.* [37]. Prepared bionanocomposite films were hermetically sealed in a permeation cell ($3.0 \times 6.5 \times 2.0$ cm) that stored at 25°C in desiccators to maintain a 75% RH gradient across the film, silica gel (0% RH) was placed inside the cell, and a sodium chloride (NaCl) saturated solution (75% RH) was used in the desiccators. Water vapour transport was determined from the weight gained on the permeation cell. The equilibrium conditions were reached after about 2 hours. Six weight measurements were taken over 6 h. Changes in the weight of the cell were weighed using a four-digit balance and plotted as a function of time. At least three samples of each type of film were tested and WVP was calculated [38]. After the permeation tests, the film thickness and WVP ($\text{g}/\text{Pa}\cdot\text{s}/\text{m}$) were measured.

2.5.6. Tensile properties

Tensile tests were performed using a H50KS Hounsfield. The tensile specimens were cut in rectangular shapes with dimensions of 40 mm in length and 10 mm in width. The gauge length was fixed at 20 mm and the speed of the moving clamp was $10\text{ mm}/\text{min}$. All tests were carried out on a minimum of five samples and the reported results are average values.

3. Results and discussion

The composition of Alfa grass is 40.5% of pure cellulose, 22.8% of hemicellulose, 22.5% of lignin, 2.3% of hot water extractives, 10.2% of organic solvents extractives and 1.7% of ash. The ash content was analysed according to the standard method ASTM D 1102 84 (Reapproved 1990), hot water extracts were determined using the standard method ASTM 1110 56 (Reapproved 1977), organic solvents extracts were analysed using the standard method ASTM D 1107 (Reapproved 1972) modified by replacing benzene with toluene, the hemicellulose content was determined according to ASTM D 1104 56 (Reapproved 1978), the lignin content was analysed using ASTM D 110656 (Reapproved 1977) and, finally, the determination of α -cellulose was carried out according to ASTM D 1103 60 (Reapproved 1978).

The morphological and chemical characteristics of NC were analysed by AFM, FTIR spectroscopy, XRD and TGA. FTIR spectra of Alfa fibres (Alfa-F), Alfa-cellulose (Alfa-C) and NC samples are given in Figure 1. The dominant peaks at approximately 3300 cm^{-1} and 2900 cm^{-1} were attributed to OH-stretching and CH-stretching of the cellulose present in the all samples. The band observed in the spectra of both samples at 1034 cm^{-1} is due to the C–O–C stretching vibration and the peak at 895 cm^{-1} indicates C–H rocking vibration of cellulose present in the Alfa-C and NC. Other peaks, such as the peak at 1512 cm^{-1} is attributed to the C=C bond elongation of the lignin aromatic ring, and symmetric CH_2 bending vibration [39]. The band at 1735 cm^{-1} is attributed to the acetyl group of hemicellulose uronic ester or the carboxylic ester group of the ferulic ring and *p*-coumaric acid of lignin and/or hemicellulose [40, 41]. This result indicates that the extraction of lignin and hemicellulose has been effective. Interestingly, no difference was found between the spectrum of NC and Alfa-C. This result suggests that the acid hydrolysis of Alfa-C did not affect the chemical structure of the cellulose fragments [42]. During the hydrolysis process, the esterification reaction occurred, giving the appearance of a small peak at 1206 cm^{-1} in the NC spectrum assigned to the S=O vibration. This result is reported in the literature [43, 44].

Figure 1: FTIR spectra of a) Alfa-F, b) Alfa-C and c) NC

The XRD patterns of Alfa-F, Alfa-C as well as NC are shown in Figure 2. Both diffractograms showed at 2θ of 22.6° and a shoulder in the 2θ range $10\text{--}18^\circ$, which represent typical cellulose structure [45]. However, the intensity of the peaks of NC was significantly higher than that of the Alfa-F and Alfa-C, respectively [46–48]. On the other hand, the higher diffraction peak of 2θ of 22.6° of NC indicated that the crystallinity index of NC is greater than that of the Alfa F and Alfa-C (Table 1).

The crystallinity index of three samples of Alfa-F, Alfa-C and NC was 46%, 64% and 71%, respectively, using Segal's empirical method. The crystallinity index significantly increased because the removal of amorphous components from Alfa-F to Alfa-C and amorphous region from Alfa-C to NC by the acid hydrolysis [49]. It was indicated that the intermolecular hydrogen bonds of

Figure 2: XRD patterns of cellulose samples studied

cellulose were broken, causing the collapse of crystal structure during the whole process [50].

To get a more accurate idea about the dimension scale of the as-extracted of NC, AFM observations were carried out on

Table 1: Results obtained from the X-ray diffraction analysis for the cellulose samples studied

Sample	d-spacings (nm) ^a			CrI (%) ^b
		110	200	
Alfa-F	0.599	0.546	0.397	46
Alfa-C	0.597	0.546	0.393	64
NC	0.599	0.546	0.394	71

^ad-spacings of typical three equatorial peaks of cellulose samples (using XDR analysis); ^bCrystallinity index using XRD analysis

samples obtained by applying one drop of an aqueous NC dispersion on freshly cleaved mica sheets. It is well known that the AFM observation is an appropriate method for the analysis of the exact dimensions of NC [51–53]. Herein, AFM images of NC are shown in Figure 3. Excess water was removed by drying the sample in an oven at 50°C for 1 h. The dimensions and aspect ratio (length:diameter) of NC made under the optimised hydrolysis conditions 30 min at 45°C with a H₂SO₄ concentration of 64 wt% were determined by analysis of the AFM images (Figure 3), resulting in an average diameter of 8 ± 2 nm, an average length of 246 ± 64 nm, as calculated from the high profiles shown in Figure 3 taken in two different positions.

Figure 3: The AFM images show an area of 1.6 x 1.6 mm. AFM images of NC height (a) and amplitude (b) tapping mode

The average aspect ratio of as-extracted NC is calculated at 31 ± 0.7 nm.

The thermal stability is important for future applications of cellulose fibres in development of entirely biodegradable packaging materials. The TGA curves for Alfa-F, Alfa-C and NC samples are shown in Figure 4. Table 2 shows the result obtained from these curves. The drying stage for all samples occurs at a temperature range 70–160°C approximately, which

Figure 4: TGA/DTGA pyrolysis curves of cellulose samples

is due to the evaporation of water. As can be seen, the onset decomposition temperature was 267°C for Alfa-F, 291°C for Alfa-C and 239°C for NC, respectively, (Figure 3). For Alfa-F, a weight loss was observed due to degradation processes of lignin, hemicellulose and cellulose, such as dehydration, decarboxylation, depolymerisation and decomposition of glycosyl units followed by the formation of a charred residue. The NC exhibited the lowest thermal stability due to the introduction of sulphated groups to the nanocrystals during the H₂SO₄ hydrolysis of the Alfa F [54, 55].

The NC/CMC bionanocomposite films with a NC content of 3, 5, and 10% (w/w), were prepared by solution casting from water. Generally, all the dried bionanocomposite films were transparent, as shown in Figure 5.

Table 2: Results of thermogravimetric analysis of cellulose samples studied

Sample	TGA analysis		
	Onset (°C) ^a	Peak (°C) ^b	Wt (%) ^c
Alfa-F	267	378	73
Alfa-C	291	375	85
NC	239	315	80

^aOnset decomposition temperature using TGA; ^bPeak temperature of DTGA; ^cResidual weight at 600°C.

Figure 5: Pictures of films of a) neat CMC and CN/CMC nanocomposite films b) NC 3%, c) NC 5% and d) NC 10%

Figure 6 shows the FTIR spectra of CMC/NC nanocomposites films containing 3, 5, and 10% NC, respectively. Hence, this analysis attempted to characterise the incorporation of NC into the CMC films matrix and distinguish the IR bands and vibrations shifts related to NC interactions. Few differences can be observed in the whole IR region after addition of NC into film matrix because NC was a similar chemical structure to that CMC. The presence of hydrogen-bound O–H sulphate groups caused a low shift of absorption to lower frequencies with the disappearance of peak at 1643 cm^{-1} present in NC. The absorption peaks of all films (CMC and CN/CMC films) can be assigned to the stretching vibrations of O–H and C–H stretching of the $-\text{CH}_2$ groups at about 3400 cm^{-1} and 2920 cm^{-1} , respectively. The region from 1200 to 1650 cm^{-1} corresponds to the typical vibration modes of CMC associated with vibrations relating to the degree of order that is observed for typical cellulosic materials. A peak at 1430 cm^{-1} could be attributed to a reduced resonance of methylated residues from CMC after NC addition (asymmetric bending vibration of $-\text{CH}_3$). The band at 1319 cm^{-1} could be attributed to a more crystalline pattern in the conformation of the oxymethyl groups (bending vibration of $\text{O}-\text{CH}_2$) from cellulose induced by NC addition.

TGA and DTGA curves for different films CN/CMC: 0/100, 03/97, 05/95 and 10/90 are shown in Figure 8. The TGA curves show weight decreasing pattern of film due to the thermal degradation and the DTGA curves show the maximum decomposition temperature at each stage of thermal degradation. The CMC and NC/CMC bionanocomposites exhibited three major weight loss regions (Figure 7), a maximum decomposition occurred around 210 , 315 and 500°C for the initial, second and the decomposition processes, respectively. After, the evaporation of moisture, the first major decomposition process at a temperature of $140\text{--}275^\circ\text{C}$ was due to the evaporation of free hydroxyl groups present in both phases, NC and CMC, with the weight loss of about 19 wt%. The second major degradation occurred at around $280\text{--}350^\circ\text{C}$, which was due to the thermal degradation of the biopolymer chain. The complex decomposition behaviour of sulfonated NC was studied in literature, and the multiple decomposition steps are thought

to correspond to different degradation processes, that is., hydrolysis of the outer sulphated cellulose at a first step and decomposition of amorphous traces, followed by dehydration and depolymerisation [54, 55].

WVP of CMC materials is an important challenge for the use CMC in new applications. Figure 8 shows the effect of NC content on the WVP of the CMC films.

The values of WVP decreased sharply as the content of NC in the films increased. Indeed, the WVP values of CMC films were 116, 112, 109 and $106 (10^{-4}\text{ g/h.m.Pa})$ for films containing 0, 3, 5, and 10% NC, respectively. The low WVP value in the NC/CMC films can be explained by the removed zone amorphous during NC production, provoking an increase in the crystallinity and promotes a better dispersion of this nanoparticle in the polymeric matrix, producing a network of hydrogen bridges between the CMC chains and the NC. This arrangement increase the tortuosity in the NC/CMC films, leading to slower

Figure 6: FTIR spectra of a) CMC, b) NC/CMC: 03/97 (w/w), c) NC/CMC: 05/95 (w/w), and d) NC/CMC: 10/90 (w/w)

Figure 7: a) TGA and b) DTGA curves of CMC and its bionanocomposite films

diffusion processes and, hence, to a lower permeability [56]. In addition, the interactions of NC with CMC films components as well as the interactions between nanofibres may have enhanced the water vapour barrier [57]. Chang *et al.* and Azeredo *et al.* reported that the WVP of starch films [56] and chitosan films [58], respectively, improved significantly by the addition of cellulose nanoparticles.

The mechanical properties, as tensile strength (σ_b), elongation at break (ϵ_b) and Young's modulus (E) of neat CMC film and its bionanocomposite films with different filler content of NC were studied by simple tensile test. Figure 9 (a) shows the typical stress–strain curves of the all studied films. From these curves, the mechanical properties are extracted and presented as function of NC percentage.

The CMC films exhibit a Young's modulus of 1.39 GPa, an elongation at break of 19.17% and a tensile strength of 57.2 MPa. For NC/CMC bionanocomposite films, we note after the addition of NC into CMC polymer, an important increase of tensile strength and Young modulus. This could be due to the formation of a network between NC and CMC biopolymer. The network formed generates a strong interaction and hydrogen-bonding formation between the hydroxyl and sulphate groups of NC and the CMC polymer. The Young's modulus and tensile strength of the NC/CMC bionanocomposites increased by 60% from 1.39 to 2.29 GPa and by 47% from 57.2 to 119.3 MPa when

10 wt% NC was added. This results show the improvement of the mechanical properties of the NC/CMC bionanocomposite films compared to the neat CMC. The elongation at break of CMC is affected by the addition of NC, a decrease from 19.7% for unloaded CMC to 11.6% when 10 wt% NC is added. So the addition of NC improves the rigidity of the biopolymer.

Figure 8: WVP of NC/CMC bionanocomposites

Figure 9: a) Typical stress–strain curves, b) tensile strength, c) elongation at break, and d) Young's modulus of the neat CMC and the bionanocomposite films

This significant reinforcement impact on the mechanical properties of CMC polymer can be explained by the large surface area and the very high Young's modulus of NC. In addition, homogeneous dispersion of NC along with the favourable interfacial interactions between NC and the polymeric matrix are the key points to achieve improvement final tensile properties for the as-prepared bionanocomposite films, resulting in mechanically strong and flexible bio-plastic films.

4. Conclusion

NC prepared from Alfa-F, one of the most abundant sources of cellulose in Northern Morocco, has properties similar to those of vegetal NC. NC was isolated from Alfa-C fibre using H₂SO₄ hydrolysis method and the NC was used to prepare NC/CMC bionanocomposite films with varying concentration of the NC. CN/CMC bionanocomposite films were prepared in water by a casting method. The results revealed that the film properties, such as water vapour barrier and mechanical properties, have significantly improved with lower amount of the NC inclusion. Remarkable increase in tensile properties is clearly visible, especially for the ultimate tensile strength and the Young modulus. These properties can make NC from Alfa-F, a potential material for the preparation of a new class of bionanocomposite films.

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