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Characterization of films made with chayote tuber and potato starches blending with cellulose nanoparticles

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ABSTRACT

The aim of this study was to characterize chayotextle starch films reinforced with cellulose (C) and cellulose nanoparticle (CN) (at concentrations of 0.3%, 0.5%, 0.8% and 1.2%), using thermal, mechanical, physicochemical, permeability, and water solubility tests. C was acid-treated to obtain CN. The films were prepared by casting; potato starch and C were used as the control. The solubility of the starch films decreased with the addition of C and CN compared with its respective film without C and CN. No statistical difference ($\alpha = 0.05$) was found in the films added with different concentrations of C and CN. In general, the mechanical properties were improved with the addition of C and CN, and higher values of tensile strength and elastic modulus were determined in the films reinforced with CN. The melting temperature and enthalpy increased with the addition of C and CN, and the values of both thermal parameters were higher in the films with CN than with C; the enthalpy value of the film decreased when the concentration of C or CN increased in the composite. Low concentration of C and CN is better distributed in the matrix film. The addition of C and CN in the starch films improved some mechanical, barrier, and functional properties.

1. Introduction

Nowadays, a large number of research studies are focusing on solving the problems of plastic waste to obtain environmentally friendly material. Among the many kinds of candidates of polymers friendly with the environment, starch is one of the most promising materials for biodegradable plastic because it is a versatile biopolymer with immense potential and can be obtained at a low price for use in non-food industries (Choi, Kim, & Park, 1999; Mohanty, Misra, & Hinrichesen, 2000). Starch has been investigated widely for its use in the potential manufacture of products such as water-soluble pouches for detergents and insecticides, flushable liners and bags, and medical delivery systems and devices (Fishman, Coffin, Konstance, & Onwulata, 2000). The production of biodegradable and edible films from polysaccharides adds value to the low cost raw materials and can play an important role in food preservation (Avérous, Fringant, & Moro, 2001). In this sense, the use of new sources of starch such as those obtained from the chayote tuber (chayotextle) (Hernandez-Uribe, Agama-Acevedo, Gonzalez-Soto, Bello-Pérez, & Vargas-Torres, 2011), fruits (Espinosa-Solis, Sanchez-Ambriz, Hamaker, & Bello-Perez, 2011), and pulses (Hoover, Hughes, Chung, & Liu, 2010) could provide interesting data in the elaboration of biofilms. Recently, chayote starch has been isolated from a variety growing in the center of the country (Hidalgo State) due to the fact that the tuber contains an important amount of starch (60% dry basis), and the use of this tuber is limited to local consumers. However, high production of chayote tuber (approximately 100 452 tonns/year) has been reported (Hernandez-Uribe et al., 2011). Before this study, only one report of starch isolated from chayote was reported with limited information available on starch yield and its structural and physicochemical features (Jiménez-Hernández, Salazar-Montoya, & Ramos-Ramírez, 2007).

Several studies have reported the use of starches from different sources to prepare films by melt processing or casting with different properties, and they indicated that this polysaccharide is promising material in this regard (Jiménez, Fabra, Talens, & Chiralt, 2012; Mali, Sakanaka, Yamashita, & Grossmann, 2005). However, films formed from starch are brittle and difficult to handle. For this reason, the addition of water or other plasticizers such as sorbitol and glycerol has been done to improve some mechanical properties of the films (Jiménez et al., 2012). Unfortunately, plasticizers generally decrease the film water vapor permeability (Jiménez et al., 2012; Muller, Yamashita, & Laurindo, 2008). In order to improve

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starch-based film characteristics, the use of natural fibers such as cellulose and cellulose nanocrystals as a suitable reinforcing component has increased. There are studies that report an increase in the mechanical and thermal properties of the films for addition of these cellulose particles because they have a similar chemical structure to that of starch (Chang et al., 2010; Jiménez et al., 2012; Kaushik, Singh, & Verma, 2010; Lu, Weng, & Cao, 2006). In the same sense, Muller, Laurindo, and Yamashita (2009) studied the effect of the addition of cellulose fibers on starch-based films, reporting that the increase of cellulose fibers decreased the water vapor permeability, solubility, and water diffusion compared with starch films without fibers. Similar behavior was reported in starch films added with nanoparticles (Chang et al., 2010). These results are related with the introduction of a tortuous path for water molecules to pass through the matrix film due to the presence of the nanoparticles (Kristo & Biliaderis, 2007).

The objective of this work was to evaluate the addition of cellulose and cellulose nanocrystals in films made with chayotextle and potato starch, and to determine their effect on the mechanical properties, water solubility, thermal, and water vapor permeability.

2. Materials and methods

2.1. Materials

Chayote (*Sechium edule* Sw.) tubers were collected in Tulancingo, Hidalgo, Mexico. Potato starch (PS) was purchased from KMC Kartoffelmelcentralen Amba (Brande, Denmark) and characterized by Palma-Rodriguez et al. (2012). They reported a granule size between 10 and 100 μm, amylose content of 28.5%, crystallinity percentage of 29.31, and B-type X-ray diffraction pattern. Cotton cellulose with catalog number S3504 and Type 20, 20 μm, was purchased from Sigma–Aldrich de Mexico (Toluca, State of Mexico, Mexico).

2.2. Starch isolation

The starch was isolated according to the methodology reported (Flores-Gorosquera et al., 2004). The tubers were cut into 2 × 2 cm cubes and immediately macerated at low speed in a blender (500 g root: 500 g tap water) for 2 min. The homogenate was consecutively sieved and washed through screens number 50, 100, 200, 270 and 325 US mesh, until the washing water was clean and was pelleted overnight and decanted. This material was dried in convection oven at 35 °C overnight. Dry starch was ground in a blender until obtain a powder, and it's was passed through a standard 100 mesh sieve and stored in sealed container until required. Chayote starch presented a purity of 89%, granule size between 10 and 25 μm, amylose content of 26%, and B-type X-ray diffraction pattern (Hernandez-Uribe et al., 2011).

2.3. Preparation of cellulose nanoparticle

Cellulose was subjected to acid hydrolysis for producing the cellulose nanoparticle according to the procedure of Morán, Álvarez, Cyras, and Vázquez, (2007). The acid hydrolysis was carried out with sulphuric acid (H_2SO_4) solution 60 wt.% at 45 °C for 30 min under continuous agitation. The cellulose nanoparticle was dried in convection oven at 35 °C overnight and was ground using a laboratory blender and sieved in 235 US meshes.

2.4. Characterization of the cellulose nanoparticle

Transmission electron micrographs of cellulose nanoparticle were taken with a transmission electron microscope (JEOL – JEM1010, Japan), with an acceleration voltage of 80 KV. The Cellulose nanoparticle was deposited from an aqueous dilute dispersion (1:10) on a micro grid covered with a thin carbon film (~200 nm). This was subsequently stained with a 1.5% uranyl acetate solution to enhance the microscopic resolution.

2.5. Film preparation

Films were prepared with a concentration of 4% of chayote tubers starch or potato starch (w/w, dry basis), 2% of glycerol (w/w), cellulose or cellulose nanoparticle and water (170 mL). For details of the formulation, see Table 1. The solution was placed in a mini-reactor (300 mL) and stirred at 125 rpm with a Lightnin Lab Master SPX-Mixer. The dispersions were heated at 90 °C for 10 min. The films were prepared by casting and the suspensions were poured in glass container (11 cm × 11 cm of length and width respectively, with 3 mm thickness). The starch suspensions were dried at 40 °C in an oven for 24 h. Afterward, the films were removed from the glass container and stored at 25 ± 2 °C and a relative humidity (RH) of 57%, which was provided by a saturated solution of NaBr.

2.6. Mechanical properties

The mechanical measurements consisted of a test to determine the tensile strength (TS), percentage elongation at break (%E), and Elastic modulus (EM). The mechanical properties (TS, %E, and EM) were obtained from force versus deformation curves according to the ASTM standard method D882-95a (ASTM, 1995a, 1995b); with a texture analyzer equipped with 50 kg load cell (TA-HDi) (Stable Micro Systems, Haslernere, UK, and Texture Technologies Corp., Scarsdale, NY). For the tests of tension, films were cut into rectangles 7 cm long and 1 cm wide. The rectangles were maintained for at least 3 days in a desiccator containing a saturated NaBr solution (57% RH). The separation among the gauges was 6 cm. The ends of the film were fixed in each of the subjection gauges. The speed of deformation was 24 mm/min. The thickness of the films was assessed with a manual micrometer (Mitutoyo Co., Kobe, Japan) in 5 random positions of the film. This average value was used to calculate the cross-sectional area of the films (the area was equal to the thickness multiplied by the width of each film).

2.7. Thermal analysis

The thermal properties of films, such as temperature and enthalpy of fusion were measured using a differential scanning calorimeter (DSC, TA Instrument, 2010, New Castle, NJ, USA) previously calibrated with indium. The samples (1–5 mg) were weighed (dry basis) on aluminum pan. The pans were sealed and scanned at a heating rate 10 °C/min with temperature ranging from 25 to 260 °C. The fusion temperature (T_m) of transition and transition enthalpy (ΔH) were obtained directly from the analysis with the software TA Instruments, 4.4A version.

2.8. Water vapor permeability

Water vapor permeability (WVP) test was conducted using ASTM standard method E 96-95 (ASTM, 1995a, 1995b), with some modifications. Each sample was sealed over a circular opening of 0.000282 m^2 in a permeation cell that was stored at 25 °C in a desiccator 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 desiccator. Water vapor transport was determined from the weight gained on the permeation cell. After the steady-state conditions were reached (ca. 2 h). Eight weight measurements were taken over 8 h. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by

Table 1
Formulations of blends containing starch, cellulose, cellulose nanoparticle and glycerol (% wet-weight basis).

Sample identification	Chayotextle starch (CS)	Potato starch (PS)	Cellulose (C)	Cellulose nanoparticle (CN)	Glycerol
Control-PS		4			2
PS-0.3C		4	0.3		2
PS-0.5C		4	0.5		2
PS-0.8C		4	0.8		2
PS-1.2C		4	1.2		2
PS-0.3CN		4		0.3	2
PS-0.5CN		4		0.5	2
PS-0.8CN		4		0.8	2
PS-1.2CN		4		1.2	2
Control-CS	4				2
CS-0.3C	4		0.3		2
CS-0.5C	4		0.5		2
CS-0.8C	4		0.8		2
CS-1.2C	4		1.2		2
CS-0.3CN	4			0.3	2
CS-0.5CN	4			0.5	2
CS-0.8CN	4			0.8	2
CS-1.2CN	4			1.2	2

0.3, 0.5, 0.8, and 1.2 are the concentrations of C and CN.

linear regression ($r^2 > 0.98$), and the water vapor transmission rate was calculated from the slope of the straight line (g/s) divided by the cell area (m^2). After the permeation tests, the film thickness and WVP (g/Pa/s/m) were measured.

2.9. Film solubility in water (FSW)

Samples of 2 cm × 3 cm were cut and stored 7 days in a desiccator (approximately 0% RH). The samples were weighed and placed in glass vessels with 80 mL of deionized water. The samples were kept with constant agitation for 1 h at 25 °C. The same process was realized by 60 °C. Immediately the samples were dried at 60 °C for 2 h.

The percentage of the soluble total material was calculated as follows:

$$\text{Solubility}(\%) = \frac{\text{initial dry weight} - \text{final dry weigh}}{\text{initial dry weight}} \times 100$$

2.10. Statistical analysis

Experiments were arranged in a completely randomized design. An analysis of variance (ANOVA) was carried out with the statistical program Sigma-Stat version 11.0 (Fox, Shotton, & Ulrich, 1995). Media comparison was done by Tukey's multiple test ($\alpha = 0.05$).

3. Results and discussion

3.1. Morphological characterization of the cellulose nanoparticle

Fig. 1 shows the cellulose nanoparticles (CN) with sizes between 5 and 15 nm. This microscopic analysis by transmission electron microscopy (TEM) showed that the acid treatment reduced the commercial cellulose of 20 μm in length. De Teixeira et al. (2009) reported similar values in the sizes of CN of 2–11 nm. This reduction in size of the cellulose is due to the fact that the amorphous parts of the cellulose were removed during the acid hydrolysis, leaving intact the crystalline parts of smaller size (De Azeredo, 2009).

3.2. Mechanical properties

The tensile strength (MPa), elastic modulus (MPa) and elongation at break (%) values of the films are shown in Figs. 2–4, respectively. Films elaborated with chayotextle and potato starch showed an increased in tensile strength (TS) (Fig. 2) and elastic modulus (EM) (Fig. 3) from the addition of C and CN, and the values increased when the concentration of both cellulose materials increased in the composite. Higher values of TS were found in the films added with CN than with C, and no differences were observed in the films made with the different starches with the formulation. The chemical structure of C and starch is similar. When they are mixed to produce a filmogenic solution, interactions among the OH groups of both polymers are produced by hydrogen bridges, producing a rigid network that increases the TS (Curvelo, De Carvalho, & Agnelli, 2001; Gáspar, Benkó, Dogossy, Réczey, & Czigány, 2005; Lu et al., 2006; Ma, Yu, & Kennedy, 2005; Muller et al., 2009). Films added with CN had the highest TS values; this pattern could be due to the fact that higher reinforcement is produced for the higher contact surface between the CN and the polysaccharide chains for the nanometer sizes (5–15 nm) of CN, increasing the hydrogen bonds

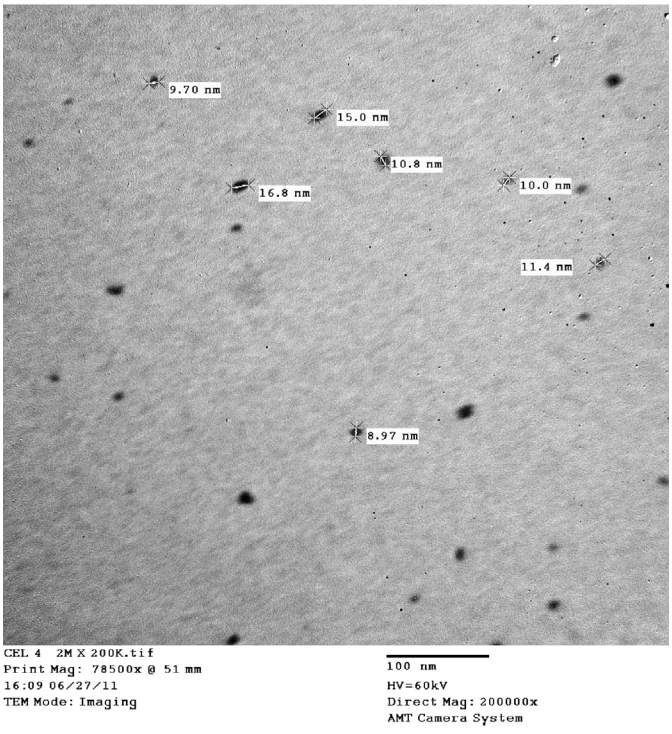

Fig. 1. Transmission electron micrographs of cellulose nanoparticle.

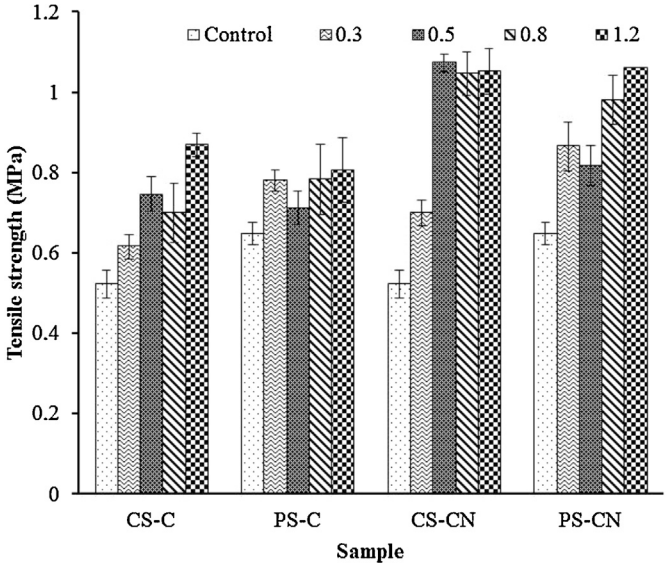

Fig. 2. Effect of cellulose and cellulose nanoparticle content on the tensile strength of chayotextle and potato starch films. Average of ten replicates ± standard deviation. For sample identification, see Table 1.

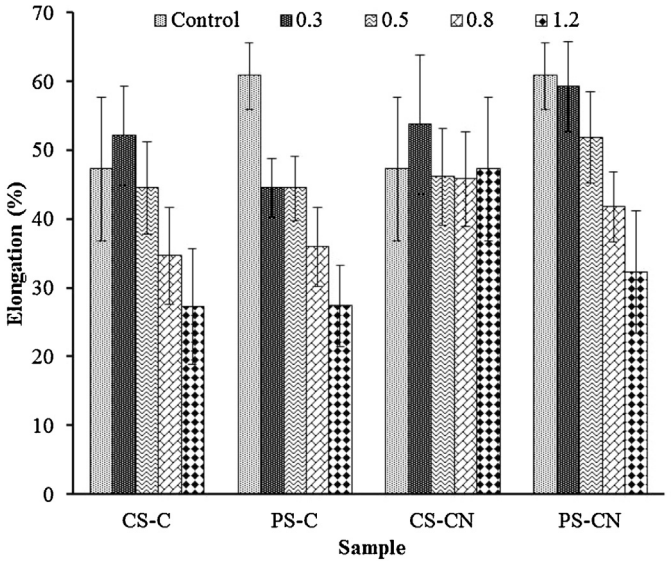

Fig. 4. Effect of cellulose and cellulose nanoparticle content on the elongation at break of chayotextle and potato starch films. Average of ten replicates ± standard deviation. For sample identification, see Table 1.

in the polymeric matrix of the film (Bras et al., 2010; Chang et al., 2010; De Teixeira et al., 2011; Siqueira, Bras, & Dufresne, 2009).

In general, the addition of C at the highest concentration studied (0.8 and 1.2%) to both starches decreased the elongation (Fig. 4) of the composite films. A similar pattern was found for potato starch with CN, and the elongation values of these films were similar to their counterpart with C. Films elaborated with CS and added with CN presented similar elongation values, which means that the concentration of CN did not modify this mechanical property. Thus, at the highest concentrations (0.8 and 1.2%) of CN, the elongation values were higher than their counterpart with C, indicating that more rigid films were obtained. The higher rigidness of the films with CN can be attributed to the higher dispersion of the nanoparticles in the matrix of the film due to the higher hydrogen bridges with the OH groups of the starch (Lu, Weng, & Cao, 2006; Dufresne, 2008; Angellier, 2005, 2006). The films of PS and CS added with C or CN showed a similar behavior in the elongation values, a pattern which is related to the similar physicochemical and molecular characteristics of both starches (Hernandez-Uribe et al., 2011).

3.3. Water vapor permeability (WVP)

Fig. 5 shows the water vapor permeability of composite films of PS and CS with CN and C. Control samples of both starches showed similar WVP values. The addition of C and CN decreased the WVP in the composite films, compared with in the control films. No appreciable difference was found in the WVP values between both starches at the different concentrations evaluated for the same cellulosic materials, but the films with CN presented a lower WVP value than those with C. The low WVP value in the starch films with CN can be due to their nanometric size, which increases the surface-volume ratio and promotes a better dispersion of this nanoparticle in the polymeric matrix, producing a network of hydrogen bridges between the starch chains and the CN. This arrangement produces a more tortuous path for the water molecules, decreasing their diffusion through the film (Bras et al., 2010; De Azeredo, 2009; Dufresne,

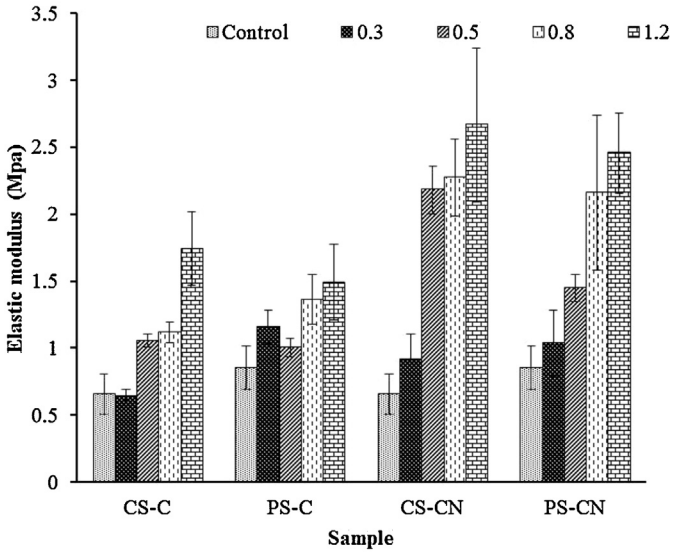

Fig. 3. Effect of cellulose and cellulose nanoparticle content on the elastic modulus of chayotextle and potato starch films. Average of ten replicates ± standard deviation. For sample identification, see Table 1.

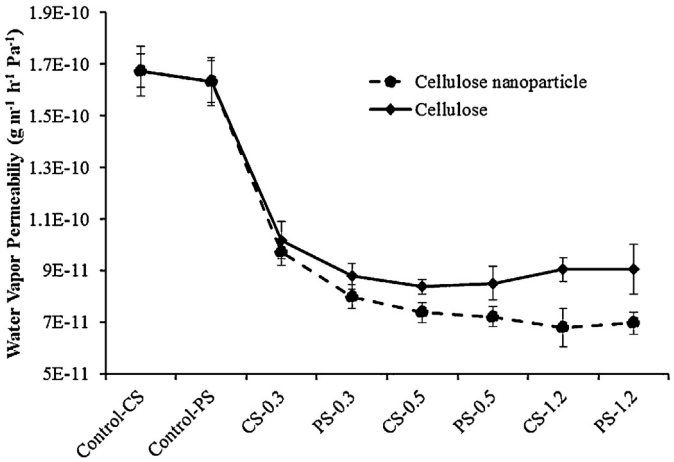

Fig. 5. WVP of chayotextle and potato starch films added with cellulose and cellulose nanoparticle at different concentrations. Average of three replicates. For sample identification, see Table 1.

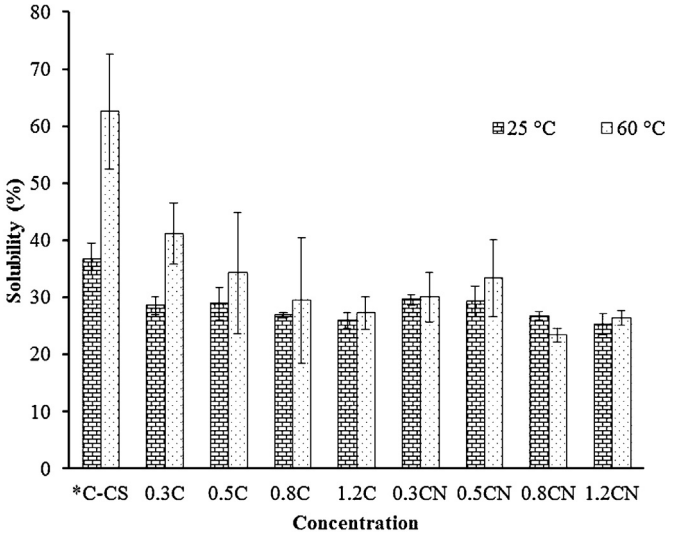

Fig. 6. The water solubility of chayotextle starch films as a function of cellulose and cellulose nanoparticle content. Average of three replicates ± standard deviation. For sample identification, see Table 1. *C = control.

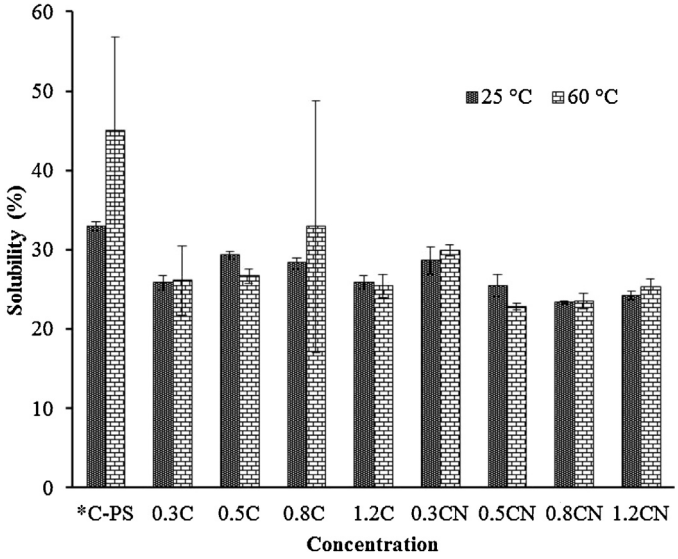

Fig. 7. The water solubility of potato starch films as a function of cellulose and cellulose nanoparticle content. Average of three replicates ± standard deviation. For sample identification, see Table 1. *C = Control.

Dupeyre, & Vignon, 2000; Kristo & Biliaderis, 2007; Svagan, Mikael, & Lars, 2009). In addition, the cellulose is less hydrophilic than starch, due to its higher crystallinity and compact microfibrillar arrangement, making it more hydrophobic (Bras et al., 2010; Curvelo et al., 2001). De Azeredo (2009) reported that during CN production, the amorphous zone is removed, provoking an increase in the crystallinity of this nanoparticle, which explains the reduction rate and the difference in the WVP values in both composite films. A similar pattern was found in starch films added with cellulose nanoparticles (Chang et al., 2010).

3.4. Water solubility of films

The control films of CS presented slightly higher water solubility than their counterpart of PS, and in both control films the water solubility increased to a higher temperature (Figs. 6 and 7). However, the addition of C or CN at different concentrations in the starch films did not change the water solubility, indicating that no effect for the starch, particle type, or temperature was found. It is well known that starch is non-soluble in water at an ambient temperature, but when a filmogenic solution is prepared to make the films, a disorganization of the semicrystalline structure is produced, increasing the solubility. However, the addition of C or CN (with a crystalline nature) in the film promotes interactions among the OH groups of both polysaccharides, producing more crystalline zones that reduce the water solubility (Amash & Zugenmaier, 2000; De Azeredo, 2009; Ma, Jian, Chang, & Yu. 2008; Muller et al., 2009). However, the concentrations of C and CN used in the film preparation did not promote a major increase in the crystalline zones in the composite films.

3.5. Thermal properties

Table 2 shows the melting temperature (T_m) and the melting enthalpy (ΔH) of the composite films. In general, a higher T_m temperature was recorded for CS than for PS films, and those films with CN presented a higher T_m than their counterpart with C. Also, the addition of C and CN increased the T_m, but no important difference was found at the different C and CN concentrations. The increase in the T_m of the composite films with C and CN is attributed to the crystallinity of both cellulosic materials, which promotes interactions between both polysaccharides, increasing the crystalline arrangement in the composite films (Amash & Zugenmaier, 2000; Kaushik et al., 2010; Ma et al., 2005; Muller et al., 2009). The highest T_m values recorded in the films with CN are due to the small size of this nanoparticle, which increase the contact area between both polysaccharides and consequently their ordering, which requires a higher temperature to disorganize. The addition of C and CN increased the enthalpy value of the composite films; the values were higher for CS than for PS, and for CN than for C. This pattern can be related to the higher gelatinization enthalpy determined in CS

Table 2
Thermal properties of chayotextle and potato starch films with different cellulose and cellulose nanoparticle contents[a].

[b]Sample	T_m (°C)		ΔH (J/g)	
	CS	PS	CS	PS
Control	89.40 ± 0.58[a]	84.23 ± 0.42[a]	28.25 ± 1.44[a]	2.21 ± 0.87[a]
0.3-C	116.28 ± 0.39[b]	104.12 ± 0.30[b]	66.99 ± 0.35[b]	51.77 ± 0.65[b]
0.5-C	113.66 ± 0.77[c]	114.19 ± 0.61[c]	51.09 ± 0.68[c]	44.26 ± 0.20[c]
1.2-C	117.54 ± 0.91[b]	106.50 ± 1.11[d]	46.64 ± 0.57[d]	34.81 ± 0.31[d]
0.3-CN	124.24 ± 1.12[d]	130.33 ± 0.86[e]	121.07 ± 0.44[e]	91.79 ± 0.69[e]
0.5-CN	124.14 ± 0.48[d]	123.87 ± 0.89[f]	112.54 ± 0.50[f]	46.27 ± 0.56[f]
1.2-CN	121.36 ± 0.50[e]	120.63 ± 0.76[g]	97.70 ± 0.54[g]	48.24 ± 0.70[g]

Means with different letters within a column indicate significant differences ($P \leq 0.05$).
T_m = melting temperature and ΔH = melting enthalpy.
[a] For sample identification see, Table 1.
[b] Average of three replicates ± standard deviation.

than in PS (Hernandez-Uribe et al., 2011). The ΔH value decreased when the concentration of CN and C increased for both starches. Similar behavior was reported by Kaushik et al. (2010), reporting values of 197 J/g, 190 J/g, and 169 J/g for starch films added with 5%, 10%, and 15% of cellulose nano-fibers, respectively. The arrangement of the polysaccharide chains with the addition of C and CN did not produce an ordering in the double helices due to the steric hindrances between polysaccharides, and the effect was higher when the concentration of both cellulosic materials increased in the composite films.

4. Conclusions

The addition of cellulose nanoparticles (CN) reinforced the film matrix, improving the tensile strength, the elastic modulus, and elongation at break. The mechanical properties of the starch films with CN were better than those for films with cellulose (C). Starch films added with CN presented the lowest water vapor permeability values. The addition of CN increased the melting temperature of the starch films. The films made with tuber starches blended with CN can have an alternative use as packing materials.

Conflict of interest statement

The authors declare that no conflict of interest exist related with this publication.

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