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Edible films from alginate-acerola puree reinforced with cellulose whiskers

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ABSTRACT

Fruit purees, combined or not with polysaccharides, have been used in some studies to elaborate edible films. The present study was conducted to evaluate tensile properties and water vapor barrier of alginate-acerola puree films plasticized with corn syrup, and to study the influence of cellulose whiskers from different origins (cotton fiber or coconut husk fiber, the latter submitted to one- or multi-stage bleaching) on the film properties. The whiskers improved the overall tensile properties (except by elongation) and the water vapor barrier of the films. The films with coconut whiskers, even those submitted only to a one-stage bleaching, presented similar properties to those of films with cotton whiskers, despite the low compatibility between the matrix and the remaining lignin in coconut whiskers. This was probably ascribed to a counterbalancing effect of the higher aspect ratios of the coconut whiskers.

1. Introduction

Edible films from several film-forming biopolymers have been studied and used in food packaging to reduce the need for non-biodegradable petroleum-derived polymers. The elaboration of edible films from fruit purees has been recently studied (Azeredo et al., 2009; McHugh & Senesi, 2000; Rojas-Graü et al., 2006, 2007; Senesi & McHugh, 2002). Such application of fruit purees is related to the presence of film-forming polysaccharides in their composition, such as pectin and starch (Kaya & Maskan, 2003), and is an interesting way of combining the mechanical and barrier properties of those polysaccharides with the sensory and nutritional properties of the fruit.

Biopolymers used in edible films usually have poor mechanical and barrier properties when compared to petroleum-based polymers. Several composites have been developed by adding reinforcements (fillers) to biopolymers to enhance their performance and applicability. Fillers with at least one nano-sized dimension (nanofillers or nanoreinforcements) have better interfacial adhesion with the polymer matrices, when compared to the respective micro/macroscopic reinforcements. A uniform dispersion of nanofillers leads to a very large matrix/filler interfacial area, changing the molecular mobility, the relaxation behavior, and the consequent thermal and mechanical properties of the resulting nanocomposite (Ludueña, Alvarez, & Vasquez, 2007). High aspect ratio fillers, because of their high specific surface area, are particularly interesting, providing great reinforcing effects (Azizi Samir, Alloin, & Dufresne, 2005; Dalmas, Cavaillé, Gauthier, Chazeau, & Dendievel, 2007).

Cellulose crystals with nano-sized diameters, commonly referred to as whiskers, can be isolated from cellulose microfibrils (Azizi Samir et al., 2005; Azizi Samir, Alloin, Sanchez, & Dufresne, 2004). They have been used to elaborate low cost, lightweight, and very strong nanocomposites (Azizi Samir et al., 2005; Bhatnagar & Sain, 2005; Helbert, Cavaillé, & Dufresne, 1996). Cotton fiber has been one of the cellulose sources of choice for extraction of whiskers, because of its very high cellulose contents. Cellulose accounts for more than 95 g/100 g of the dry weight of mature cotton fiber, and the cotton fiber wall contains no lignin (Kim & Triplett, 2001). On the other hand, unripe coconut husk is an abundant and cheap agroindustrial byproduct in Brazil, which requires new end uses (Rosa et al., 2009). Coconut husk fiber is rich in lignin, which hinders fiber separation by acid hydrolysis; so, partial delignification (bleaching) of coconut husk fiber is required in order to help fiber separation and further whisker extraction (Rosa et al., 2010).

The objectives of this study were: (a) to characterize an edible film obtained from acerola puree and alginate plasticized with corn

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Table 1
Dimensions of CW as determined from TEM images.

Type	Diameter (D, nm)	Length (L, nm)	Aspect ratio (L/D)
CcO-CW	5.5 ± 1.5	194 ± 70	39 ± 14
CcM-CW	5.3 ± 1.3	210 ± 78	42 ± 16
Ct-CW	12.0 ± 4.0	114 ± 55	10 ± 5

CcO-CW: cellulose whiskers from coconut fiber submitted to one-stage bleaching; CcM-CW: cellulose whiskers from coconut fiber submitted to multi-stage bleaching; Ct-CW: cellulose whiskers from cotton fiber. Values expressed as means ± standard deviations.

syrup, in terms of tensile properties and water vapor barrier; and (b) to evaluate the effects of incorporation of cellulose whiskers (CW) from cotton or, alternatively, from coconut husk fibers submitted to different bleaching levels, on tensile and water vapor barrier of films.

2. Materials and methods

For the alginate-acerola puree (AAP) film formulation, 100 g of acerola puree (AliPolpa, Aquiraz, CE, Brazil, with a total solid content of 6.4 g/100 g) were added with 1.6 g sodium alginate (Grinsted® FD175, provided by Danisco Brasil Ltda.) and 50 mL of distilled water. Four grams of corn syrup (Karo, Unilever, São Paulo, SP, Brazil) was added as both plasticizer and sweetener, since acerola films without a sweetener would be too acid. The proportions of the ingredients were based on preliminary tests.

Cellulose whiskers from cotton fibers (Ct-CW) were extracted by a 90-min acid hydrolysis, according to Cranston & Gray (2006) and adapted by Rosa et al. (2010). A sulfuric acid solution (64 g/100 mL in water) was used, with a fiber-to-acid solution ratio of 1 g:10 mL. CW from coconut husk fibers were extracted by a 120-min hydrolysis preceded by one- (CcO-CW) or multi-stage bleaching (CcM-CW). Bleaching was carried out according to Wise, Murphy, and D'Addieco (1946), one- and multi-stage bleaching being defined by Rosa et al. (2010). Briefly, for one-stage bleaching, 5 g of dried fibers were heated (60°–70 °C) in 150 mL of water containing 1.5 g $NaClO_2$ and 8–10 drops of glacial acetic acid. The suspension was periodically stirred for 1 h, cooled in an ice bath, filtered and washed in cold water. For multi-stage bleaching, this procedure was repeated three more times under the same conditions. In the end, the bleached pulps were treated with 0.05 mol equi/L nitric acid solution for 1 h at 70 °C, sieved in a 120 μm mesh sieve and washed extensively in water. The CW suspensions were then concentrated to 4–5 g/100 g.

The dimensions of the CW (diameter, length, and the resulting aspect ratio) were measured from TEM images, carried out by using a CM12 scanning-transmission electron microscope (STEM, FEI Co., Inc., Hillsboro, OR, USA) operating in the bright field mode at 80 kV (Rosa et al., 2010). Digital images were captured with the STEM's associated XR41 CCD camera system (AMT, Danvers, MA, USA). Data were collected using Image Pro Plus 6.3 (Media Cybernetics, Inc., Bethesda, MD, USA) and analyzed using Microsoft Excel 2003.

Nine nanocomposite films were produced by adding each of three concentrations (5, 10 or 15 g/100 g, on a dry basis) of each of the three types of CW suspensions (Ct-CW, CcO-CW or CcM-CW) to the AAP film formulation. The concentrations were defined as the ratio between the solid matter content of the CW suspensions and the solid matter content of films (including alginate, acerola puree, and corn syrup).

For all film formulations, the mixtures were firstly homogenized for 60 min at 200 rpm with a magnetic stirrer (Fisatom 752A, Aaker Solutions Ltda., Porto Alegre, Brazil) at 50 °C, and then in a cell disruptor (DES500, Unique Group, Indaiatuba, SP, Brazil) for 18 min at 90 W. The mixture was vacuum degassed by using a vacuum pump V-700 (Büchi Labortechnik AG, Flawil, Switzerland) at 30 mbar for 45 min, then cast on 0.3 × 0.3 m glass plates and leveled with a draw-down bar to a thickness of 1.2 mm. The films were placed on a lab bench (24 °C ± 1 °C, RH 76% ± 2%) for 24 h to dry. A test was carried out by immersing films in $CaCl_2$ solutions with different concentrations (2–4 g/100 mL) in order to obtain crosslinked sodium alginate with better water resistance, but the resulting films were salty, so this step was eliminated. Then, samples were cut and detached from the surface. Prior to film properties determination, the detached, free-standing films were conditioned for 24 h at 25 °C in desiccators containing $MgNO_3$ saturated solution (50% RH). The water vapor permeability (WVP) determination, with eight replicates, was based on the method E96-80 (ASTM, 1989) at 24 °C and 85% RH, using silica gel as the desiccant material, and at least seven measurements within a 24-hour period. Tensile properties of 100 mm × 15 mm film strips (with five replicates) were measured according to D882-97 (ASTM, 1997), in an Emic DL 2000 Universal Testing Machine with a load cell of 500 N, initial grip separation of 0.05 m, and crosshead speed of 10 mm/min (1.67×10^{-4} m/s). Five replicates were used for each treatment. Analyses of variance (ANOVA) were carried out for all responses, in order to verify which of them were significantly affected by CW type and/or concentration. Depending on the results for each response, appropriate difference tests were applied to study differences among CW concentrations (Tukey tests) and/or CW types (Dunnett tests).

3. Results and discussion

The plain AAP film presented the following properties: tensile strength, 3.16 MPa; elongation at break, 28.26%; Young's modulus, 15.35 MPa; water vapor permeability, 3.19×10^{-13} kg m Pa^{-1} s^{-1} m^{-2}. The strength and modulus of the films were higher when compared

Table 2
F values resulting from ANOVA for physical properties of the films.

Properties	Source of variation					
	CW type		CW concentration		CW type × concentration interactions	
TS	*F*	1.15	*F*	50.64	*F*	0.30
	p	0.33	*p*	<0.01	*p*	0.93
EB	*F*	0.06	*F*	54.10	*F*	0.31
	p	0.94	*p*	<0.01	*p*	0.93
YM	*F*	0.13	*F*	151.11	*F*	0.34
	p	0.88	*p*	<0.01	*p*	0.91
WVP	*F*	2.61	*F*	65.49	*F*	0.55
	p	0.08	*p*	<0.01	*p*	0.77

TS: tensile strength; EB: elongation at break; YM: Young's modulus; WVP: water vapor permeability.

Table 3
Tensile strength (MPa) of films (means ± standard deviation).

CW (g/100 g)	CW types		
	Ct-CW	CcO-CW	CcM-CW
0	(3.16 ± 0.61) b	(3.16 ± 0.61) b	(3.16 ± 0.61) b
5	(3.63 ± 0.07) b	(3.86 ± 0.23) b	(3.29 ± 0.49) b
10	(4.72 ± 1.42) ab	(5.19 ± 0.60) a	(4.94 ± 0.47) a
15	(5.91 ± 0.45) a	(6.10 ± 0.31) a	(5.65 ± 0.40) a

Ct-CW: cellulose whiskers from cotton fiber; CcO-CW: cellulose whiskers from coconut fiber submitted to one-stage bleaching; CcM-CW: cellulose whiskers from coconut fiber submitted to multi-stage bleaching. Values at the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$).

Table 5
Young's modulus (MPa) of films (means ± standard deviation).

CW (%)	CW types		
	Ct-CW	CcO-CW	CcM-CW
0	(15.35 ± 1.68) b	(15.35 ± 1.68) c	(15.35 ± 1.68) d
5	(39.83 ± 10.59) a	(38.25 ± 3.06) b	(38.30 ± 3.67) c
10	(46.70 ± 5.57) a	(45.74 ± 4.10) a	(43.45 ± 2.27) b
15	(48.10 ± 3.60) a	(50.58 ± 3.12) a	(50.16 ± 1.82) a

Ct-CW: cellulose whiskers from cotton fiber; CcO-CW: cellulose whiskers from coconut fiber submitted to one-stage bleaching; CcM-CW: cellulose whiskers from coconut fiber submitted to multi-stage bleaching. Values at the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$).

to those observed for mango (Azeredo et al., 2009) but lower than those reported for peach (McHugh & Olsen, 2004), alginate-apple (Rojas-Graü et al., 2007) and mango (Sothornvit & Rodsamran, 2008) fruit puree films. The water vapor permeability of the AAP film was lower than those reported for other fruit-based films in all above-mentioned studies, which apparently suggests a better moisture barrier of the film in the present study when compared to those, although the test was conducted under different conditions – for example, an air-circulating system was not included as in the previous studies. Then, some caution is needed when comparing the present results with those mentioned in the beginning of this paragraph, since the lack of air circulation may retard moisture transfer, thus possibly leading to an underestimation of the WVP.

The dimensions and aspect ratios of the CW incorporated to the nanocomposite films are presented in Table 1. The CW from coconut fibers had lower diameter and higher lengths when compared to those obtained from cotton fibers, and their resulting aspect ratio was about four times higher.

The tensile properties and WVP were not significantly affected by CW type or CW type × concentration interaction (Table 2). So, the effects of CW from coconut husk fiber (submitted to one- or multi-stage bleaching) on tensile properties and water vapor permeability of the films were similar to those of CW from cotton fiber. The films with cotton CW had probably a better filler-matrix compatibility, because of the absence of lignin in the cotton fiber wall (Kim & Triplett, 2001). Although lignin has been reported to improve matrix-fillers adhesion and mechanical properties of hydrophobic matrices such as rubber (Alexy et al., 2008) and poly(lactic acid) (Graupner, 2008), this seems not to be true for hydrophilic matrices such as alginate-acerola puree, because of the relatively high hydrophobicity of lignin. In fact, Baumberger et al. (1998) reported incompatibility between lignin and a starch matrix. In this study, the incompatibility of the (hydrophilic) matrix and the remaining lignin present in CW from coconut fibers was expected to impair the film tensile and barrier properties. On the other hand, the much higher aspect ratios of the CW from coconut husk fibers probably counterbalanced those negative effects.

Differently from CW type, the effect of the CW concentration on all properties was highly significant (Table 2). So, Tukey tests were carried out to study the differences among films with different CW concentrations (Tables 3–6).

Tukey tests for tensile properties (Tables 3–5) indicate that increasing the concentration of any CW suspension resulted in films with increased tensile strength and Young's modulus, but lower elongation at break. The most dramatic changes occurred in modulus, which increased by 200% or more by incorporation of CW at 10–15 g/100 g. Other authors have reported remarkable effects of CW on modulus of polymer matrices (Bhatnagar & Sain, 2005; Helbert et al., 1996; Ljungberg et al., 2005). According to Helbert et al. (1996), such a great effect is ascribed not only to the geometry and stiffness of the whiskers, but also to the formation of a fibril network within the polymer matrix, the cellulose fibers being probably linked through hydrogen bonds. Some studies have described the effects of CW on improving both modulus and tensile strength (Ten, Turtle, Bahr, Jiang, & Wolcott, 2010) but hindering elongation of films (Jiang, Morelius, Zhang, & Wolcott, 2008; Ljungberg et al., 2005; Roohani et al., 2008; Siqueira, Abdillahi, Bras, & Dufresne, 2010). Such a behavior indicates that the whiskers incorporated into the matrix strongly interacted with the biopolymer matrix, restricting its chain motion (Lu, Weng, & Zhang, 2004).

Fig. 1 presents representative stress–strain curves obtained from films without CW (control) and with CW from one-stage-bleached coconut fibers (CcO-CW, 10 g/100 g). Both curves exhibit typical brittle behavior, characterized by a linear-elasticity to fracture, but it is possible to observe the positive effects of the CW on strength and modulus of the films, although the elongation has been reduced.

Table 6 indicates reduction in water vapor permeability of the films from increasing the concentration of any CW suspension, corroborating other studies which reported enhanced water vapor barrier of films by cellulose nanoreinforcements (Azeredo et al., 2009, 2010; Paralikar, Simonsen, & Lombardi, 2008; Sanchez-Garcia, Gimenez, & Lagaron, 2008; Svagan, Hedenqvist, & Berglund, 2009).

Tables 3–6 indicate that, in most cases, the performance of the films added with CW at 10 g/100 g was not significantly different

Table 4
Elongation at break (%) of films (means ± standard deviation).

CW (g/100 g)	CW types		
	Ct-CW	CcO-CW	CcM-CW
0	(28.26 ± 2.88) a	(28.26 ± 2.88) a	(28.26 ± 2.88) a
5	(19.32 ± 1.85) b	(18.52 ± 1.38) b	(18.08 ± 1.15) b
10	(16.60 ± 4.03) b	(18.00 ± 2.14) b	(17.74 ± 1.20) b
15	(19.44 ± 1.84) b	(18.22 ± 1.70) b	(18.39 ± 2.71) b

Ct-CW: cellulose whiskers from cotton fiber; CcO-CW: cellulose whiskers from coconut fiber submitted to one-stage bleaching; CcM-CW: cellulose whiskers from coconut fiber submitted to multi-stage bleaching. Values at the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$).

Table 6
Water vapor permeability ($\times 10^{-13}$ kg m Pa^{-1} s^{-1} m^{-2}) of films, at 24 °C/75% RH (means ± standard deviation).

CW (%)	CW types		
	Ct-CW	CcO-CW	CcM-CW
0	(3.19 ± 0.47) a	(1.15 ± 0.47) a	(1.15 ± 0.47) a
5	(2.50 ± 0.45) b	(2.42 ± 0.39) b	(2.14 ± 0.39) b
10	(2.28 ± 0.31) bc	(2.20 ± 0.33) bc	(2.09 ± 0.22) b
15	(1.67 ± 0.42) c	(1.83 ± 0.31) c	(1.47 ± 0.17) c

Ct-CW: cellulose whiskers from cotton fiber; CcO-CW: cellulose whiskers from coconut fiber submitted to one-stage bleaching; CcM-CW: cellulose whiskers from coconut fiber submitted to multi-stage bleaching. Values at the same column followed by the same letter are not significantly different (Tukey, $p < 0.05$).

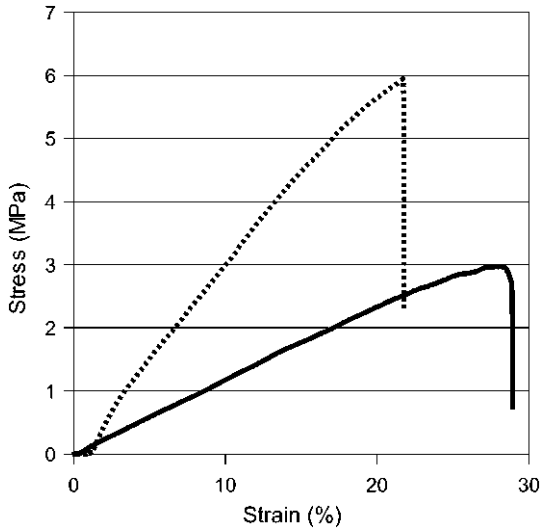

Fig. 1. Representative stress–strain curves from alginate-acerola puree films without CW (control, continuous line) and with CW from coconut husk fibers submitted to one-stage bleaching (CcO-CW at 10 g/100 g, dotted line).

from that of films with the highest whisker concentration used (15 g/100 g), suggesting that the CW addition at 10 g/100 g is probably more interesting from the economic point of view.

4. Conclusions

The incorporation of cellulose whiskers to alginate-acerola puree films improved their water vapor barrier, as well as tensile strength and modulus, indicating that the whiskers improve the film applicability as edible packaging. Cellulose whiskers obtained from coconut husk fibers have shown to be comparable to those from cotton fibers in terms of their positive effects on the film properties, in spite of their remaining lignin, probably because of their higher aspect ratios when compared to those from cotton fibers. The films can be used as edible coatings for several foods such as fresh fruits and vegetables, extending their shelf life. Moreover, alginate-acerola films without cellulose whiskers can be consumed as snacks, since such an application does not require great mechanical or barrier properties.

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References

Alexy, P., Feranc, J., Kramárová, Z., Hajsová, M., Duracka, M., Mosková, D., et al. (2008). Application of lignins in rubber compounds. *Kautschuk und Gummi Kunststoffe, 61*(1–2), 26–32.

ASTM. (1989). Standard test methods for water vapor transmission of materials. E96–80. In *Annual book of American standard testing methods*. Philadelphia: ASTM.

ASTM. (1997). Standard test method for tensile properties of thin plastic sheeting. D882–97. In *Annual book of American standard testing methods*. Philadelphia: ASTM.

Azeredo, H. M. C., Mattoso, L. H. C., Avena-Bustillos, R. J., Ceotto Filho, G., Munford, M. L., Wood, D., et al. (2010). Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content. *Journal of Food Science, 75*(1), N1–N7.

Azeredo, H. M. C., Mattoso, L. H. C., Wood, D., Williams, T. G., Avena-Bustillos, R. J., & McHugh, T. H. (2009). Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. *Journal of Food Science, 74*(5), N31–N35.

Azizi Samir, M. A. S., Alloin, F., & Dufresne, A. (2005). Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules, 6*, 612–626.

Azizi Samir, M. A. S., Alloin, F., Sanchez, J. Y., & Dufresne, A. (2004). Cellulose nanocrystals reinforced poly(oxyethylene). *Polymer, 45*, 4149–4157.

Baumberger, S., Lapierre, C., Monties, B., & Della Valle, G. (1998). Use of kraft lignin as filler for starch films. *Polymer Degradation and Stability, 59*, 273–277.

Bhatnagar, A., & Sain, M. (2005). Processing of cellulose nanofiber-reinforced composites. *Journal of Reinforced Plastics and Composites, 24*(12), 1259–1268.

Cranston, E. D., & Gray, D. G. (2006). Morphological and optical characterization of polyelectrolyte multilayers incorporating nanocrystalline cellulose. *Biomacromolecules, 7*, 2522–2530.

Dalmas, F., Cavaillé, J. Y., Gauthier, C., Chazeau, L., & Dendievel, R. (2007). Viscoelastic behavior and electrical properties of flexible nanofiber filled polymer nanocomposites. Influence of processing conditions. *Composites Science and Technology, 67*, 829–839.

Graupner, N. (2008). Application of lignin as natural adhesion promoter in cotton fibre-reinforced poly(lactic acid) (PLA) composites. *Journal of Materials Science, 43*(15), 5222–5229.

Helbert, W., Cavaillé, C. Y., & Dufresne, A. (1996). Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and mechanical behaviour. *Polymer Composites, 17*(4), 604–611.

Jiang, L., Morelius, E., Zhang, J., & Wolcott, M. (2008). Study of the poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/cellulose nanowhisker composites prepared by solution casting and melt processing. *Journal of Composite Materials, 42*(24), 2629–2645.

Kaya, S., & Maskan, A. (2003). Water vapour permeability of pestil (a fruit leather) made from boiled grape juice with starch. *Journal of Food Engineering, 57*(3), 295–299.

Kim, H. J., & Triplett, B. A. (2001). Cotton fiber growth in planta and in vitro. Models for plant cell elongation and cell wall biogenesis. *Plant Physiology, 127*, 1361–1366.

Ljungberg, N., Bonini, C., Bortolussi, F., Boisson, C., Heux, L., & Cavaillé, J. Y. (2005). New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion characteristics. *Biomacromolecules, 6*(5), 2732–2739.

Lu, Y., Weng, L., & Zhang, L. (2004). Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. *Biomacromolecules, 5*, 1046–1051.

Ludueña, L. N., Alvarez, V. A., & Vasquez, A. (2007). Processing and microstructure of PCL/clay nanocomposites. *Materials Science and Engineering: A, 460–461*, 121–129.

McHugh, T. H., & Olsen, C. W. (2004). Tensile properties of fruit and vegetable edible films. *United States-Japan Cooperative Program in Natural Resources*, 104–108.

McHugh, T. H., & Senesi, E. (2000). Apple wraps: A novel method to improve the quality and extend the shelf life of fresh-cut apples. *Journal of Food Science, 65*(3), 480–485.

Paralikar, S. A., Simonsen, J., & Lombardi, J. (2008). Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. *Journal of Membrane Science, 320*(1–2), 248–258.

Rojas-Graü, M. A., Avena-Bustillos, R. J., Friedman, M., Henika, P. R., Martín-Belloso, O., & McHugh, T. H. (2006). Mechanical, barrier, and antimicrobial properties of apple puree edible films containing plant essential oils. *Journal of Agricultural and Food Chemistry, 54*, 9262–9267.

Rojas-Graü, M. A., Avena-Bustillos, R. J., Olsen, C., Friedman, M., Henika, P. R., Martín-Belloso, O., et al. (2007). Effects of plant essential oil compounds on mechanical, barrier and antimicrobial properties of alginate-apple puree edible films. *Journal of Food Engineering, 81*, 634–641.

Roohani, M., Habibi, Y., Belgacem, N. M., Ebrahim, G., Karimi, A. N., & Dufresne, A. (2008). Cellulose whiskers reinforced polyvinyl alcohol copolymers nanocomposites. *European Polymer Journal, 44*, 2489–2498.

Rosa, M. F., Chiou, B., Medeiros, E. S., Wood, D. F., Williams, T. G., Mattoso, L. H. C., et al. (2009). Effect of fiber treatments on tensile and thermal properties of starch/ethylene. *Bioresource Technology, 100*, 5196–5202.

Rosa, M. F., Medeiros, E. S., Malmonge, J. A., Gregorski, K. S., Wood, D. F., Mattoso, L. H. C., et al. (2010). Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydrate Polymers, 81*, 83–92.

Sanchez-Garcia, M. D., Gimenez, E., & Lagaron, J. M. (2008). Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydrate Polymers, 71*, 235–244.

Senesi, E., & McHugh, T. H. (2002). Film e coperture eduli com matrici a base di fruta. *Industrie Alimentari, 41*(420), 1289–1294.

Siqueira, G., Abdillahi, H., Bras, J., & Dufresne, A. (2010). High reinforcing capability cellulose nanocrystals extracted from *Syngonanthus nitens* (Capim Dourado). *Cellulose, 17*, 289–298.

Sothornvit, R., & Rodsamran, P. (2008). Effect of a mango film on quality of whole and minimally processed mangoes. *Postharvest Biology and Technology, 47*(3), 407–415.

Svagan, A. J., Hedenqvist, M. S., & Berglund, L. (2009). Reduced water vapour sorption in cellulose nanocomposites with starch matrix. *Composites Science and Technology, 69*, 500–506.

Ten, E., Turtle, J., Bahr, D., Jiang, L., & Wolcott, M. (2010). Thermal and mechanical properties of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/cellulose nanowhiskers composites. *Polymer, 51*(12), 2652–2660.

Wise, L. E., Murphy, M., & D'Addieco, A. A. (1946). Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on hemicelluloses. *Paper Trade Journal, 122*, 35–43.