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How properties of cellulose acetate films are affected by conditions of iodine-catalyzed acetylation and type of pulp

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Abstract The present study has been carried out to consider the effect of acetylation conditions and type of bleached pulps [Kraft and SO₂–ethanol–water (SEW) pulps] on the properties of obtained cellulose acetates (CA) and their films. The acetylation reaction in the absence of solvent was performed by using acetic anhydride and iodine as a catalyst. The efficiency of acetylation and the degree of substitution, crystallinity, transparency, tensile strength, young modulus, differential scanning calorimetry, water vapor permeability

(WVP), scanning electron microscope and atomic force microscopy images were studied. The results showed that the while the Young's modulus and transparency increased by up to 8% of the catalyst due to the increase in iodine charge; higher iodine levels led to embrittlement of the film. The increase in the ratio of acetic anhydride to pulp (A:P) from 10:1 to 20:1 with 4% catalyst led to a reduction of the DS by 8–10%, the crystallinity by 25%, the Young's modulus by 13–25%, and transparency by 1–34% of a CA obtained from SEW and Kraft pulp, respectively. With the use of higher amounts of the catalyst (8%) and a ratio of A:P equal to 20:1, all properties of CA were suitable for film preparation. WVP of films from Kraft pulp and SEW pulp showed a decrease of about 8.5% and 18% respectively when increasing the iodine amount from 4 to 8% in acetylation. The tensile strength of CA films was initially increased by enhancing the amount of iodine, but then reduced in a similar way to other properties. The condition of acetylation can be adjusted to produce a high-quality CA film according to the characteristics of the pulp used as raw material.

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Graphical abstract

Keywords Acetylation · Iodine · Substitution degree · Transparency · Young modulus

Introduction

One of the crucial problems in recent years is the consumption of plastic materials which causes accumulation of these materials in the environment. The use of recyclable polymers as a substitute for plastics has drawn a lot of attention. These materials are accessible and have various advantages (Mohanty et al. 2000; Zhang et al. 2005). Polysaccharides, such as thermoplastic polymers, are a type of natural polymer that cannot be processed easily by common technologies (Schroeter and Felix 2005; Heinze and Liebert 2001; Pereira et al. 1997). Cellulose esters such as CA, propionate cellulose acetate (CAP), and thermoplastic cellulose acetate butyrate (CAB) are produced through esterification of cellulosic raw materials such as cotton, wood, and bagasse (Ferreira-Harrar and Dairi 2014). CA is an important derivative of cellulose; it is a transparent thermoplastic which softens at 60–97 °C and has a melting temperature of 260 °C. It is used in packaging, textile industries, construction and as biodegradable plastics (Tessler and Billmers 1996; Rodrigues Filho et al. 2008). CA is obtained through the substitution of hydroxyl groups with an acetyl group, and when fully substituted the degree of substitution is 3. These groups have shown different reactivity in the esterification stage. Regiani et al. (1999) reported that the reactivity of the hydroxyl groups of cellulose follows

the order $C2 < C3 < C6$, and in other cases the order $C3 < C2 < C6$ (Marson and Seoud 1999; Miyamoto et al. 1985). CA with a degree of substitution of 2–2.5 is soluble in acetone, dioxane and methyl acetate; at a higher degree of substitution it can be dissolved in dichloromethane (Fischer et al. 2008). CA with a 2.5° of substitution is used as a raw material for the production of fiber, filter, membranes and thermoplastic materials (Schaller et al. 2013). The CA production is performed by two methods: the homogeneous and heterogeneous process. In the homogeneous process (traditional), CA is obtained from the reaction of cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid as a catalyst (Fischer et al. 2008). In the heterogeneous process no solvent or diluent is added to the system to produce the CA-insoluble residue. The heterogeneous conversion of cellulose into cellulose triacetate (CTA) leads to a product with higher crystallinity than with homogeneous acetylation (Cerqueira et al. 2006).

Cheng et al. (2010) found that more yield can be obtained by esterification of cotton byproducts without cellulose purification by using iodine as a catalyst as compared to acetylation by Acetic acid, anhydric acid and sulfuric acid as catalysts. Moreover, Biswas et al. (2006) achieved yields of 25% (based on dry initial material) in the production of CA from agricultural byproducts using sulfuric acid as a catalyst. The acetylation of cellulose by an iodine catalyst has shown that the increase of iodine raised the degree of substitution (Biswas et al. 2008). Also, Hu et al. (2011) indicated that this process is efficient, economic and environmentally friendly.

CA films with high efficiency and flexibility, optical transparency, thermal stability, mechanical strength, biodegradability and gas barrier properties have a wide range of applicable programs. Yang et al. (2013) used sulfuric acid as a catalyst in the production of CA from a nano-whisker; the maximum transparency, the Young's modulus, and the tensile strength were 84%, 1.5 GPa and 44 MPa, respectively. Another parameter under consideration in CA production is the crystallinity of CA, which has an effect on the mechanical and chemical properties of CA film. For instance, cellulose diacetate is more amorphous and biodegradable than cellulose triacetate (Samios et al. 1997). In this study the production of CA was carried out by a heterogeneous process with iodine as a catalyst. The aim was to investigate the influence of the reaction conditions of acetylation and pulp type on the properties of CA and its films. Unlike previous studies, an additional goal was to optimize the acetylation of inferior pulp with iodine as a catalyst in order to produce a high-quality CA film.

Experimental

Raw materials

In this research, two bleached pulps obtained from our previous research (Yadollahi et al. 2018) were used to study the effects of acetylation conditions with iodine and different types of pulps on CA properties. The properties of these pulps are indicated in Table 1.

In the acetylation stage the accessibility of hydroxyl groups affects the degree of substitution (DS). The crystallinity of pulps was measured with X-ray diffraction (XRD). X-ray diffraction of specimens were recorded at temperatures from 0 to 100 °C at a scanning speed of 0.02°/s by a Rigaku Ultima IV. The operating voltage and current was 40 kV and 40 mA. The crystallinity index of cellulose, I_c , was calculated by the formula below (Regiani et al. 1999).

$$I_c = 1 - \frac{I_{min}}{I_{Max}} \times 100 \quad (1)$$

where I_c is the crystallinity index, I_{min} is the intensity minimum between $2\theta = 18^\circ$ and 19° , and I_{max} is the intensity of the crystalline peak at the maximum between $2\theta = 22^\circ$ and 23° C.

Production of CA

Following the method in Cheng et al. (2010), an iodine catalyst with acetic anhydride was used for acetylation of these pulps to achieve a substitution degree of 2–2.5. This simple method was carried out in the absence of solvent using the determined amount of iodine (based on dry weight of pulp 2–12%), the ratio of acetic anhydride to pulp was 10–20, the time duration was 10–20 h, and the temperature was 85 and 95 °C in some treatments. After completion of the reaction in the determined conditions, the reaction balloon was exited from the oil bath and cooled down in the laboratory environment. Then 2 ml of a saturated solvent of sodium thiosulfate was used to

Table 1 Characterization of pulps for producing CA (Yadollahi et al. 2018)

	Bleached SEW pulp (BSP)	Bleached Kraft pulp (BKP)
Yield (% on raw material)	38.9	39
Kappa number	0.3	2.1
Viscosity	714.3	695.2
ISO brightness (%)	90.6	83.2
Cellulose (% on pulp)	90.1	80
Xylan (% on pulp)	3.0	14.3
GLMA (% on pulp)	4.9	2.0
lignin content (% on pulp)	0.6	0.72
Hexuronic acid (HexA) content (meq/kg)	0.90	2.58
Number-average MM	53,319	73,054
Weight-average MM	614,386	547,165

transform iodine to iodide and change the mixture color from dark brown to colorless. Next, for the sediment of CA, 50 ml ethanol was added to the reaction environment and they were mixed for 30 min. The obtained CA was separated by filter paper and washed with warm water to eliminate extra chemical materials. After washing and dewatering under vacuum conditions, the materials were put in an oven at 60 °C to be dried.

Preparation of film

To prepare the film, a solution of CA in methylene chloride with the constant concentration of 10% was prepared. The obtained solution was kept in an air tight container for 2 h to completely remove all bubbles. The solution was cast on a smooth glass by an adjusted blade (Dr.blade) on $250 \pm 10 \mu\text{m}$. Then, 5–10 min after evaporation of the solvent, the film was immersed in ethanol for 5 min. Next, the films were put between paper sheets at room temperature to be dried and prevent distortion.

Characterization of CA and obtained films

The yield (%Weight gain) and substitution degree

The yield was calculated based on Eq. 2 and the substitution degree of CA samples were determined using ¹H NMR, a Bruker 400 MHz Ultra Shield device and TopSpin 3.5 software. Standard dimethyl sulfoxide (DMSO) was used as the CA solvent to prepare the NMR sample.

$$Y = \frac{M2 - M1}{M1} \times 100 \quad (2)$$

Y is the CA yield, M2 is the weight of CA, and M1 is the weight of pulp (Li et al. 2009).

Determination of the films' thickness and transparency

The films' thickness was measured using a micrometer as a mean of 5 different points. The films' thickness was considered as 10–20 μm . In order to keep the same thickness in all films, the concentration of CA and blade gap were considered as 10% and $250 \pm 10 \mu\text{m}$, respectively. Transparency of CA films with a thickness of 20 was measured by a

spectrophotometer UV-2550 UV-Vis at the wavelength of 550 nm according to standard test method for light transmittance of transparent plastics (2007).

Strength properties

Stress and strain were applied to films using a universal device (Instron, Model 33R4204) with a constant force (100 N) and velocity of 0.5 mm/min for each sample (the mean of dimensions were $20 \times 5.30 \times 0.01 \text{ mm}^3$) at 23 °C and relative moisture of 50%.

Differential scanning calorimetry (DSC)

Degree of crystallinity, glass transition temperature (T_g), melting temperature (T_m), and fusion enthalpy of CA films were measured by the analysis of DSC, (Mettler Toledo DSC 821e, Gerifensee, Switzerland) under N_2 gas. The samples were heated at a pace of 10 °C/min to 330 °C along with 2 min isothermal at this temperature and then they were cooled down at the same rate (10 °C/min) to 100 °C using N_2 gas. In the reheating stage the samples were heated again to 330 °C at a pace of 10 °C/min, and the enthalpy of fusion (ΔH_f), T_g , and T_m were measured. The degree of crystallinity CA was determined by enthalpy of fusion in the cooling down stage (ΔH_f), the enthalpy of fusion of a perfect crystal (ΔH_f°) is equal to 58.8 J/g (Cerqueira et al. 2006).

$$\% C = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100 \quad (3)$$

Water vapor permeability

Water vapor permeability was determined based on the ASTM E 96/E 96 M-05 standard (ASTM 2005). The films were quite stiff and were closed on an aluminum container with a cap containing 43 g of calcium carbonate as a desiccant (Labuza et al. 1985). Dishes were placed in a cabinet equipped with a fan with the velocity of 0.15 m/s for uniform distribution of air at the top of the samples. The temperature of the cabinet was 22 °C and its relative moisture was kept at 54% by using a saturated solution of $\text{Mg}(\text{NO}_3)_2$. The weight of the dish with the desiccant material inside was measured once a day for 5 days. Also, in the

weighting stage the temperature and relative moisture of the cabinet were recorded using a Rotronic HygroPalm. The water vapor transition rate was calculated using a regression for the linear slope of weight gain vs. time divided by the mouth area of the test cell. The specific pressure of the films' water vapor was also calculated using the modified method of Gennadios et al. (1994). Water vapor permeation (WVP) was calculated by multiplying the water vapor transition rate by film thickness and the partial pressure of both sides of the film. Each type of film was tested twice and their thicknesses were measured at 5–10 points with the accuracy of 1 μm .

Surface characterization (SEM and AFM)

Each type of film was covered by a layer of platinum with the thickness of 3 nm using a Emitech K100X. Then a photo of the films' surface and a cross-section were taken by the electron microscopic device Zeiss Sigma VP with the voltage of 3 kw. Atomic force microscope (AFM) images were recorded from the surface of several films by a Multimode 3000 (Digital Instruments, Santa Barbara, USA) with an amplitude set point of 1.3–1.6 V at room temperature (25 °C) and an area of 2 $\times$ 2 μm^2 .

Results and discussion

X-ray diffraction of the pulps revealed a higher crystallinity for the BKP (82%) than for the BSP (77%) (Fig. 1). The crystallinity and impurity of pulps led to different behavior in the acetylation stage. The

BSP had low crystallinity and subsequently more accessible hydroxyl groups as compared to the BKP. Crystallinity of both pulps was in a range of 70–85%, which corresponded to the range reported by Park et al. (2010).

Effect of iodine consumption

The esterification results of BSP and BKP showed that an increase in iodine consumption led to an increased degree of substitution. This is in line with the findings of Hu et al. (2011), Biswas et al. (2008), and Li et al. (2009). The acetylation of both pulps after increasing the iodine consumption from 2 to 8%, based on oven dry pulps, initially led to a decrease in the yield of CA but then increased as the iodine consumption increased (Table 2). While the acetylation yield of BSP pulp remained between 54 and 69% irrespective of the iodine charge, the increase in the iodine charge of BKP cellulose from 2 to 4% initially led to a decrease in the acetylation yield to 42%, but a further increase in the iodine dosage to 8% again led to a slight increase in the acetylation yield to 45%. It can be speculated that the BKP pulp contains a higher concentration of non-cellulosic impurities, such as HexA and xylan, than the BSP pulp, which reacts with the iodine in a side reaction and is therefore no longer available as a catalyst for acetylation. If the amount of iodine is increased to 8%, more iodine is available as a catalyst for acetylation despite the side reactions with the oxidizable impurities, which leads to an increased yield of acetylation.

Effect of acetic anhydride to pulp ratio (A:P)

The DS and yield of obtained CA from both pulps decreased when the ratio of A:P increased from 10:1 to 20:1 because the concentration and effect of iodine decreased in a high ratio of A:P.

In addition, the results of NMR showed that the CA of both pulps had a higher degree of substitution at C-6 than at C-2 and C-3. This phenomenon is attributed to the lower steric hindrance of C-6 than C-2 or C-3 (Fig. 2). These results correspond well with those reported by Marson and Seoud (1999) and Miyamoto et al. (1985).

Fig. 1 X-ray diffraction spectra of BKP and BSPs

Table 2 Acetylation condition of BSP (S-codes) and BKP (K-codes) with the properties of obtained CA

Samples	Ratio of A:P (by weight)	Iodine (%)	T (°C)	Yield ^a (%Weight gain)	DS (total)	DS6	DS2	DS3
S2-10	10:1	2	85	65	1.51	0.61	0.46	0.44
S4-10 (10 h) ^b		4		54	1.56	0.63	0.51	0.41
S4-10		4		63	2.38	0.95	0.75	0.68
S8-10		8		69	2.62	1.00	0.85	0.78
S4-20	20:1	4	85	62	2.21	0.86	0.68	0.67
S8-20		8		61	2.60	1.00	0.85	0.75
S12-20		12		64	2.66	1.00	0.89	0.78
K2-10	10:1	2	85	61	0.78	0.05	0.09	0.04
K4-10 (10 h) ^b		4		54	1.19	0.46	0.39	0.33
K4-10		4		42	2.03	0.85	0.70	0.65
K8-10		8		45	2.59	1.00	0.93	0.75
K4-20	20:1	4	85	39	1.80	0.68	0.57	0.55
K8-20		8		36	2.36	0.92	0.73	0.72
K12-20		12		39	2.53	0.93	0.85	0.76
K8-20-95	20:1	8	95	37	2.55	1.00	0.84	0.71

^a% weight gain of samples (g/g)^bDuration of this reaction was 10 h. But other reactions were 20 h **Fig. 2** NMR spectra of CA produced from BKP (K4-10) and BSP (S4-10) under comparable acetylation conditions

Effect of time and kind of pulp

As expected, the reductions of the esterification time from 20 to 10 h decreased the yield and the degree of substitution. The obtained DS and yield of CA produced from the BSP were higher than those from the BKP under comparable acetylation conditions (Table 2 and Fig. 2). This is due to the higher crystallinity and impurities, such as xylan and HexA, in BKP and the associated low reactivity compared to the BSP (Table 1). The results of the current study

corresponded with a previous study by Peredo et al. (2015) in which xylan led to a slight decrease in the DS and yield of obtained CA from the BKP. Also, BSP has a thinner primary wall, similar to AS pulp (Iakovlev et al. 2014), which may be partly responsible for the increased reactivity. According to the results of the DS obtained by NMR from the CA, DS achieved under comparable acetylation conditions of BSP (S2-10) was higher than that of BKP (K2-10). This was presumably due to higher cellulose purity, a thinner primary wall (Iakovlev et al. 2014), and lower crystallinity of BSP as compared to BKP. CA obtained from BKP at a 2% charge of the catalyst (K2-10) had a DS of less than one and wasn't soluble in dichloromethane, and no film could be prepared from it.

Effect of temperature was studied only on acetylation of BKP because it needs more reaction intensity compared to BSP to receive approximately the same DS (Table 2). The increase in the temperature of BKP (K8-20-95) in acetylation showed that the yield and the DS of the obtained CA increase with the same amount of catalyst and acetic anhydride.

Characterization of produced CA films

Effect of iodine and pulp

In this study, the optimal conditions for the esterification reaction were determined based on films strength, DS, and the yield. The stress–strain behavior of CA films obtained from BKP (CAF-K) and BSP (CAF-S) showed that when the catalyst dosage and catalyst concentration was low as for S2-10 and K4-20, respectively, the films tolerated more strain. This may be due to a low DS and less degraded cellulose as well as more hydrogen bonds (Fig. 3). The increase in iodine consumption initially increased the tensile strength, but further increasing it caused it to drop as shown for S8-10 and S12-20 (Fig. 3). The tensile strain of K8-10 and K12-20 decrease, but their tensile stress did not decrease due to the additional impurity and crystallinity in BKP, only the tensile stress showed a different behavior. In fact, increasing iodine consumption led to increased brittleness and modulus of CA films obtained from both pulps (up to 8% iodine) (Figs. 3, 4). Previous studies on starch esterification indicated that the increase of iodine charge caused starch hydrolysis and reduced the molecular weight

(Biswas et al. 2008). Cellulose was hydrolyzed by increasing the amount of catalyst in the acetylation stage of both pulps to 12% (on dry matter), which resulted in a decrease in film modulus and tensile strain in both CA films (Figs. 3, 4).

In the esterification of BKP, the increase in DS to 2.5 with 12% iodine based on oven dry BKP (K12-20) resulted in a decrease in tensile stress, strain, and modulus by 1%, 58%, and 6% respectively, compared to K8-20. In addition, the stress, strain and modulus of S12-20 decreased 29%, 56% and 20%, respectively, in comparison to S8-20 (Figs. 3, 4). This showed that the brittleness of the films increased. Peredo et al. 2015 reported that xylans in acetylated BKP increased the hydrogen bond interaction. So hydrogen bonds in cellulose acetate film with low DS (created by hydroxyl group remaining on the cellulose and remaining xylans) led to more tensile strain. However, in a large amount of catalyst (12%) the CA films were brittle. Actually, the mechanical properties of the films were mostly affected by the condition of acetylation. The results of maximum tensile stress and young modulus of films (Figs. 3, 4) obtained from both pulps (K8-20 and S8-20) showed higher mechanical strength compared to previous studies (Yang et al. 2013; Lu

Fig. 3 Tensile stress and strain of CAF-K and CAF-S with different amounts of catalyst (2–12%) and two ratios of A:P (10:1 and 20:1)

Fig. 4 Modulus of CAF-K and CAF-S by different amounts of catalyst (2–12%) and two ratios of A:P (10:1 and 20:1)

and Drzal 2010; Rodriguez et al. 2012a) (Table 3). Lu and Drzal (2010) improved the tensile modulus and the tensile strength of Neat CA film to 4.1 GPa and 63.5 MPa, respectively. The mechanical strength of the films described by Lu and Drzal was lower than that of the films obtained from both pulps in the current study.

Effect of acetic anhydride to pulp (A:P) ratio and time

The improvement in the ratio of A:P from 10 (8–10 in treatments) to 20 (8–20 in treatments) for both pulps led to higher tensile stress and elongation, and thus to lower brittleness of the films (Figs. 3). Since a large amount of iodine leads to depolymerization (Biswas et al. 2008), increasing the ratio of A:P led to a

Table 3 Comparing mechanical properties of films with pervious literature

Kind of films	Thickness of films (mm)	Maximum tensile stress (MPa)	Maximum modulus (GPa)	Transparency in wave length 550 nm (%)
S8-20	0.0120 ± 0.007	132 ± 4	5.3 ± 0.4	91 ± 1
K8-20	0.0124 ± 0.008	158 ± 5	6.6 ± 0.3	89.5 ± 0.5
CTA film (Gutierrez et al. 2017)	–	–	–	91.5
Commercial Cellulose diacetate (Tabuchi et al. 1998)	–	150	2.9	–
Commercial Cellulose triacetate (Tabuchi et al. 1998)	–	70	2.9	–
CA nanocomposites (Yang et al. 2013)	0.4	44	1.5	70–84
CA nanocomposites (Romero et al. 2009)	–	–	3.3	–
MFC/CA composites (Lu and Drzal 2010)	0.2	63.5	4.1	–
Neat CA (Lu and Drzal 2010)	0.2	38	1.9	–
CA nanocomposites (Rodriguez et al. 2012a)	0.058	58 ± 3.5	1.8	–
Cellulose film (Yang et al. 2011)	0.03–0.06	150	6.0	90

decreased concentration of iodine and its effects. Most likely depolymerization occurred when the concentrations of iodine (K8-10 and S8-10) or the amounts of iodine (K12-20 and S12-20) increased.

The Young's modulus of CA films, especially those made of BKP, was reduced by increasing the weight ratio of A:P, essentially reducing the brittleness of the films (Fig. 4). The tensile strength of S8-20 and K8-20 films with a DS of 2.6 and 2.36, respectively, were higher than the other films. Tensile stress of CA film obtained during a smaller amount of time acetylation [S4-10 (10 h)] showed lower tensile stress compared to the S4-10 (20 h) film. So, the time of acetylation affected the DS of CA and the mechanical strength of its film. Therefore, the properties of CA films depend on the properties of pulps and the esterification conditions.

Transparency

Based on the results of the transparency test at a wavelength of 550 nm, the transparency of the film was increased firstly when the catalyst dosage was increased from 2% to 4% and 8%. In large amounts of catalyst (12%), transparency at 4% and 6% decreased for S12-20 and K12-20 compared to S8-20 and K8-20, respectively (Fig. 5). This was due to the slight brown color of the films at this consumption dosage (12%). The transformation of iodine to iodide and the change of the color from dark brown to colorless did not occur completely.

Moreover, the transparency of some film at low levels of iodine (S2-10) were reduced significantly due to an increased ratio of A:P in the low amount of iodine especially for BKP (K4-20) and low time (K4-10_{10h}). These factors led to a low DS and homogeneity in the acetylation stage due to lower solubility and transparency in the CA film (Figs. 5).

By comparing the results of previous studies on cellulose films (Lu and Drzal 2010; Yang et al. 2011, 2013; Romero et al. 2009; Rodriguez et al. 2012a) and the results of the present study, we found that the CA films obtained from both pulps under optimal esterification conditions (8% catalyst and the ratio of A:P equal to 20 at 85 °C for 20 h) exhibit higher tensile strength and transparency than the results of previous studies (Table 3). Therefore, despite the high proportion of impurities in the BKP, transparent and resistant CA films were produced with this acetylation process.

Thermal properties

DSC analysis was carried out in order to investigate the effect of acetylation on the thermal properties of the acetylated product. Glass transition temperature (T_g), crystallinity (X_c), and melting point (T_m) were recorded for the product (Fig. 6 and Table 4). Glass transition temperatures for all samples were in the range of 158 to 164 °C. DS, crystallinity, and melt enthalpy decreased by increasing the ratio of A:P. The amount of iodine consumed had an influence on the

Fig. 5 UV–Vis transmittance spectra of CAF-K and CAF-S with different amounts of catalyst (2–12%) and two ratios of A:P (10:1 and 20:1)

Fig. 6 DSC curve of CAF produced from BKP and BSPs with different amounts of catalyst (4 and 8%) and two ratios of A:P (10:1 and 20:1)

Table 4 DSC results of CAF produced from BKP and BSPs with different amounts of catalyst (4 and 8%) and two ratios of A:P (10:1 and 20:1)

	DS	% Crystallinity	ΔH_f (J/g) ^a	ΔH_f (J/g) ^b	T _m (°C) ^b	T _g (°C) ^b
S4-10	2.4	40	24	20	272	164
S4-20	2.2	29	17	18.5	272	158
S8-20	2.6	39	23	21.6	271	158
K4-10	2.0	30	18	18	276	161
K4-20	1.8	—	—	—	—	—
K8-20	2.4	24	14	16.8	276	162

^aObtained from scan of the DSC cooling

^bObtained from the second scan of DSC thermogram

crystallinity of CA. The crystallinity of S8-20 was higher than for S4-20. It seems that the iodine catalyst increased the DS by entering both amorphous and crystalline zones of the cellulose. An increase of the ratio of A:P from 10:1 to 20:1 at 4% catalyst led to a reduction in CA crystallinity. This is due to a reduction in the concentration of iodine and its degradation effect. As it is shown in Fig. 3, the films' strength dropped sharply when the catalyst dosage increased from 4 to 8% when the ratio of A:P was 10:1. An increase of the ratio of A:P (at the same level of catalyst, 8%) increased the strength of CA films. Therefore, increasing the ratio of A:P reduced the degradation effect of the catalyst. The strength of CA film in the treatment of S8-20 was higher as compared to the other films.

The CA of the BKP had a lower DS and crystallinity and little higher melt enthalpy in comparison to the CA of the BSP; the result of such a phenomenon may be attributed to the high cellulose purity and the low crystallinity of BSP.

There was no difference between the maximum glass transition temperatures of CAF from both pulps. The melting temperature of CAF-K was 5 °C higher than that of CAF-S. This may be due to the lower DS of CAF-K. So, impurities such as HexA and xylan did not have a significant negative effect on the physical properties of the CA, which corresponds to the results of Peredo et al. (2015). The maximum temperature of T_g and T_m in the present study were 20–30 °C less and 35–50 °C more, respectively, than the results of Ferfera-Harrar and Dairi (2014) and Rodriguez et al. (2012b). Also the melting temperature and T_g of the CA obtained in this study were 100 °C and 30 °C higher than the results of Rodriguez et al. (2012a). This may be due to the type of CA and the type of acetylation. High melting temperature leads to more heat resistance, which can be an advantage.

Water vapor permeability (WVP)

According to Fig. 7, the water vapor permeability of the films dropped with the increase in iodine consumption in the acetylation stage. As mentioned above, increasing the ratio of A:P reduced DS and crystallinity; but, WVP increased due to lower DS. Actually, increasing the degree of substitution led to a higher hydrophobicity of the CA and lower WVP. S4-10 and K4-10 had a slightly lower WVP than K8-20 and S8-20 due to a higher crystallinity. This is due to the accessibility of the remaining hydroxyl groups in the crystalline zone of CA which make water vapor permeability difficult and leads to a decrease in WVP. The results of WVP showed that CA is not a good barrier and must be coated with a barrier material. The results of WVP in the current study (480–680 g/m² day at 50% relative humidity and a temperature of 22 °C) were comparable with the results of Shogren (1997). The water vapor permeability of biodegradable polymers, such as CA, is much higher than good barrier materials such as low density polyethylene (Shogren 1997).

Fig. 7 Water vapor permeability and DS of some CAF-K and CAF-S obtained with two amounts of catalyst (4 and 8%) and two ratios of A:P (10:1 and 20:1)

Fig. 8 SEM from the cross section and surface of some CAF-K and CAF-S with different amounts of catalyst (4 and 8%) and two ratios of A:P (10:1 and 20:1)

Surface characterization

According to the SEM images (Fig. 8), there was no significant difference between the surfaces of the films; all surfaces were flat and without pores and roughness. The cross-sections of S4-10 and K4-10 were more strongly uniform than S8-20 and K8-20; this could be due to more DS, higher solubility and more homogeneity. The AFM image showed only some dark particles in the CAF-K compared to CAF-S. Probably, impurities of BKP, such as HexA, led to these dark particles in the AFM image (Fig. 9). These particles may have slightly affected the properties of CA films but the condition of acetylation and consequently the DS of obtained CA had a much greater effect on all properties of CA. Reaction conditions of acetylation, such as consumption amount of iodine and ratio of A:P, duration of reaction, and kind of pulps affected the DS. Hence, producing high quality CAF with low grade pulp is possible.

Conclusions

Based on the results obtained, increasing the dosage of the catalyst increases the DS. The acetylation yield

initially decreases and then increases with increasing iodine as a catalyst. The yield increase of CA from BKP was lower than for BSP. It appears that impurities in BKP were removed during the esterification of pulp and the washing stage of CA. The increase of the catalyst quantity at a ratio of A:P equal to 10:1 led to a loss of tensile strength and increased brittleness of the films due to higher crystallinity. Increasing DS with a high amount of iodine (S12-20 and K12-20) and a low ratio of A:P at high levels of iodine like S8-10 and K8-10 led to the removal of amorphous zones, depolymerization, and a decrease in accessible hydroxyl groups in the cellulose chain by substitution and increasing crystalline zones. Hydrogen bonds decrease due to the low accessibility of hydroxyl groups. CA films with more DS and low hydrogen bonds had low tensile strain and were brittle. Mechanical properties of the films were mostly affected by the condition of acetylation. The optimal acetylation conditions according to the properties of the films (acetylation yield, degree of substitution, tensile strength and transparency) were 8% iodine charge (based on the weight of the pulp) and an A:P ratio of 20:1 at 85 °C for 20 h. The modulus of elasticity was increased when the catalyst quantity rose to 8%, but a further increase in the catalyst quantity (12%) reduced

Fig. 9 AFM images from the surface of CAF-K and CAF-S with 4% catalyst and a ratio of A:P equal to 10:1

the modulus and transparency of the film. Consequently, the properties of CA and its film depend on the properties of pulp dissolution and acetylation conditions. The crystallinity and DS of CA had more influence on the mechanical strength and WVP of films. WVP was more affected by iodine consumption and subsequently the DS of the obtained CA. The production of CA films with high transparency and mechanical strength is also possible with inferior cellulose and iodine as catalyst. This kind of transparent CA film can be applied as a functional material utilizing its high mechanical strength; it can also be used for packaging after improving its permeability.

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