ORIGINAL RESEARCH PAPER

PHYSICAL, BARRIER, AND THERMAL PROPERTIES CHARACTERIZATION OF EDIBLE FILMS FROM COMPOSITE MIXTURES OF STARCH AND STARCH DERIVATIVES

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Abstract

In the search for sustainable and ecological alternatives in food packaging, the use of starch as one of the most abundant biopolymer resources to formulate edible films has been studied. Nonetheless, compatibility with other starch derivatives, such as dextrin and/or chemically modified starch, has not been explored yet. The objective of this research was to characterize opacity, water vapor barrier capability, and thermal properties of composite edible films, by a mixture design approach, formulated with three types of commercial chemical modified starch mixed with native corn starch and dextrin. Lower opacity in edible films was related to more soluble material, where the main effect of dextrin was the rise of soluble material and lower water vapor permeability. A more permeable film can be obtained with Nifrastarch and lower permeability with Gelamil. The type of chemically modified starch used in edible films for edible packaging can be decided according to the characteristics of the food in question, *i.e.*, moisture, color, permeability, or edible film solubility for active packaging.

Keywords: edible films, starch derivatives, WVP, DSC, FTIR, mixture design approach

Introduction

Starch is a cheap alternative to polymeric materials since it can be obtained from several renewable crops. In addition, starch satisfies the principal aspects of renewable resources, such as availability, high extraction yield, nutritional value, low cost, biodegradability, biocompatibility, and edibility. These features make

starch coatings and films a promising material being edible, odorless, tasteless, colorless, nontoxic, and semipermeable to moisture and gases (Shah *et al*., 2016), due to its ability to form a continuous matrix by the prior disruption of starch granules through a gelatinization process in an excess of water media (Jiménez *et al*., 2012). A particularly interesting fact is that films made of native starch are strong and exhibit good oxygen barrier properties, being suitable as biodegradable and/or compostable packaging material when the required lifetime of the material is short (Koch, 2018). Edible films as a thin layer can be used as food coatings or free-standing films as a barrier for oxygen and moisture and consumed with no residual taste, that can be used when synthetic packaging cannot be applied, with the addition of antioxidants or antimicrobials (Gupta *et al*., 2012).

Starch derivatives are produced and marketed on a commercial scale; commercial interest arises when manufacture becomes economically feasible at a lower cost. Starch derivatives include those modifications which change the chemical structure of some of the D-glucopyranosyl units in the molecule, modifying the gelatinization and enhancing hydrophilic character (Rutenberg and Solarek, 1984). The modification of starches by physical and chemical processes has been an effective way to improve the performance of starch films, increasing water solubility, degree of crystallinity, and gel strength of starch with the concomitant decrease of molecular weight and viscosity, properties desired for the ease of handling of the dispersion, pasting, casting and drying processes in the preparation of edible films (Zhang *et al*., 2019). On this, edible films from composite mixtures made of different starch types will improve environmental characteristics, such as biodegradability. Starch mixed with starch derivatives can be used to develop different edible film characteristics according to the requirements and characteristics of the food and environment, where degradability is related to water vapor permeability and solubility of the edible films.

The aim of this research was to characterize the physical properties, water vapor barrier capability, and thermal properties of edible films formulated with three components: native starch, dextrin, and chemically modified starch.

Materials and methods

Formulation of edible films

In the formulation of the edible films, three different chemical modified starches were employed: Nifrastarch TS (ADISA, Mexico City, Mexico), Gelamil 100 (FABPSA, Mexico City, Mexico), and National 1317 (Ingredion, Mexico City, Mexico). These modified starches presented higher viscosities, according to their respective datasheet. Native corn starch Nifrastarch 05B (ADISA) and dextrin N-Dulge SA1 (Ingredion, Mexico City, Mexico) were employed as well in the formulation of the composite edible films. A mixture of 5 g (w/w) of starch, dextrin, and one chemically modified starch (in accordance with the experimental design) was dissolved in 90mL of water with 5% (v/v) of glycerol. The mixture was constantly stirred and heated to 75°C until solubilization of all the

components, cooled at room temperature before pouring the solution onto 144 cm^2 glass plates. The filmogenic solution was dehydrated at room temperature and 59% of relative humidity during 36-48 h. The molded by casting edible films were carefully detached from glass plates and kept individually in plastic bags until their analysis.

Opacity and total soluble material

Film opacity was determined according to the recommendations of Pereda *et al*. (2011), by employing rectangular edible film samples mounted in visible spectrophotometer test cells without front and back walls. Film opacity was calculated as the area under absorption curve (collected by scanning from 400 to 800 nm in a Genesys 10 spectrophotometer (Thermo Fisher Scientific, Waltham, USA) divided by average film thickness (Absorbance (nm) per millimeter). Film thickness was determined as the average of at least 5 random locations measured using a Mitutoyo IP 65 digital micrometer (Mitutoyo, Kanagawa, Japan).

Total soluble material was measured employing 2×2 cm samples previously stabilized at 70°C overnight. Samples' weight was recorded before being immersed in 30 mL of distilled water at room temperature for 24h. The undissolved material was carefully recovered and dried in aluminum pans at 80°C overnight. Weight difference calculated from the initial gross weight and final dry weight was reported as the total soluble material or solubility (Jangchud and Chinnan, 1999).

Water vapor permeability at different RH gradients

To determinate the water vapor permeability at different relative humidity gradients, film samples were first stabilized at 70°C overnight and kept in a desiccator until the test. Films were mounted on glass flasks containing a saturated solution of $NaNO_3$ 10.94 M (65% RH), NaCl 6.33 M (75% RH) or distilled water (100% RH) at 25°C and 50% RH, to obtain the RH gradient between edible films of 15%, 25%, and 50%, respectively. Flasks weights were recorded at 60 min intervals during 6-8 h, observing a steady state. From the steady-state, a linear regression of the slope was calculated to calculate water vapor permeability (WVP) was calculated according to Equation 1:

$$\text{WVP (g/Pa s m)} = \frac{(\text{WVTR} \times \text{L})}{\Delta p} \qquad (1)$$

where WVPR is the water vapor permeability rate (slope of water vapor loss × exposed area), L as the average film thickness, and Δp was calculated based on the RH inside and outside the flask, as the vapor pressure difference across the film (Gennadios *et al*., 1996).

Differential scanning calorimetry

Thermal properties were determined using a Mettler DSC1 differential scanning calorimeter (Mettler Toledo, Columbus, USA), calibrated with indium. Edible film samples were weighed (0.005 ± 0.001 g) in 40 μL aluminum crucible pans and

sealed. Samples were heated from 30 to 120°C at 10°C min^{-1} with nitrogen flow purge (20 mL min^{-1}), using an empty pan as reference. The endothermic peaks and peak areas on DSC thermograms were used to determine thermal transition temperatures and enthalpies.

Fourier transform infrared spectroscopy

Single-beam spectra of the edible film samples were collected against a background of air in an infrared spectrophotomer Buck M530 (Buck Scientific, East Norwalk, USA), by scanning from 4000 to 1000 cm^{-1}, at a nominal resolution of 10 cm^{-1}.

Experimental design and data analysis

To determine the degree of interaction among the different components of the mixtures, the interaction between starch and derivatives as dextrin plus chemically modified starch, a mixture design was employed (Cornell, 2011). The mixtures of the different components are listed in Table 1. Data were analyzed to obtain regression coefficients of estimated parameters and iso-response curves with SAS statistical analysis software version 9.0, into the ADX interface (SAS Institute, Cary, USA).

Table 1. Starch and starch derivatives as components of the mixture for the mixture design approach.

Mixture	Starch	Dextrin	Chemically modified starch
1	0.000	0.000	1.000
2	0.000	0.333	0.667
3	0.000	0.667	0.333
4	0.000	1.000	0.000
5	0.333	0.000	0.667
6	0.333	0.333	0.333
7	0.333	0.667	0.000
8	0.667	0.000	0.333
9	0.667	0.333	0.000
10	1.000	0.000	0.000

Results and discussion

Opacity and total soluble material

According to the regression analysis, when Gelamil was employed in the edible films formulation, films opacity was highly significant ($p<0.01$) affected by the linear terms for both dextrin and chemically modified starch, and there was a significant ($p<0.05$) effect due to starch×chemically modified starch interaction, presenting an acceptable correlation coefficient ($R^2= 80.29$). In formulation with National modified starch, there was as well highly significant ($p<0.01$) effect by dextrin and chemically modified starch linear terms, with a significantly ($p<0.05$) effect by the starch and the starch×chemically modified starch interaction, presenting a good correlation coefficient ($R^2= 83.16$). Finally, for edible films

formulated with Nifrastarch, only the dextrin linear parameter presented a highly significant (p<0.01) effect, and both linear starch parameters for starch and chemically modified starch presented a significant (p<0.05) effect. Also, starch×dextrin and starch×chemically modified starch interactions presented a significant (p<0.05) effect (R^2= 86.30) (Table 2). According to these results, the component with a strong effect on edible films opacity was dextrin since higher opacity values can be observed at both dextrin vertex and dextrin−starch mixtures side in the iso-response contour curve. Nifrastarch resulted in the more translucid edible films, since on the chemically modified starch−starch side as the Nifrastarch proportion increased, the opacity values decreased, as compared with the other formulations (Figure 1a).
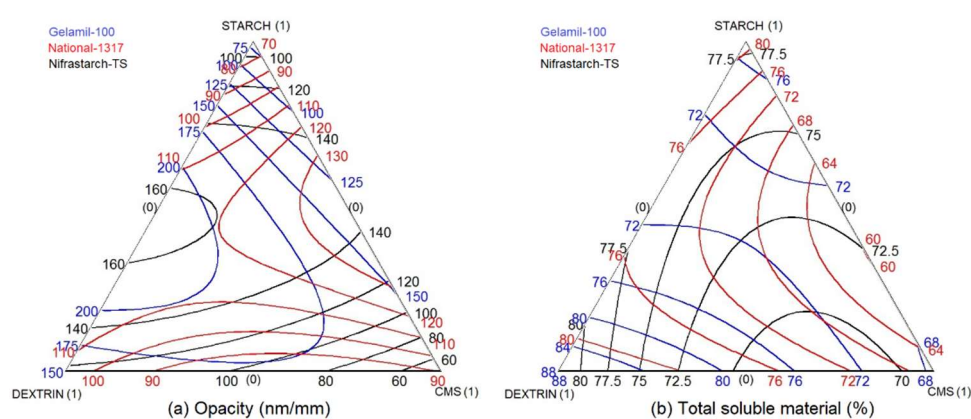

Figure 1. Isoresponse contour plots for the regression equation for edible films (a) opacity and (b) total soluble mater.

Regarding the total soluble matter, edible films formulated with Gelamil presented a highly significant (p<0.01) effect for the linear parameters, and an R^2= 45.81. A similar tendency was observed in the samples formulated with National modified starch, with a highly significant (p<0.01) effect due to starch, dextrin, and chemically modified starch linear parameters (R^2=59.61). When Nifrastarch was employed, linear parameters also presented a highly significant (p>0.01) effect, in addition to a significant (p<0.05) but with a negative effect of the dextrin×chemical modified starch interaction (and a high R^2= 92.26) (Table 2). In the iso-response curve, lower total soluble material was observed in the chemically modified vertex, corresponding to the lower estimated parameter values in the regression analysis. In contrast, dextrin seems to increase the total soluble material. In general, increasing chemically modified starch proportion decreased total soluble material, irrespective of the chemically modified starch employed (Figure 1b).

Translucid edible films were more soluble. Since dextrin resulted in glossy, fractured, and tacky coatings (Trezza and Krotcha, 2000), the increase in dextrin proportions resulted in less translucent and more soluble composite films.

Although acid-modified starch had similar amylose content to native starch, acid hydrolysis could lead to a reduction in the average molecular weight of linear chains, modifying film-forming capacity (López *et al.*, 2010).

Table 2. Regression coefficients and correlation for the adjusted model to the experimental data in mixture design approach.

Variable	β1	β2	β3	β12	β13	β23	R2
Opacity (nm/mm)							
Gelamil	55.34	149.77**	153.34**	453.26*	91.96	79.74	80.29
National	65.75*	105.77**	91.52**	117.22	247.99*	-70.95	83.16
Nifrastarch	82.42*	116.14**	44.43*	322.11*	250.75*	57.24	86.30
Total soluble material (%)							
Gelamil	78.40**	88.08**	66.97**	-48.24	-5.18	4.03	45.81
National	82.07**	82.56**	65.61**	-28.22	-5.44	13.45	59.61
Nifrastarch	78.09**	82.27**	71.69**	-13.85	-5.51	-30.04*	92.26
Water vapor permeability ΔRH= 50 (g/Pa s m)							
Gelamil	1.125**	0.750**	0.880**	-2.276	-0.139	0.233	75.02
National	1.220**	0.664**	2.062**	0.079	-3.435**	-1.389	93.16
Nifrastarch	1.167**	0.708**	1.820**	-0.044	-2.412**	-0.885*	98.52
Water vapor permeability ΔRH= 25 (g/Pa s m)							
Gelamil	1.773**	1.010**	0.767**	-0.632	-1.315	-0.516	75.57
National	1.843**	0.911**	1.734**	-1.769*	-4.173**	-2.039	94.95
Nifrastarch	1.074**	0.944**	1.709**	-2.119**	-1.582**	-1.720*	92.80
Water vapor permeability ΔRH= 15 (g/Pa s m)							
Gelamil	1.706**	1.030**	0.875**	-1.219	-1.266	-0.767	88.22
National	1.822**	0.894*	1.693**	-1.863*	-4.035**	-2.051*	96.03
Nifrastarch	1.826*	1.422*	2.094**	-2.265*	-3.335**	-2.899	91.11
Melting temperature (° C)							
Gelamil	128.68**	161.39**	154.37**	-115.23	-148.11	-185.73	67.49
National	118.91**	165.12**	143.36**	-82.02	-44.64	-177.62	67.70
Nifrastarch	126.16**	155.34**	135.56**	-139.87	-83.31	-165.25	56.36
Denaturation enthalpy (J/g)							
Gelamil	215.04	148.33	97.19	-33.15	108.79	148.55	14.52
National	214.92	149.61	115.19	-41.69	41.97	148.72	10.07
Nifrastarch	220.44	151.45	125.97	-13.34	19.45	145.48	10.41

* Significant p<0.05, **Highly significant p<0.01

Water vapor permeability at different RH gradients

In the regression analysis, water vapor permeability at 50% RH gradient for Gelamil containing samples presented a highly significant (p<0.01) effect only in linear terms, this is, no additive effect or interaction was detected for this parameter (R^2= 75.02). In the edible films formulated with National modified starch, there was a higher significant (p<0.01) effect due to linear terms (starch, dextrin, and chemically modified starch), and for the starch×chemically modified starch interaction, with a good correlation coefficient R^2= 93.16). And for the edible films formulated with Nifrastarch, there was as well a highly significant (p<0.01) effect for

the linear parameters. In addition, the starch×chemically modified starch interaction presented a highly significant (p<0.01) effect, and the dextrin×chemically modified starch presented a significant (p<0.05) effect as well (R^2= 98.52) (Table 2). In iso-response contour plots, at 50% RH gradient, higher WPV values were observed when Gelamil proportion increased, with a similar tendency for National and Nifrastarch samples, but with lower WVP values (Figure 2a).

For Gelamil edible films at 25% RH gradient, only linear terms presented a highly significant (p<0.01) effect (R^2= 75.57). When National modified starch was employed in the mixtures, a highly significant (p<0.01) effect was due to the linear terms (starch, dextrin, and chemically modified starch) and starch×chemically modified starch interaction (negative sign) was detected. The starch×dextrin interaction resulted significantly (p<0.05), with a good R^2 of 93.16. For the edible film containing Nifrastarch, the linear terms, together with both starch×dextrin and starch×chemically modified starch cross-product terms, presented a highly significant (p>0.01) effect, where the negative sign in the interactions signifies a decrease in WVP (R^2= 92.80) (Table 2). The reduction in the RH gradient drastically changed the shape of the iso-response contour plot curves. Lower values were observed at dextrin vertex and similar values at both starch and chemically modified starch vertices. With no significant effect in cross-product terms, Gelamil presented the lowest WVP values (around 0.8) (Figure 2b).

In regression analysis at the lowest relative humidity gradient (15%) for edible films formulated with Gelamil, linear terms presented a highly significant (p<0.01) effect (R^2= 88.22). For the National modified starch edible film samples, the linear terms, and starch×chemically modified starch interaction (negative) presented a highly significant (p<0.01) effect, in addition to a significant (p<0.05) effect with a negative sign of starch×dextrin interaction and dextrin×chemically modified starch interaction, plus a good R^2 of 96.03. For Nifrastarch containing samples, linear terms and the starch×chemically modified starch interaction presented a highly significant p<0.01) effect, in addition to a significant (p>0.05) effect of starch×dextrin interaction (R^2=91.11). Interactions presented a negative sign, indicating a reduction in the permeability of the edible films at this RH gradient (Table 2). Iso-response contour curves for 15% RH gradient presented similar behavior to that observed at 25% RH gradient, higher values at both starch and CMS pure component vertices, and lower at the dextrin vertex. With no significant effect in cross-product terms, Gelamil-100 presented the lowest WVP values (around 1.0) (Figure 2c).

Soluble material in edible films seems to be related to higher WVP, moreover when the RH gradient decreased from 50% to 15%. In the edible films, water vapor interacts strongly with polymer structure, where diffusion and solubility of the gas depend on the driving force, *i.e.* the difference in the partial pressure of the gas on the two surfaces of the barrier (Bertuzzi *et al.*, 2007; Hagenmaier, 2012). WVP depends on the intermolecular forces between the polymer chains and the plasticizer, regulating the free volume and movement of molecular chains, promoting the dissemination of water molecules through the film, and the swelling

of the hydrophilic matrix due to different structural changes in the film, which are a result of the strong interactions of starch molecules that lead to differences in the packaging of the starch network and compacting of the adjusted structure by the plasticizer (Adjouman *et al*., 2017). The increase in film permeability indicates a water affinity of hydrophilic compounds (Koch, 2018), and this affinity is related to crystalline zones within the edible film matrix. Crystalline zones in edible films bond a greater amount of water than amorphous zones (López *et al*., 2008; Myllärinen *et al*., 2002), and since for starch matrices, the crystalline structure was mainly attributed to the spontaneous recrystallization of amylose molecules after gelatinization during film casting (Cano *et al*., 2014). More translucent and soluble edible films will allow a higher WVP, and edible films formulated with Nifrastarch presented in general higher WVP than the other chemically modified starches.
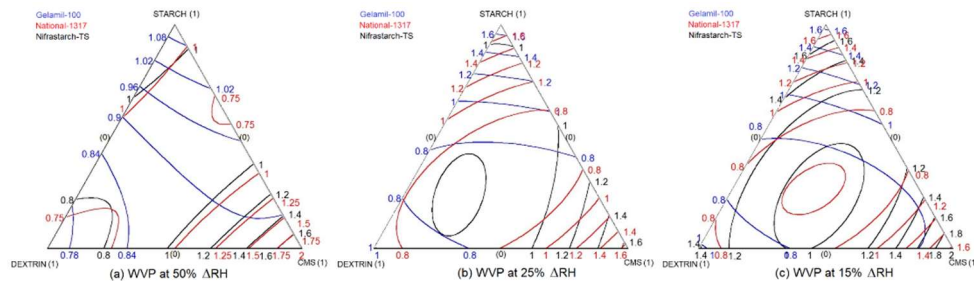

Figure 2. Isoresponse contour plots for the regression equation for the edible films water vapor permeability at (a) 50% relative humidity gradient, (b) 25% relative humidity gradient, and (c) 15% relative humidity gradient.

Differential scanning calorimetry

Regression analysis established that for thermal transition temperature, only linear terms presented a highly significant (p<0.01) effect for the three chemically modified starches used. Similar correlation coefficient values were observed in Gelamil samples (R^2= 67.49) and National chemical modified starch (R^2= 67.70), and a lower one in Nifrastarch samples (R^2= 56.36) (Table 2). In the iso-response contour plot, higher thermal transition temperature values can be observed at the dextrin vertex, where the increase in chemically modified starch proportions reduced the thermal transition temperature (dextrin×chemically modified starch side). In contrast, on the starch×chemically modified starch side, the increase in chemically modified starch proportions increased thermal transition temperature, with higher values observed in Nifrastarch samples (Figure 3a).

In the enthalpy regression analysis, there was no significant (p>0.05) effect for any of the chemically modified starch used in the edible film formulation, with concomitant low regression coefficients (14.52, 10.07, and 10.41 for Gleamil, National, and Nifrastarch, respectively) (Table 2). The iso-response contour plot presented higher denaturation enthalpy values at the dextrin vertex, with similar

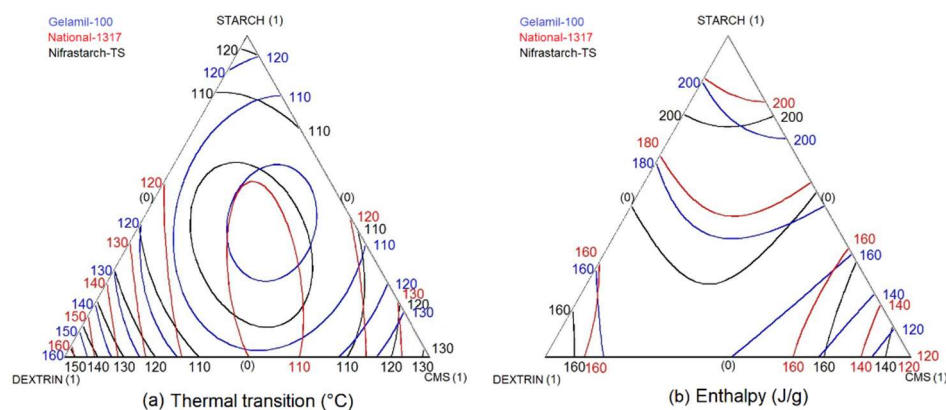enthalpy values for the three chemically modified starches at this vertex (≈120 J/g) (Figure 3b).

Figure 3. Isoresponse contour plots for the regression equation for the edible films (a) thermal transition temperature and (b) enthalpy.

According to Ghanbarzadeh *et al.* (2010), three characteristic thermal transitions may exist for semi-crystalline polymers such as starch: a glass transition for the amorphous fraction, a melting transition for the crystalline fraction, and a transition due to crystallization. The glass transition of plasticized starch films is difficult to determine because the change in heat capacity is quite low. Melting thermal transition could be associated with several processes, such as the crystal growth of short chains (products of hydrolysis) and recrystallization of amylose or other long lateral amylopectin chains (García *et al.*, 2009). The melting of co-crystallized amylose and amylopectin and crystallized amylopectin resulted in an endothermic peak above 110-120°C, where cocrystals seem to be located in starch strands and amylopectin-like structures (Rindlav-Westling *et al.*, 2002). Melting temperature, typical of a semi-crystalline polymeric system such as edible starch film, has been associated with the melting of crystalline starch domains reorganized during the retrogradation, and chemical modification in the structure of the starch polymer backbone which causes a higher degree of crystallinity (Ghanbarzadeh *et al.*, 2010). In this respect, the more translucent, soluble, and permeable edible films formulated with Nifrastarch with more crystalline zones as a result of the relatively high amylose/amylopectin ratio, presented higher melting temperatures.

Fourier transform infrared spectroscopy

For edible starch films, broadband around 3400 cm^{-1} corresponds to the stretching of hydrogen-bonded hydroxyl groups, attributed to the complex vibrational stretches of the free, inter- and intra-molecular bond groups in the gross structure of starch, associated with complex vibrational stretching with the free hydroxyl groups, evidencing the formation of inter- and intra-molecular hydrogen bonding in plasticized starch films (Fang *et al.*, 2001; Kibar and Us, 2014; Bof *et al.*, 2015). A

sharp band around 1300 cm^{-1} corresponds to C-H stretching associated with the ring of methine hydrogen atoms, and changes in this region indicate the formation of inter- and/or intra-hydrogen bonds between polymer chains and/or plasticizer molecules in edible films (Fang *et al*., 2001; Kibar and Us, 2014). In the same way, the infrared spectra of starches between 900-1300 cm^{-1} represent a domain that is more sensitive to molecular conformation, and changes in the bands between 1400-1300 cm^{-1} are related to molecular changes, such as C-H and C-O-H bending (Vicentini *et al*., 2005). Three characteristic peaks appear, attributed to C-O bond stretching. In this range, the stretching vibrations of C-O bonds in the C-O-H and C-O-C groups in the anhydroglucose ring within the starch structure are at 1157, 1082 and 929 cm^{-1}, respectively (Fang *et al*., 2001; Kibar and Us, 2014) (Figure 4).

The spectra of the different edible films analyzed showed the typical bands or peaks previously reported for edible starch films in general, with differences in intensity and band shifts at $\approx$3400 cm^{-1} and $\approx$1350 cm^{-1} frequencies. Differences between the different chemically modified starches seem to be related to changes in peak frequency mainly within these two spectra regions, as a consequence of the respective chemical modification. The IR spectra of edible films with Gelamil chemically modified starch presented both 2900 cm^{-1} and 3100 cm^{-1} peaks, with similar intensity and lower frequency shift when native starch increased in the edible film formulation. The intensity of both 2900 cm^{-1} and 3100 cm^{-1} peaks for the IR spectra of edible films containing National chemically modified starch was similar. In contrast, Nifrastarch chemically modified starch presented major differences, such as the lack of two peaks around 2900 cm^{-1} and 3100 cm^{-1}, although when the proportion of native maize starch increased, the intensity of both peaks seems to recover. This was the highest band shift in the FTIR spectra of the edible film mixtures for the incorporation of high proportions of native starch (from 0.00 to 0.67) (Figure 4). In this respect, Gelamil edible films presented lower water vapor permeability WVP due to a more compact structure developing during the filmogenic process, as indicated by the infrared spectra. The reduction of constant force brought about by some interaction is directly related to the frequency (or wavenumber) shift of stretching vibrations, thus, the lower the peak frequency the stronger the interaction (Pawlak and Mucha, 2003). An appreciable band shift in the FTIR spectra for the addition of another component is related to distinct chemical interactions, such as hydrogen bonding, between the components (Wu *et al*., 2009). This explains the higher total soluble material values and WVP of Nifrastarch composite edible films. Edible film composites containing Nifrastarch chemically modified starch were less opaque and more soluble, with higher WVP, due to the more crystalline zones that resulted in higher melting temperatures according to DSC and less compact structure, as indicated infrared spectra.
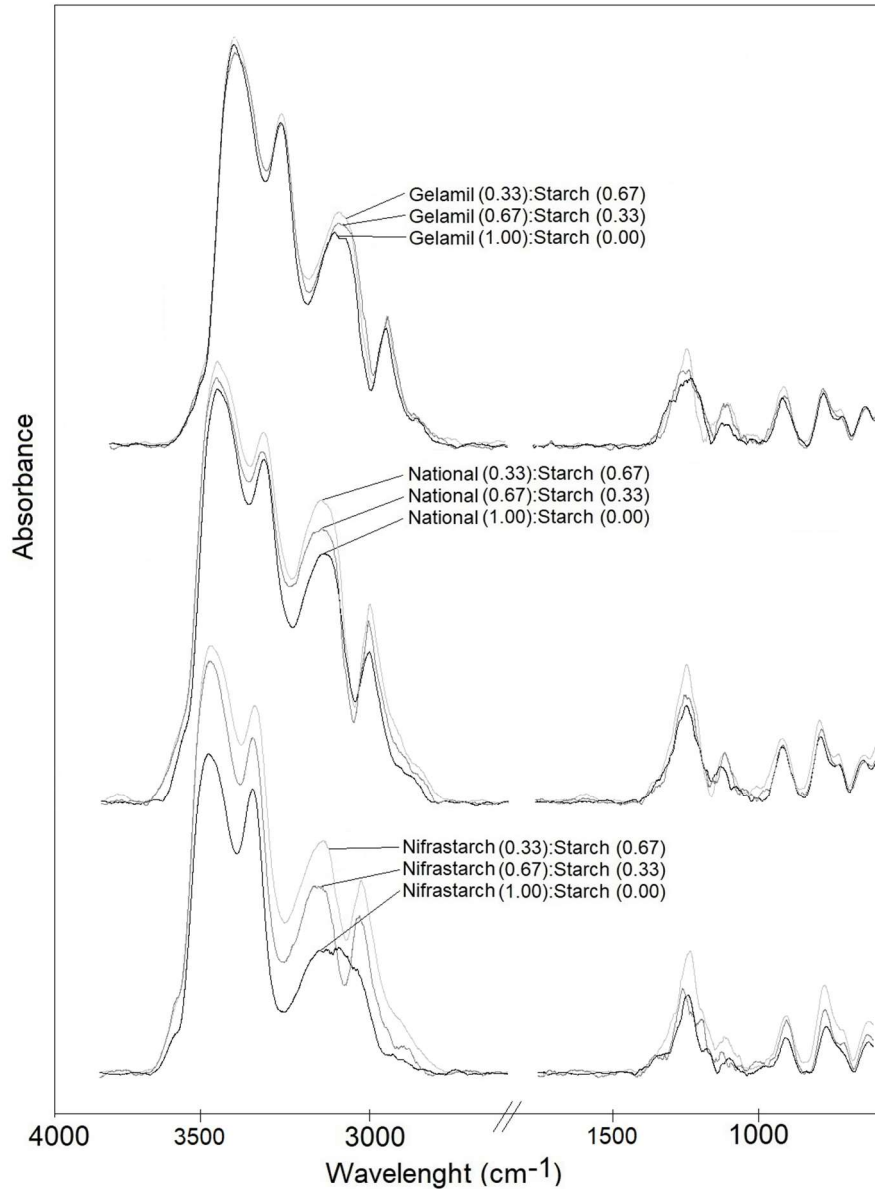
Figure 4. FTIR spectra of the edible films formulated with mixtures of starch, dextrin, and different chemically modified starches.

Conclusions

Lower opacity in edible films was associated with more soluble material, a concomitant effect of the abundance of crystalline regions, moreover when Nifrastarch chemically modified starch was used. Less translucid and less soluble edible films were obtained with Gelamil modified starch. The main effect of

dextrin also seems to be related to clear and more soluble edible films. Higher solubility was related to higher WVP, even at different relative moisture gradients. A more permeable film can be obtained with Nifrastarch and lower permeability with Gelamil. Dextrin seems to reduce WVP due to its higher hygroscopic properties. Strong interaction between the mixture components and Gelamil chemically modified starch was demonstrated with DSC and FTIR. A more homogeneous structure was developed in this mixture since enthalpy was not significantly different, and the lower peak frequency shift in the FTIR spectra indicates a strong interaction. The type of chemically modified starch used in edible films for edible packaging can be decided according to the characteristics of the food in question, *i.e.*, moisture, color, permeability, or edible film solubility for active packaging.

Acknowledgments

References

Adjouman, Y.D., Nindjin, C., Tetchi, F.A., Dalcq, A.C., Amani, N.G., Sindic, M. 2017. Water vapor permeability of edible films based on improved cassava (*Manihot esculenta Crantz*) native starches. *Journal of Food Processing and Technology,* **8**, 665.

Bertuzzi, M.A., Castro Vidaurre, E.F., Armada, M., Gottifredi, J.C. 2007. Water vapor permeability of edible starch based films. *Journal of Food Engineering,* **80,** 972-978.

Bof, M.J., Bordegaray, V.C., Locaso, D.E., García, M.A. 2015. Chitosan molecular weight effect on starch-composite film properties. *Food Hydrocolloids,* **51,** 281-294.

Cano, A., Jiménez, A., Cháfer, M., González, C., Chiralt, A. 2014. Effect of amylose:amylopectin ratio and rice bran addition on starch films properties. *Carbohydrate Polymers,* **111,** 543-555.

Cornell, J.A. 2011. *A Primer on Experiments with Mixtures.* John Wiley & Sons.

Fang, J.M., Fowler, P.A., Tomkinson, J., Hill, C.A.S. 2001. The preparation and characterization of a series of chemically modified potato starches. *Carbohydrate Polymers,* **47,** 245-252.

García, M.A., Pinotti, A., Martino, M.N., Zaritzki, E. 2009. Characterization of starch and composite edible films and coating. In *Edible Films and Coatings for Food Applications*. Embuscado, M.E., Huber, K.C., Springer Science, pp. 169-209.

Gennadios, A., Weller, C.L., Hanna, M.A., Froning, G.W. 1996. Mechanical and barrier properties of egg albumen films. *Journal of Food Science,* **61**, 585-589.

Ghanbarzadeh, B., Almasi, H., Entezami, A.A. 2010. Physical properties of edible modified starch/carboxymethyl cellulose films. *Innovative Food Science and Emerging Technologies,* **11**, 697-702.

Gupta, M., Brennan, C., Tiwari, B.K. 2012. Starch-based edible films and coating. In *Starch-Based Polymeric Materials and Nanocomposites. Chemistry, Processing, and Applications*. Ahmed, J., Tiwari, B.K., Imam, S.H., Rao, M.A., CRC Press, pp. 239-254.

Hagenmaier, R.D. 2012. Gas-exchange properties of edible films and coatings. In *Edible Coating and Films to Improve Food Quality*, 2nd ed. Baldwin, E.A., Hagemmaier, R.D., Bai, J., CRC Press.

Jangchud, A. Chinnan, M.S. 1999. Peanut protein film as affected by drying temperature and pH of film forming solution. *Journal of Food Science,* **64**, 153-157.

Jiménez, A, Fabra, M.J., Talens, P., Chiralt, A. 2012. Edible and biodegradable starch films: A review. *Food Bioprocessing and Technology,* **5,** 2058-2076.

Kibar, E.A.A., Us, F. 2014. Evaluation of structural properties of cellulose ether-corn starch based biodegradable films. *International Journal of Polymeric Materials and Polymeric Biomaterials,* **63**, 342-351.

Koch, K. 2018. Starch-based films. In *Starch in Food, Structure, Function, and Applications*, 2nd ed., Sjöö, M., Nilsson, L, Woodhead Publishing, pp. 747-768.

López, O.V., García, M.A., Zaritzky, N.E. 2008. Film forming capacity of chemically modified corn starches. *Carbohydrate Polymers,* **73**, 573-581.

López, O.V., Zaritzky, N.E., García, M.A. 2010. Physicochemical characterization of chemically modified corn starches related to rheological behavior, retrogradation and film forming capacity. *Journal of Food Engineering*, **100,** 160-168.

Myllärinen, P., Partanen, R., Seppälä, J., Forssell, P. 2002. Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers,* **50**, 355-361.

Pawlak, A., Mucha, M. 2003. Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica Acta,* **396**, 153-166.

Pereda, M., Amica, G., Marcovich, N. 2011. Development and characterization of edible chitosan/olive oil emulsion films. *Carbohydrate Polymers,* **87,** 1318-1325.

Rindlav-Westling, A., Stading, M., Gatenholm, P. 2002. Crystallinity and morphology in films of starch, amylose and amylopectin blends. *Biomacromolecules,* **3,** 84-91.

Rutenberg, M.W., Solarek, D. 1984. Starch derivatives: Production and uses. In *Starch: Chemistry and Technology*, 2nd ed. Whistler, R.L., BeMiller, J.N., Paschall, E.F., Academic Press.

Shah, U., Naqash, F., Gani, A., Masoodi, F.A. 2016. Art and science behind modified starch edible films and coatings: A review. *Compressive Reviews in Food Science and Food Safety,* **15,** 568-680.

Trezza, T.A., Krochta, J.M. 2000. The gloss of edible coatings as affected by surfactants, lipids, relative humidity, and time. *Journal of Food Science,* **65,** 658-662.

Vicentini, N.M., Dupuy, N., Leitzelman, M., Cereda, M.P., Sobral, P.J.A. 2005. Prediction of cassava starch edible film properties by chemometric analysis of infrared spectra. *Spectroscopy Letters,* **38,** 749-767.

Wu, Y., Geng, F., Chang, P.R., Yu, J., Ma, X. 2009. Effect of agar on the microstructure and performance of potato starch film. *Carbohydrate Polymers,* **76,** 299-304.

Zhang, H., Hou, H., Liu, P., Wang, W. Dong, H. 2019. Effects of acid hydrolysis on the physicochemical properties of pea starch and its film forming capacity. *Food Hydrocolloids,* **87,** 173-179.