Classification of Cassava Starch Films by Physicochemical Properties and Water Vapor Permeability Quantification by FTIR and PLS

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ABSTRACT: Cassava starches are widely used in the production of biodegradable films, but their resistance to humidity migration is very low. In this work, commercial cassava starch films were studied and classified according to their physicochemical properties. A nondestructive method for water vapor permeability determination, which combines with infrared spectroscopy and multivariate calibration, is also presented. The following commercial cassava starches were studied: pregelatinized (amidomax 3550), carboxymethylated starch (CMA) of low and high viscosities, and esterified starches. To make the films, 2 different starch concentrations were evaluated, consisting of water suspensions with 3% and 5% starch. The filmogenic solutions were dried and characterized for their thickness, grammage, water vapor permeability, water activity, tensile strength (deformation force), water solubility, and puncture strength (deformation). The minimum thicknesses were 0.5 to 0.6 mm in pregelatinized starch films. The results were treated by means of the following chemometric methods: principal component analysis (PCA) and partial least squares (PLS) regression. PCA analysis on the physicochemical properties of the films showed that the differences in concentration of the dried material (3% and 5% starch) and also in the type of starch modification were mainly related to the following properties: permeability, solubility, and thickness. IR spectra collected in the region of 4000 to 600 cm^{-1} were used to build a PLS model with good predictive power for water vapor permeability determination, with mean relative errors of 10.0% for cross-validation and 7.8% for the prediction set.

Keywords: chemometrics, modified starch, PCA, physicochemical properties, PLS

Introduction

The packaging industry has experienced a substantial growth in the last few years, both in terms of materials and processes. The use of plastic materials in food packaging is increasing and being considered as one of the most economic and safe forms of food preservation. About 60% of the polyethylene and 27% of the polystyrene produced is consumed in packaging production and a large part of it is specifically used for food products (Alvin and Gil 1994).

However, motivated by the question of the environmental impact of conventional synthetic packaging materials, the search for new biodegradable materials, especially biodegradable polymers is, today, a great challenge. Biodegradable polymers are flexible films that can be prepared from biological macromolecules capable of forming a continuous matrix (Gontard and Guilbert 1996). The biopolymers that are used for preparation of the films are biodegradable, and even edible when only additives with nutrition values are included in their formulation.

According to this viewpoint, the challenge today is to substitute conventional packaging by biodegradable films that have the same shelf life and efficiency in the inhibition of humidity, oxygen, carbon dioxide, aroma, and lipid migration (Kester and Fennema 1986; Krochta and De Mulder-Johnston 1997).

Among the polymers used in biodegradable polymer production, the most important are starch, pectin, cellulose and its derivatives, collagen, gelatin, and myofibril proteins (Vanin and others 2005).

According to Garcia and others (1997), the advantages of using biodegradable polymers are to increase the product lifetime by slowing down the migration of gases and solute transport and to allow the conservation of organoleptic, nutritional, and mechanical characteristics of the product, besides its texture.

Starch-based biodegradable polymers are among those frequently studied, with cassava starch being the most suitable raw material due to its transparency and brightness (Cereda and others 1992).

Starches can be modified to acquire specified characteristics if compared to regular or native starches, such as the property to form films. The literature on biodegradable native starch-based films is relatively abundant, but very rare on modified starches. Brazilian industry has produced acetylated cassava starches and evaluated these modified products for their surface impermeability in rigid and flexible packaging, with the intention to improve the characteristics of biopackaging. Oxidation processes with agents such as hypochlorite and hydrogen peroxide were employed to produce a starch paste with reduced viscosity and other modified properties. Such procedures resulted in the formation of compounds in which some of hydroxyl groups were oxidized into carbonyl or carboxylate groups. Due to the fact that the carbonyl and carboxylate groups are larger than hydroxyl groups, the amylose chains tend to be more separated and, thus, prevent starch retrogradation. This chain separation is facilitated by the ionization of carboxylate groups that causes a steric effect (Bobbio and Bobbio 2003). The starch oxidation does not promote grain rupture, but preserves its original structure. Oxidized starch is insoluble in cold water and forms a clear paste with

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low tendency to thicken or retrograde. After drying, the films formed by oxidized starches are clear and firm. This starch type is quite useful in the paper industry as a glue for surfaces and in the textile and adhesive industries. The starch forms films on the threads of the fabrics, increasing their resistance to tears, accentuating the color, and increasing the shine of the fabrics. The starch transformed in dextrines is in soluble water, has adhesives properties, and is used in envelopes and stamps.

In this work, the films of modified starch were made and characterized by the following physical properties: film thickness (TH), grammage (GM), water vapor permeability (WVP), water activity (WA), tensile strength - deformation force (TS), water solubility (WS), and puncture strength – deformation (PS). Two chemometrics tools were applied: (i) principal component analysis (PCA) method was used to explore how the physicochemical properties of modified cassava starch films are affected by the differences in concentration of the dried material (3% and 5% starch) and also in the type of starch modification; (ii) diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) associated with the multivariate calibration method PLS was used to propose a nondestructive method for determining the water vapor permeability. This property has been specifically selected to illustrate that a time- and labor-consuming physicochemical property determination can be accomplished by a fast and reliable method. The application of Fourier transform infrared spectroscopy (FTIR) and chemometric methods has made it possible to perform the analysis of rather complex mixtures without prior separation of their components (Geladi and Kowalski 1986; Martens and Naes 1988; Beebe and others 1998; Ferreira and others 1999).

Materials and Methods

Materials

The starch extracted from the plants is called natural or native starch. The starches are modified by physical, chemical, and enzymatic processes to improve characteristics or to accentuate functional properties. As a function of the modification of the starches, physicochemical properties can be changed, for example, to improve solubility in organic or inorganic solvents with respect to native one and increase the pH.

In the estherified starch of the acetate type, a carboxyl group is added in the carbon 6 of the glucose molecule in a percentile of 3% (number of substitutions for 100 glucose units in the starch chain) as is verified in the reaction below.

In the etherified starch of the carboxymethyl type, an organic acid salt group is formed in the carbon 6 of the glucose molecule as is verified below.

Both modified starches (ether or ester) are water soluble because of their pH. The cassava native starch has pH 6.0 but the modified ones presented pH 12.0 for the ether (CMA) and 9.0 for the ester. The alkaline pH opens the starch granule structure and makes it soluble in cold water. The higher the pH increase, the greater the starch solubility in cold water.

The following commercial-modified cassava starches were used as raw materials: pregelatinized (amidomax 3550 – Cargill®), carboxymethylated starch (CMA) of low and high viscosities (Flexamid – Celuflok®), and esterified starches (Lorenz®). Two starch filmogenic suspensions were prepared. One of them contained 3% of starch in water and the other 5%. The abbreviations are defined in Table 1.

Methods

The formulations were prepared by gelatinizing a water suspension of starch in the temperature of 70 °C. To obtain 3% and 5% starch concentrations, 30 g and 50 g of starch were suspended in 1 L of distilled water, respectively.

The films with modified cassava starches were prepared by casting, that is, dehydration of filmogenic solutions in Bioplass glass Petri dishes with 15 cm dia. The suspensions were dehydrated and dried with forced air stove for 24 h at 40 °C and left standing at 21°C ± 2 at a relative humidity of 54% (NaCl) for 3 d before removing the films. Slow drying conditions were used to avoid physical alteration in the films with the temperature (Yang and Paulson 2000). Mass control was carried out using a semianalytical balance. The thicknesses of the films were controlled by the volume to area ratio of the solution. The thicknesses of films can vary if the surface of the Bioplass glass Petri is not perfectly level.

The films were characterized for their TH, GM, WVP, WA, TS, WS, and PS (Gnanasambandam and others 1997). The methods used for determination of these properties are described below.

Thickness. Defined as the perpendicular distance between the two principal surfaces of the material, this is an important parameter of plastic film. Knowing its thickness, it is possible to obtain information about mechanical resistance and migration of gases. According to Cuq and others (1996), the variation in the filmogenic solution thickness (initial) does not affect the possible molecular rearrangements during the drying process. Crank (1980) emphasized that the film thickness should not affect water vapor permeability.

Table 1 – Experimental mean and standard deviation (sd) values for modified starch film properties. All the mean values were obtained from 5 replicates.

	Mean (±sd)						
Samples (Titles)	TH (mm)	GM (g/m^2)	PS (%)	TS (N)	WS (%)	WVP ($g.mm\ m^{-2}.\ h^{-1}.kPa^{-1}$)	WA
High CMA, 3%	0.06	423.90	0.55	10.78	23.39	0.15	0.55
(CMAH3)	(±0.006)	(±20.50)	(±0.043)	(±3.65)	(±1.87)	(±0.010)	(±0.023)
Low CMA, 3%	0.09	341.00	0.63	10.57	53.85	0.17	0.55
(CMAL3)	(±0.019)	(±19.26)	(±0.089)	(±3.92)	(±2.23)	(±0.010)	(±0.011)
High CMA, 5%	0.10	380.70	1.07	16.03	14.14	0.19	0.56
(CMAH5)	(±0.019)	(±9.11)	(±0.352)	(±4.65)	(±1.06)	(±0.023)	(±0.014)
Low CMA, 5%	0.11	457.90	0.83	8.85	45.99	0.20	0.56
(CMAL5)	(±0.023)	(±10.38)	(±0.332)	(±4.32)	(±1.63)	(±0.038)	(±0.018)
Pregelatiniz., 3%	0.07	321.90	1.35	12.18	56.47	0.12	0.56
(PG3)	(±0.010)	(±20.78)	(±0.702)	(±5.68)	(±2.08)	(±0.017)	(±0.048)
Pregelatiniz., 5%	0.12	335.30	1.30	15.82	32.04	0.21	0.55
(PG5)	(±0.010)	(±25.73)	(±0.778)	(±7.73)	(±1.10)	(±0.036)	(±0.028)
Esterefied, 3%	0.08	371.00	1.03	13.02	73.76	0.12	0.54
(Ester3)	(±0.016)	(±26.28)	(±0.201)	(±4.33)	(±1.40)	(±0.020)	(±0.026)
Esterefied, 5%	0.08	382.90	1.02	15.09	82.97	0.18	0.55
(Ester5)	(±0.009)	(±27.88)	(±0.289)	(±1.98)	(±1.06)	(±0.032)	(±0.024)

This property was determined by a digital micrometer and expressed in millimeters (mm). Each measurement was carried out 9 times, and each thickness was considered as the mean of the measured values (Sobral 1999).

Grammage. Defined as the mass of a specific area and expressed in g/m^2 (Oliveira and others 1996). Grammage is directly related to the mechanical resistance. In other words, greater grammage yields greater mechanical resistance. This property was determined from the relation $GM = 10000\ m/a$, where GM is grammage (g/m^2), m = mass (g), and a = area (cm^2) of the film.

Tensile and puncture strengths. These properties were determined as described by Gontard and others (1992), and the ASTM standard method (ASTM 1996). The mechanical properties were measured using a Texture Analyzer (TA.XT2, Texture Technologies, Corp., N.Y., U.S.A.). The results are given by the software Texture Expert V.1.15 (SMS).

For the tensile strength determination, the films were cut into 18-mm × 100-mm strips. The strips were fixed in 2 grips separated by 80 mm. The grips were dislocated at 1 mm/s up to film rupture. The values used in the data analysis were related to the deformation force (N).

To determine the puncture strength, the films were cut in a circular format with approximately 6 cm dia and fixed in a glass cell with circular cap opening. The glass cell was supported in a circular support with an opening of 52.6 cm dia and punctured by a probe of 3 mm dia at a speed of 1 mm/s. The values used in the data analysis relate to the deformation (%).

Water solubility. Two samples of 2-cm dia were taken per film, for each repetition. The thin grating containing the weighted samples was immersed into a vessel containing 200 mL of demineralized water at 20 °C and gently and periodically agitated with a magnetic stirrer for 5 min. After noticeable solubilization, the solution was transferred to a dryer at 105 °C for 24 h, and the mass of the dissolved material was determined (Gontard and others 1992).

Water vapor permeability. Water vapor permeability was determined gravimetrically, according to an ASTM technique (1996), modified by Gontard and others (1992). The film was placed in cell containing silica gel (UR = 0%; 0 kPa), constituting a membrane, and the cell was then placed inside of a desiccator containing distilled water (UR = 100%; 32.3 kPa) in room acclimatized to 22 °C. The cell was weighed in semianalytic scale every 24 h.

Water activity. Water activity was measured 3 times by means of levy block treatment. An Aqualab series 3 Quick Start with direct reading was used for the measurements, and the results were expressed in WA.

All physicochemical properties were determined in 5 repetitions for each film formulation, and average values were used for the data analysis.

FTIR measurements. Infrared spectra of the films were recorded in the reflectance mode using a Perkin-Elmer spectrophotometer (Spectrum One) supplied with a device for attenuated reflectance (ATR) with a diamond crystal in the Laboratorie de Spectrochimie Infrarouge et Raman (LASIR)/Université dês Sciences et Technologie de Lille (France). The spectra were collected from 4000 to 650 cm^{-1} at least 3 times per sample, with 200 sweepings in each repetition at a resolution of 2 cm^{-1}. The spectra were obtained on three different regions of the film and the mean WVP values of the film were considered for each spectrum. The spectra considered emphasized the "fingerprint" region from 2000 to 700 cm^{-1} that makes an investigation of the molecular structure of the analyzed compositions possible. All readings were done directly on the films.

Data analysis

The analysis of the experimental data was performed in 2 parts: qualitative (exploratory) and quantitative (multivariate calibration) analyses.

The exploratory data analysis was carried out for the physicochemical results by means of PCA (Beebe and others 1998; Ferreira and others 1999). PCA is a projection method in which complex data are compressed in such a way that the relevant information becomes more obvious. The experimental data were organized in a matrix $\mathbf{X}_{\mathbf{pca}}$, in which the samples are described by the rows and the physicochemical properties (variables) are described by the columns. PCA in this work was carried out on autoscaled data (meancentered and scaled to unit variance).

The calibration model for WVP determination was built using the spectral data and the method of partial least squares (PLS) (Geladi and Kowalski 1986; Martens and Naes 1988; Ferreira and others 1999). The input data for PLS modeling are the data matrix $\mathbf{X}_{\mathbf{pls}}$, where each row corresponds to a given spectrum from casssava starch film and the **y** vector whose entries are the experimentally obtained WVP.

The model structure is given by the 2 equations

$$X_{pls} = TP^t + E \tag{1}$$

$$y = Tq + f \tag{2}$$

where the matrix **P** and the vector **q** are called loadings and **T** is the scores matrix. The number of columns (*k*) in **T** may be thought of as a small set of latent variables accounting for the systematic variation in both $\mathbf{X}_{\mathbf{pls}}$ and **y**. The matrix **P** and vector **q** describe how the variables in **T** are related to the original data matrices $\mathbf{X}_{\mathbf{pls}}$ and **y**. The matrix **E** and the vector **f** represent the noise or irrelevant variability in $\mathbf{X}_{\mathbf{pls}}$ and **y**, respectively. PLS regression attempts to find factors which capture variance and achieve correlation. The loadings in **P** and **q** are estimated by regression of $\mathbf{X}_{\mathbf{pls}}$ and **y** onto **T**, and the residual matrices are found by subtracting the estimated versions of $\mathbf{TP}^t$ and **Tq** from $\mathbf{X}_{\mathbf{pls}}$ and **y**, respectively. The estimated model parameters can be combined into the regression vector **b** to be used in the prediction equation (Naes and others 2002).

$$\hat{y} = b_0 + \mathbf{x}^t\hat{\mathbf{b}} \tag{3}$$

The number of factors in the model was determined by cross-validation applying the leave-one-out method, based on the calculation of root mean square errors of cross-validation (RMSECV) given in Equation 4 and on the correlation coefficient ($\mathbf{r}_{\mathbf{cv}}$) between the estimated values by cross-validation and the true ones. The predictive ability of the model for unknown samples was given by the root mean square errors of prediction (RMSEP) calculated for an external validation set (Equation 5).

$$RMSECV_k = \sqrt{\frac{\sum_{i=1}^{I} (c_i - \hat{c}_i)_k^2}{I}} \tag{4}$$

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{N} (\hat{y}_i - y_i)^2}{N}} \tag{5}$$

In Equation 4, $\hat{\mathbf{c}}_{\mathbf{i}}$ is the estimated WVP for sample i, not included in the model formulation, k is the number of factors in the model, and I is the number of samples for internal validation.

The root-mean-square error of prediction (RMSEP) was used for model evaluation when the model was applied to an external data set (prediction set). In Equation 5, the predicted values ($\hat{y}_i$) are based on the final model, and N is the number of samples in the prediction set.

Once the model has been constructed and validated, it can be used for prediction of WVP for new film samples using Equation 3.

Data analysis was performed using the computational package PLS˙Toolbox® (Eigenvector Research, Inc. – PLS˙Toolbox version 3.02.) and Matlab® 6.5 software (The MathWorks Co., Natick, Mass., U.S.A.).

Results and Discussion

Table 1 presents the mean values obtained for each physical property and the respective standard deviations. Each value was obtained from 5 replicates in accordance with the methodology presented for the 7 properties.

Classification analysis

PCA was performed on a data matrix $\mathbf{X}$ (45 × 7) containing the values for each individual replicate of the 7 physicochemical properties investigated. The purpose of this chemometric analysis was to explore the physicochemical properties of the films, with the intention to visualize the relevant aspects that could be useful in their characterization, for instance, to identify which parameters could be important for the differentiation of films with respect to their composition, that is, the type of modification and concentration (3% and 5% in water) of the starch.

The presence of highly intercorrelated variables means that it is possible to find a new set of variables to represent the original data, where a large part of the original information is preserved in a low dimensional space. This can enable better spatial visualization of the data in 2- or 3-dimensional plots. The new set of variables called principal components is defined as a linear combination of the original ones (whose coefficients are the loadings) and is oriented in such a way as to describe the maximum variance of the original data. The scores, coordinates of the projected samples in the PC coordinate system, can be seen in Figure 1A.

There are 2 distinct groups of samples along the axes of the 1st and 5th principal components, describing 33.88% of the total variance, as can be seen in Table 2. With a few exceptions, the samples with positive scores in PC1 represent the films produced by filmogenic suspensions with 5% starch concentrations, while the samples with negative scores represent the films containing 3% starch

Table 2—Loadings contributions of the original properties to the principal components. The % variance explained is in parenthesis.

	PC1 (23.26%)	PC2 (22.83%)	PC3 (15.64%)	PC4 (14.14%)	PC5 (10.62%)
TH	0.508	0.268	−0.173	−0.5434	0.200
GM	−0.019	−0.577	−0.398	0.250	0.085
WA	0.252	−0.215	0.741	−0.233	−0.126
PS	0.028	0.606	−0.321	0.059	−0.244
TS	0.261	0.332	0.320	0.737	0.025
WS	−0.484	0.229	0.191	−0.057	0.785
WVP	0.612	−0.141	−0.144	0.194	0.510

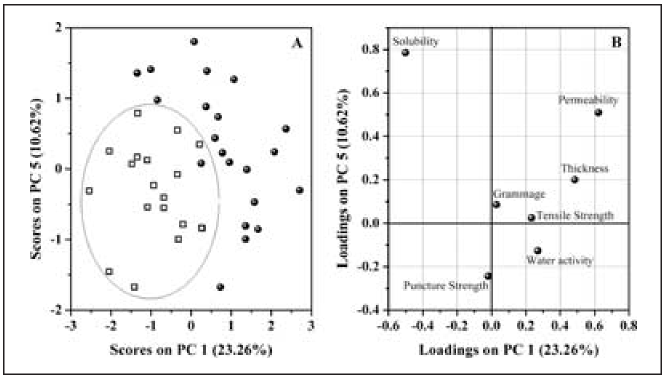

Figure 1—Scores (A) and loadings (B), PC1 × PC5 showing the distribution of the films with respect on to their concentration and variables influence, respectively. In A, the symbols (☐) and (•) indicate 3% and 5% starch concentration, respectively.

Table 3—Contribution of the original properties to the principal components. The % variance explained is in parenthesis.

	PC1 (38.85%)	PC2 (30.43%)	PC3 (18.19%)
TH	0.510	−0.555	0.146
GM	0.149	0.799	0.287
WS	−0.549	−0.224	0.803
WVP	0.646	0.063	0.501

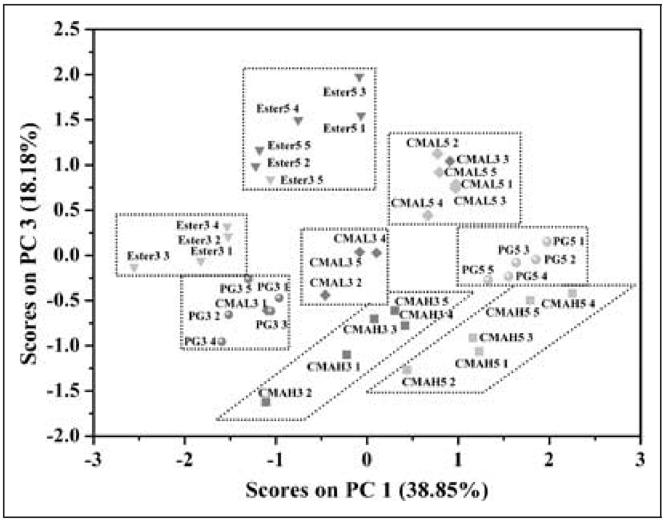

Figure 2—Scores that classify the films with respect to the chemical modification of starches

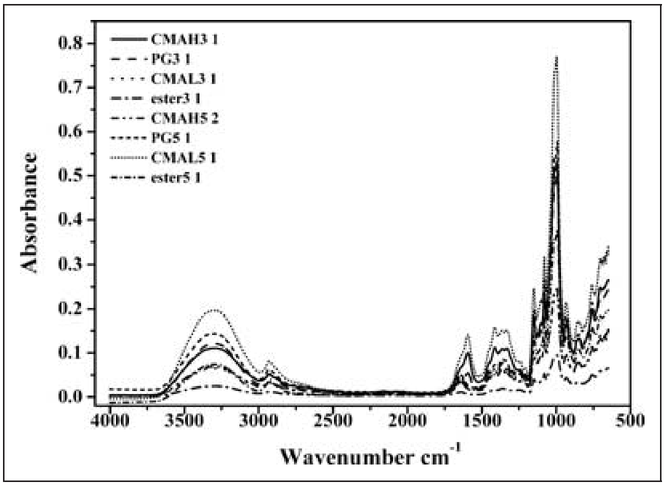

Figure 3—Spectra of some films of modified starch used in multivariate calibration

Table 4 — Parameters obtained for calibration and test set for full spectra and selected variables

	Settings		Calibration set		Test set	
Models	Preprocessing	LV	RMSECV	r_{cv}	RMSEP	r_p
Full spectra (A)	Savitsky-Golay + Meancenter	4	0.051	0.26	1.726	0.33
Selected variables (B)	Savitsky-Golay + Meancenter	4	0.022	0.80	0.016	0.92

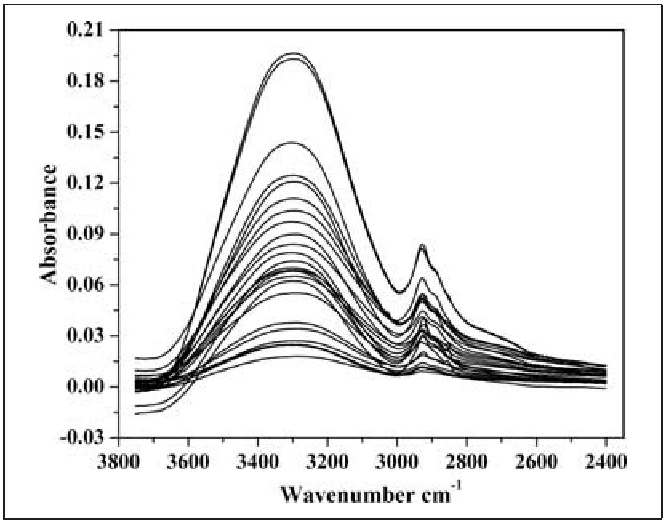

Figure 4 — The spectral region and variables selected for construction of the models for determination of WVP

concentrations. In fact, the scores plot (Figure 1A) exhibited discrimination of the samples with respect to the starch concentration.

This set of samples is primarily characterized by the influence of 3 physicochemical properties of the films: TH, WS, and WVP, as can be seen in the loadings plot in Figure 1B and also in Table 2. The loadings define the contribution of each original property to each principal component.

The group of samples originating from 5% starch concentrations was separated from the rest due to the high values of TH and WVP and relatively low WS. The samples with 3% concentration can be described by their high WS and low values of WVP and TH.

A variable selection was carried out with the purpose of characterizing the films with respect to starch chemical modification. For this purpose, the following variables were selected: TH, WVP, WS, and GM. According to the scores plot (Figure 2), it is possible to identify 8 distinct groups of samples, which are described by 4 types of starch chemical modification at the 2 concentration levels (3% and 5% of starch in water).

The separation observed in Figure 2 occurs along the 1st and 3rd principal components, describing 57.04% of the total % variance in the original data (Table 3). The WS, WVP, and TH are the most important parameters in this discrimination, as can be seen from the loadings values in Table 3. When comparing the results from Table 3 with the samples in Figure 2, it can be seen that the esterified starches (especially at 3% concentration level) tend to have smaller TH and be more soluble. The high viscosity CMA films of higher starch concentration (5%) are less soluble and tend to be more permeable and thicker.

The properties of the films in relation to the solubility in water were different from the properties of the same starches in the form of granules. This result can be explained by the physical properties of the films and not for the chemical property of the starch. The films of starch esterified were with smaller thickness and smaller grammage, although the process of preparation of the films was the same, there was difference of the films and it was not possible in this research to control that variation.

According to this analysis, it was possible to conclude that the pregelatinized (amidomax) samples films presented more significant answers, with regard to the physicochemical properties under consideration, when the starch concentration in the filmogenic solution was changed from 3% to 5%. Another aspect that is very important for characterization and evaluation of the films is the construction of quantitative models that correlate a studied physicochemical property with spectral data. The advantages of this approach are the ease in data acquisition, which requires little or no sample preparation, time, and cost saving, besides the small experimental error.

Multivariate calibration

A multivariate calibration using PLS regression method was used in this work to build a quantitative regression model for WVP determination. The experimental data in this section were the spectra registered in the mid-IR region (Figure 3) for the same samples studied in the previous analyses. As mentioned before the spectra were obtained in 3 different regions for each film (24 spectra) and the mean WVP value of 5 replicates was considered for each spectrum. The data set was split into 2 subsets: one containing 20 samples for building the model (calibration set), and the other with the 4 remaining samples to be used for external validation of the model. Each raw spectrum was smoothed and the 2nd derivative taken, by using the Savitsky-Golay algorithm (filter width = 9 and polynomial order = 2), and then the pretreated data matrix was mean-centered. Two models were built and are shown in Table 4. Model A was obtained using the full spectra (3351 variables). The high values of RMSECV and RMSEP and the low correlation coefficients r_{cv} and r_p are indicative of a poor to regular model.

With the aim to build a better quality model, a variable selection (Figure 4) was carried out to identify the most relevant regions for WVP determination, employing an algorithm based on

Table 5 — Experimental and predicted values of WVP (g.mm m^{-2}.h^{-1}.kPa^{-1}) for the external validation set and their residuals for models *A* and *B*

		Predicted		Residual		Error %	
	Measured	A	B	A	B	A	B
CMAH3 3	0.147	0.166	−2.194	−0.018	2.342	12.33	1588.5
PG3 3	0.123	0.137	0.602	−0.015	−0.479	12.14	391.1
CMAL3 1	0.139	0.138	−1.975	0.001	2.114	0.77	1520.9
CMAH5 2	0.194	0.180	−1.785	0.014	1.979	7.21	1019.3
Ester5 3	0.184	0.196	−0.709	−0.012	0.892	6.64	486.1

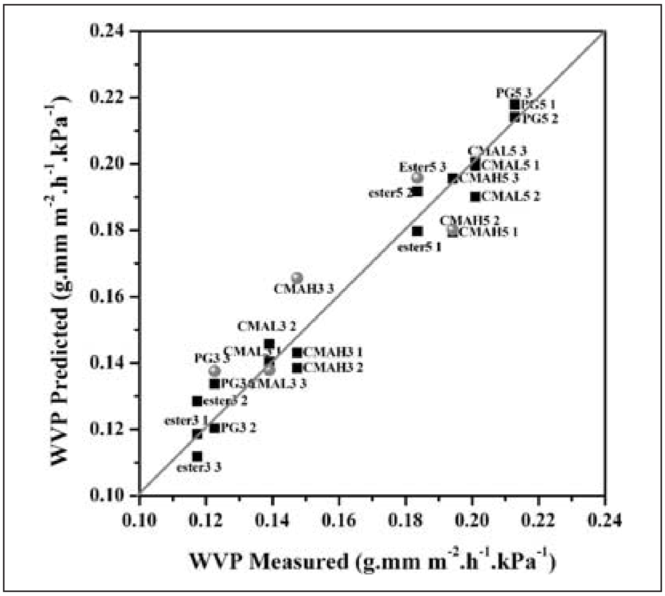

Figure 5—Predicted versus measured values of WVP for calibration model B (■) and predicted values of test set (●)

the combination of the correlogram and regression vector (Teófilo and others 2006).

Model B in Table 4 was built on the selected variables. Variable selection improved the predictive power of the model, as can be observed when comparing models A and B. The mean of relative error of cross-validation dropped from 27.9% in model A to 10.0% in model B. The predictive power of both models were tested using an external validation set formed by the following samples: Ester5 3, CMAH3 3, CMAL3 1, PG3 3, and Ester5 3, none of them used in model building. The experimental WVP and predicted values for these samples can be seen in Table 5 and in Figure 5 for model B.

High polar polymers exhibit high degrees of hydrogen bonding, resulting in extremely high values to water vapor permeability (Kester and Fennema 1986). The addition of plasticizing agent or the absorption of water molecules by the hydrophilic polymers affects negatively the barrier properties of films due to the increasing of the mobility of polymer chains, facilitating the diffusion of permeant through the film (Kumar and Balasubrahmanyam 1992; Gontard and others 1993; Ustunol and Mert 2004). In this manner, the quantity of water in film are related to its permeability; thus the selected variables in the region of the FTIR spectra, from 3750 to 2400 cm^{-1}, are related to the stretching of hydroxyl group (-OH) that is responsible by hydrogen bonding, justifying the region from variables selected.

Conclusions

Properties of the films were analyzed simultaneously by means of chemometric methods, which are more informative than the analysis of variance that compares particular properties and therefore does not consider correlations between them. When using chemometrics, it is possible to observe that permeability, solubility, and thickness are the properties most affected by the concentration of dry matter (3% and 5% initial starch concentration). According to these results, a pregelatinized and modified cross-linked starch (Amidomax 3500 - Cargill), a commercial starch, was the most sensitive. The proposed method for determination of WVP via IR spectroscopy and multivariate calibration offers different advantages as the low-time analysis, low-chemical residue production, low cost, low frequency of high-cost instrument use and, finally, the interesting characteristic of being a noninvasive method and, therefore, an excellent alternative especially at the industrial context. In this work, a good model was obtained for WVP and the variables selected indicate that the water vapor permeability can be related to the quantity of –OH group in the molecule.

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References

Alvin DD, Gil LRP. 1994. Características de materiais nacionais para embalagens flexíveis. ITAL 38:39–62.

[ASTM] American Society For Testing and Materials. 1996. Standard test methods for tensile properties of thin plastic sheeting. D882–91. Philadelphia, Pa.: ASTM.

Beebe KR, Pell RJ, Seasholtz MB. 1998. Chemometrics: a practical guide. New York: Wiley. p 360.

Bobbio FO, Bobbio PA. 2003. Introdução à química de alimentos. São Paulo: Editora Varela. p 238.

Cereda MP, Bertolini AC, Evangelista RM. 1992. Uso de amido em substituição às ceras na elaboração de "películas" na conservação pós-colheita de frutas e hortaliças. Estabelecimento de curvas de secagem. Recife: In. . . Congresso Brasileiro de Mandioca. p 107.

Crank J. 1980. The mathematics of diffusion, 2nd ed. London: Oxford Univ. Press. p 424.

Cuq B, Gontard N, Cuq JL, Guilbert S. 1996. Functional properties of myofibrilar protein-based biopackaging as effected by film tkickness. J Food Sci 61:580–4.

de Oliveira LM, Alves RMV, Sarantópoulos CIGL, Padula M, Garcia EEC, Coltro L. 1996. Ensaios para avaliação de embalagens plásticas flexíveis. Campinas: ITAL, p. 219.

Ferreira MMC, Antunes AM, Melo MS, Volpe PLO. 1999. Chemometrics I: multivariate calibration, a tutorial. Química Nova 22:724–31.

Garcia V, Colonna P, Bouchet B, Gallant DJ. 1997. Structural changes of cassava starch granules after heating at intermediate water contents. Starch 49:171–9.

Geladi P, Kowalski BR. 1986. Partial least squares regression—a tutorial. Anal Chim Acta 185:1–17.

Gnanasambandam R, Hettiarachchy NS, Coleman M. 1997. Mechanical and barrier properties of rice bran films. J Food Sci 62:395–8.

Gontard N, Guilbert S. 1996. Bio-packaging: technology and properties of edible and/or biodegradable material of agricultural origin. Boletim da SBCTA 30:3–15.

Gontard N, Guilbert S, Cuq JL. 1992. Water and glycerol as plasticers affect mechanical and water vapor barrier properties of an edible wheat gluten film. J Food Sci 53:206–11.

Gontard N, Guilbert S, Cuq JL. 1993. Water and glyceros as plasticers affects mechanical and water vapor barrier properties of an edible wheat gluten film. J Food Sci 58:206–11.

Kester JJ, Fennema OR. 1986. Edible films and coatings: a review. Food Technol 40:47–59.

Krochta JM, De Mulder-Johnston C. 1997. Edible and biodegradable polymer films: challenges and opportunities. Food Technol 51:61–73.

Kumar KR, Balasubrahmanyam N. 1992. Water-vapor transmission rates of multilayer: flexible packaging materials. J Food Sci Technol-Mysore 29:237–8.

Martens H, Naes T. 1988. Multivariate calibration. Chinchester, U.K.: NIR Publications. p 348.

Naes T, Isaksson T, Fearn T, Davies T. 2002. A user-friendly guide to multivariate calibration and classification. Chinchester, U.K.: NIR Publications. p 344.

Sobral PJA. 1999. Propriedades funcionais de biofilmes de gelatina em função da espessura. Ciência Engenharia 8:60–7.

Teófilo RF, Martins JP, Ferreira MMC. 2006. Ordered predictors Selection: an intuitive method to find the most relevant variable in multivariate calibration. Águas de Lindóia: In. . . 10th International Conference on Chemometrics in Analytical Chemistry. P066.

Ustunol Z, Mert B. 2004. Water solubility, mechanical, barrier, and thermal properties of cross-linked whey protein isolate-based films. J Food Sci 69:E129–33.

Vanin FM, Sobral PJA, Menegalli FC, Carvalho RA, Habitante AMQB. 2005. Effects of plasticizers and their concentrations on thermal and functional properties of gelatin-based films. Food Hydrocolloids 19:899–907.

Yang L, Paulson AT. 2000. Mechanical and water vapour barrier properties of edible gellan films. Food Res Intl 33:563–70.