Films of Native and Modified Starch Reinforced with Fiber: Influence of Some Extrusion Variables Using Response Surface Methodology

T. Galicia-García,[1] F. Martínez-Bustos,[1] O. A. Jiménez-Arévalo,[2]
D. Arencón,[3] J. Gámez-Pérez,[4] A. B. Martínez[3]

[1]CINVESTAV-Unidad Querétaro, Libramiento Norponiente 2000, Fracc. Real Juriquilla, Qro, CP. 76001, Mexico
[2]Universidad Nacional Aeronáutica en Querétaro, Carretera Estatal 200 Querétaro - Tequisquiapan No. 22154, C.P. 76270. Colón, Querétaro
[3]Centro Catalán del Plástico, Universidad Politécnica de Cataluña, Edifici Vapor Universitari, Carrier Colom, 114, 08222 Terrasa, Spain
[4]Grupo de Polímeros y Materiales Avanzados (PIMA), Universitat Jaume I de Castelló, 12071 Castelló, Spain

ABSTRACT: Corn starch (native and phosphorylated) and potato films containing glycerol as plasticizer, and bagasse sugar cane as fiber, were produced by extrusion-calendering process, and characterized for the mechanical properties (tensile stress at rupture σ_r, elongation at break ε_b, and Young's modulus E), water disintegration index (WDI), water absorption capacity (WAC), and luminosity. The evaluated processing variables were: feed moisture, fiber content, and type of starch. The response surface methodology was applied to analyze, and the model of significance was justified by a variance analysis (F-test). The inclusion of fiber provides a mechanical reinforcement to the starch matrix favoring the elongation at break (ε_b) in thickness films (280–350 µm). Samples formulated with potato starch within the values of feed moisture 18.25, 20.5, and 5 wt % of fiber content, showed an increment in values of tensile stress at rupture (3.80–4.4 MPa) and Young's modulus (78.47–68.04 MPa). Corn starch films with high fiber content (10%) and low feed moisture (18.25%) values showed a decrement in elongation at break (12.93%). WAC and WDI were low with minimum and intermediate levels of feed moisture and fiber content (0–5%). Luminosity values were an indicative that do not exist degradation in film materials due to condition extrusion process used. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: starch films; natural fiber; thermoplastic extrusion

INTRODUCTION

The market of starch-based bioplastics at the end of twentieth century has been estimated at about 20,000 ton/year, with a strong incidence of soluble foams for packaging and films. Bioplastics from renewable origin, either biodegradable or nonbiodegradable, still constitute a niche market that requires high efforts in the areas of material and application development; the technical and economical breakthroughs achieved in the last 3 years, however, open new possibilities for such products in the mass markets and specifically in food packaging.[1] At present, many degradable materials and products, mainly biodegradable and/or photodegradable polymers, have been developed. Polyethylene bags exhibited a greater mechanical strength, both in the unused state and over time during householding use. The severe loss of mechanical strength during the use of the starch-based sacks indicated that only thicker gauge sacks were suitable for the fortnightly kerbside collection of biodegradable municipal waste. These bags have a great efficiency due to their high resistance to heat and pressure. In addition, it has advantages like the fast and safe packaging of merchandise, as well as its transport home and can be reused, characteristics that have allowed their fast growth.[2,3] Coproducts from industrial processes and natural polymers represent an important source of renewable polymers, and can be considered alternatives for the development of new biodegradable composites to create an economic alternative and a reduction in the environmental impact.[4–8] In recent years, there has been an increasing trend toward more efficient utilization of agricultural residues.[9] Starch is an abundant raw material that can be used as a biodegradable polymer, because of its large natural abundance and low cost. Starch has been investigated widely for the potential manufacture of products such as water-soluble pouches for

Correspondence to: T. Galicia-García (thomhhas@yahoo.com.mx).

detergents and insecticides, flushable liners and bags, and medical delivery systems and devices. A number of Latin American countries generate large volumes of sugar cane bagasse that are normally used mostly as textile materials, paper production, and fuel. This bagasse consists mainly of cell-wall polysaccharides: arabinans and arabinoxylans hemicelluloses,[10] highly methylated and acetylated pectins,[11] and cellulose microfibrils.[12] About 54 million dry tons of bagasse is produced annually throughout the world.[13] Because of the high fragility in sheets and films elaborated with starch and in order to gelatinise starch, a plasticizer is necessary; therefore, the presence of a plasticizer ensures that starch undergoes gelatinization rather than degradation in the presence of heat. Water and glycerol are the most widely used plasticizers in thermoplastic starch materials.[14–19] Recently, much attention has been paid to preparing totally biodegradable composites with natural polymers and their derivatives.[20] Hydrolyzed waxy maize starch nanocrystals and cellulose nanocrystallites made by acid hydrolysis of ramie fibers have been used as reinforcing filler in glycerol plasticized-starch (GPS).[21,22] Nanoparticles from cellulose esters can also be fabricated in *N,N*-dimethylacetamide or acetone solution by a dialysis or dropping technique.[23] A new solvent system for cellulose (i.e., NaOH/urea aqueous solution precooled to $-10°C$) has been used with which the dissolution of cellulose could easily be achieved.[24] The use of ethanol into starch paste solutions and the synthesis of citrate starch nanoparticles by cross-linking starch nanoparticles with citric acid also, has been evaluated.[25] Composites reinforced with modified cellulose presented better tensile strength and adhesion between fiber and matrix than nonmodified cellulose, due to agglomeration decreases.[26] Luz et al.[27] reported similar results by mechanical testing and microstructural analysis of sugar cane bagasse fibers-reinforced polypropylene composites. The hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials; in fact, their properties depend on the ambient humidity.[28] An alternative to reduce these drawbacks is the use of modified starches.[29,30] Chemical derivatization has long been studied as a way to solve this problem and to produce low water sensitive materials.[31] Mono-phosphorylation of acidified corn starch is able to enhance the adhesion of starch to cotton and polyester fibers. Aguilar-Palazuelos et al.[19] fabricated biodegradable polymers of fiber and glycerol in blends with native corn starch using extrusion injection molding process. These researchers reported that plates showed better mechanical properties when increasing the fiber content, improving their resistance. Also, increasing the glycerol content improved the elongation and processabillity. The phosphoryla-

tion introduces hydrophilic phosphate groups onto starch, thereby markedly increasing the water-dispersibility.[32] Taking into account some drawbacks of the current technologies for biodegradable material manufacture, researches on a large scale have been performed to obtain the highest possible starch share in starch-plastics composites. The final aim of the investigations is to produce commercial disposable products from native or modified starch and eliminate traditional synthetic polymers. The so-called thermoplastic starch seems to be a perfect solution as it can be processed with conventional technologies for synthetic plastics manufacture (extrusion cooking, pressing high pressure, injection molding). Thus, the aim of this work was to evaluate the effect of some extrusion variables, fiber content, and native or modified starch in the mechanical and some physicochemical, properties of extruded biodegradable films that can be used in the fabrication of disposable bags.

MATERIALS AND EXPERIMENTAL PROCEDURE

Raw materials

Corn, waxy corn, and potato native starch food grades (NS) were acquired from Almex (Mexico D.F), glycerol-like plasticizer was used from Sigma-Aldrich (Germany), and bagasse sugar cane-like fiber source was donated by "El Modelo" sugar mill (harvested 2005, Veracruz, Mexico). Phosphorylated starch (PS) was modified according to the methodology described by Paschall.[33]

Material conditioning

The natural fiber was hammer-milled (Pulvex, mill) and sifted (Rotap, RX-29-Tyler, USA), and then was conditioned in an alkaline medium [Ca(OH)$_2$, 5% w/w] to reduce the traverse area of fiber. The modification of Bagasse sugar cane was made using controlled hydrolysis in the lignocellulose materials of fiber and unwrap the myofibrilles structure; finally, the material was sieved and separated, using the fiber with smaller diameter of 250 µm (60 mesh) to further analyses.[34]

Extrusion compounding

A compact laboratory single screw extruder (Cinvestav-Qro, Mexico) with an L/D ratio of 20 : 1, a screw compression ratio of 1 : 1, and a circular die with an internal diameter of 3 mm was used. Barrel temperatures in the feeding and final zones were kept constant at 50°C, respectively; whereas, the barrel temperature of the second zone was 80°C, with the purpose of compact and transport the material for their later process. Screw speed was 40 rpm, and the feed rate varied according to the weight of the sample.

Extrusion-calendering processing

The extrusion process was carried out with COLLIN coextrusion equipment, model E16 T, with L/D ratio of 16/25 and compression ratio of 1 : 1. Processing conditions were: (a) barrel temperatures: 60–95°C, (b) screw speed: 13–25 rpm, (c) pressure 95–230 bars, and (d) die thickness of 300 μm. Calendering process was performed using a COLLIN equipment, Model Techline CR72T, the processing conditions used were: (a) rolls speed 10–30 rpm, (b) rolls temperature: 10°C, and (c) tension speed roll: 14–20 rpm. The extrudates were stored in polyethylene bags for 12 h at 5°C, until further analysis.

Mechanical testing

A universal testing machine (Galdabini Sun 2500), with a 1 kN load cell, 5 mm/min of velocity and equipped with a videoextensometer was used to asses the mechanical properties of the films. Testing specimens (65-mm long and 5-mm wide) were prepared according to ASTM-D638-00.[35] Five repetitions of each assay were evaluated. The distance between clamps was 65 mm and 22% of the probe sample within of each clamp. The date was registered using an interface computer. The registered tensile properties were: tensile stress at rupture (σ_r), elongation at break (ε_b), and Young's modulus (E). Thickness was evaluated using a digital micrometer Mitutoyo Corp. (Tokyo, Japan).

Physicochemical properties

Water disintegration index

The water disintegration index (WDI) was measured according to the methodology of Gontard et al.[36] with some modifications.[37] Disks of 30-mm diameter were cut of films, processed by extrusion-calendering process and later weighted; the initial weight (w_i) was registered after film-dried for 24 h at 105°C. Other film samples were immersed into 50 mL of distilled water with chloroform (0.02%) utilized as an antimicrobial agent, and then the samples were dried for 24 h at 105°C and weighted (w_f). The WDI was expressed as: % MD = ($w_i - w_f$) / w_i × 100.

Water absorption capacity

The water absorption capacity (WAC) was measured following the methodology of Goia et al.[38] Film disks of 30-mm diameter were weighted and immersed in 50 mL of distilled water and stirred (100 rpm) in water bath (Reciprocal Shaker Bath, mod 1227. VWR Scientific Products, OR) for 24 h at 25°C. Finally, the sample was weighted and WAC was calculated.

Luminosity

A tristimulust colorimeter Hunter Lab (Miniscan XE, Mod 45/0-L, Hunter Associates Laboratory, Reston, VA) illuminating source D65 (light day) was used, to standard angle observation (10°) and specular component included was used to measure the luminosity (L^*) of films.

Experimental design and data analysis

Response surface methodology (RSM) was chosen to build up some mathematical models, making it possible to quantitatively interpret and describe the relationships between the selected dependent processing variables and the processing parameters. Such models have always proved to be very useful in the analysis and prediction of a process. The experiments were designed according to the theory and rules of Box and Wilson.[39] The independent variable levels were established according to preliminary tests.[40] The outline of the experimental design and its independent variables and variation levels are presented in Table I. Levels were codified in the following way:

Independent variables: X_1 = FM (feed moisture); X_2 = FC (fiber content); X_3 = TS (type of starch). Variation levels, the codification, and the used design matrix (Table I) were analyzed following a Central Design with two numeric factors (feed moisture and fiber content) and one categorical (type of starch). Central points were established and replicate the factorial point, giving a total of six experimental units. The repetition in central point allowed estimates of the variability.

The experimental data were used for the determination of coefficients (β_0) of the expansion equation of the Taylor series (quadratic polynomial) whose general expression is:

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 \\ + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \varepsilon$$

where Y_i is the generic response and X_1, X_2, and X_3 are independent variables. βs are the estimated coefficients and ε, the residue that measure the experimental error. The model of significance was justified by a variance analysis (F-test), and the influence of variables was illustrated with surface response graphics. The response variables were: tensile stress at rupture, elongation at break and Young's modulus, WAC, WDI, and luminosity.

The experimental data were analyzed using RSM, using the statistical software Design-Expert,[41] version 6.10. A polynomial of second order was used to predict the experimental behavior.

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TABLE I
Experimental Design

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	Process variables[a]			Response variables[b]					
				Mechanical properties			Physicochemical properties		
Assays	FM (%)	FC (%)	TS	σ_r (MPa)	ε_b (%)	E (MPa)	WAC (%)	WDI	L*
M1	18.25	0	PS	1.80	43.13	7.81	89.05	64.07	64.57
M11	18.25	0	NS	2.22	48.46	10.94	72.39	21.30	71.32
M13	18.25	10	NS	1.96	12.93	20.82	86.07	14.32	45.74
P5	18.25	5	NS	4.42	25.95	78.47	72.69	9.59	45.51
P6	20.50	0	NS	3.88	66.47	68.04	66.28	46.48	46.92
W15	20.50	5	NS	2.20	9.98	38.02	108.64	84.97	63.54

[a] FM, feed moisture; FC, fiber content; TS, type of starch (PS, phosphorylated starch; NS, native starch).
[b] σ_r, tensile stress at rupture; ε_b, strain at rupture; E, Young's modulus; WAC, water absorption capacity; WDI, water disintegration index; L*, luminosity. M1, phosphorylated corn starch film without fiber; M11, corn starch film without fiber; M13, corn starch film with fiber; P5, potato starch film with fiber; P6, potato starch film without fiber; W15, waxy corn starch film with fiber.

RESULTS AND DISCUSSION

Mechanical analyses

Tensile stress at rupture

The experimental values varied from 1.80 to 4.42 MPa (Table I). The regression analysis showed that σ_r was influenced by the TS ($P \leq 0.1$), the codified variables used were:

$$Y_{\delta r.} = 1.94 - 0.33^*X_1 - 0.91^*X_2 + 0.60^*X_3 - 0.78^*X_1^*X_3$$

Using original variables:

$$Y_{\delta r-PS} = -5.42565 + 0.39593^*FM + 2.50293^*FC$$
$$-0.13853^*FM^*FC$$
$$Y_{\delta r-NS} = -4.22748 + 0.39593^*FM + 2.50293^*FC$$
$$-0.13853^*FM^*FC$$

The prediction model used for σ_r explained 41.60% of the total variation ($P \leq 0.092$; Table II).

Figure 1 shows the interaction FM-FC. The highest values of σ_r (2.69 and 3.88 MPa) were found with formulations processed with PS or with NS, respectively, 20.5% FM and 0–5% FC; however, when FM and FC were decreased in the formulation, σ_r values were also decreased (0.67 and 0.51 MPa for PS and NS, respectively). The probe samples formulated with fiber (M13, P5, and W15) and analyzed in the longitudinal flow direction of the extrusion-calendering process showed the highest values of σ_r associated to the longitudinal flow direction of the fiber in the sample. According to Ref. 42, this behavior resulted in orientation and molecular organization. Other important parameters that influenced σ_r were the TS and starch modification. Potato starch films showed the highest value of σ_r (4.42 MPa), probably influenced by the form of starch granules (oval-spherical), in this sample the mechanical energy employed was lower than those used in samples where the starch form was polygonal (corn and

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TABLE II
Regression Coefficients and Analysis of Variance of First Order Equations
(Prediction Models)

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Coefficients[a]	$Y\sigma_r$	$Y\varepsilon_b$	YE	YWAC	YWDI	YL*
Intercept						
β	1.94	17.67	25.39	102.27	72.78	57.66
Lineal						
β_1	-0.33_{NS}	-9.57^*	0.64_{NS}	15.80^*	34.95^*	4.67_{NS}
β_2	-0.91^*	-37.13^{**}	-12.54_{NS}	24.60^*	17.50^*	1.91_{NS}
β_3	0.60_{NS}	1.88_{NS}	12.0_{NS}	-9.42_{NS}	-22.76^*	1.21_{NS}
Interaction						
β_{12}	-0.78_{NS}	-19.36_{NS}	-17.48^*	17.76^*	20.99^*	14.70^*
R^2	0.4160	0.9938	0.4167	0.9763	0.9902	0.8294
$P\leq$	0.092	0.1	0.092	0.022	0.1	0.058

Significance level: $^*P \leq 0.10$; $^{**} P \leq 0.05$. NS = not significant.
[a] Response variables (Y): $Y\sigma_r$, tensile stress at rupture (MPa); $Y\varepsilon_b$, strain at rupture (%); YE, Young's modulus (MPa); YWAC, water absorption capacity; YWDI, water disintegration index; YL*, luminosity.
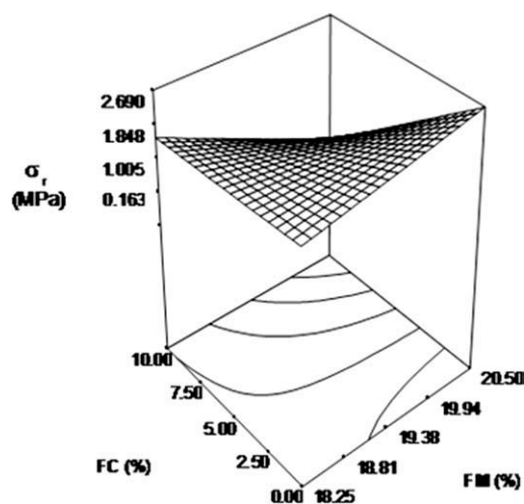
Figure 1 Effect of feed moisture-fiber content interaction in tensile stress at rupture (σ_r).

waxy corn), it resulted in a higher water retention, facilitating the interaction of OH groups with glycerol as reported by Refs. 43,44. The sample prepared with PS (M1) showed minor difference values of σ_r with relation to corn starch sample formulated with NS added with fiber. Probably, the incorporation of phosphate groups increased the number of secondary linkages, thus increasing the flexibility of the films, although, with low resistance when submitted to external tension.[45] Potato sample with fiber in the formulation (P5) showed higher values of σ_r than sample without fiber (P6), thus the incorporation of fiber reinforced the matrix of the extruded films,[46] and this behavior was not observed in corn samples probably due to the high fiber content. The values of tensile stress at rupture (σ_r) are situated between the reported values of Chien-Hsien et al.[47] and Teixeira et al.[48] (1.8–4.8 MPa) on mechanical properties of tapioca starch with the addition of diverse surfactants and plasticizing. Also our values were in agreement with those reported by Lourdin et al.,[49] who reported 3 MPa of tensile stress at rupture of starch film plasticized with 24% glycerol; whereas, Pushpadass et al.[8] registered values from 2.1 MPa of extruded films with water and glycerol. These authors mentioned that the tensile strength decreased progressively with increasing concentration of glycerol in the samples. On the other hand, Rindlav-Westling et al.[50] reported higher tensile strengths and strains in starch films. Angellier et al.[21] reported the use of waxy maize starch nanocrystals as a reinforcing agent in a thermoplastic waxy maize starch matrix plasticized with glycerol. The films prepared by casting technique showed that the increase in glycerol content leads to a more ductile behavior: the strain at break increases, whereas the stress at break decreases. The reported

values are in agreement with those found in this work, except for Young's modulus that was higher than those found in this work. Probably, the use of fiber and processing conditions modified the behavior of the films. Similar results have already been shown for potato starch[51] amylose isolated from potato starch and waxy maize starch.[52] The tensile strength increased greatly from 3.15 to 10.98 MPa in GPS/cellulose nanoparticle (CN) composites. This may be ascribed to the good interfacial interaction between CN and the GPS matrix because of similar polysaccharide structures of cellulose and starch.[53] Zullo and Iannace[54] reported values of stress at break from 0.77 to 3.42 MPa in films blowing with different starches and plasticizers. Similarly, Da Róz et al.[55] reported values of tensile stress at rupture from 1.1 to 4.8 MPa for thermoplastic starch. These values are similar to the ones found in this work. The growth of glycerol content in material mixture induced a decrease in specific mechanical energy. With material moisture and glycerol percentage growth, the specific mechanical energy value decreases; however, in the starch plasticized only with glycerol the specific mechanical energy values are higher compared to the starch plasticized exclusively with water.[56]

Strain at rupture

The ε_b values varied from 9.98 to 66.47% (Table I). The regression analysis showed that ε_b values were influenced by FC ($P \leq 0.05$), FM ($P \leq 0.1$), and FM-FC interaction ($P \leq 0.1$). The prediction model for ε_b used the codified variables:

$$Y_{\varepsilon b} = 17.67 - 9.57^*X_1 - 37.13^*X_2 + 1.88^*X_3 - 19.36^*X_1^*X_2$$

Using the original variables:

$$Y_{\varepsilon b-PS} = -115.73798 + 8.70526^*FM$$
$$+59.26664^*FC - 3.44218^*FM^*FC$$
$$Y_{\varepsilon r-NS} = -111.98781 + 8.70526^*FM$$
$$+59.26664^*FC - 3.44218^*FM^*FC$$

The prediction model used explained the 99.38% of the total variation ($P \leq 0.1$) for ε_b values (Table II). The FM-FC interaction is shown in Figure 2. The maxim values for ε_b (62.71 and 66.47%) were for the formulation with PS and NS, respectively with a range from 19.38 to 20.5% FM and from 0 to 5% FC; however, when the fiber values were increased (5–10%), the ε_b values were decreased. The probe samples analyzed in transversal direction to the exit of the extruder showed lower values than the probe samples formatted with direction to the extrusion
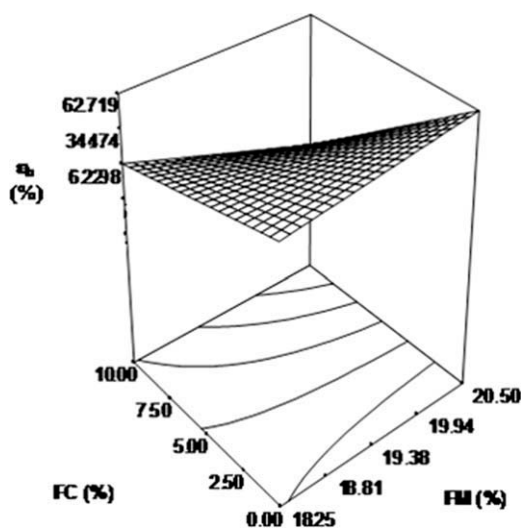
Figure 2 Efect of interaction moisture-fiber on response variable strain at rupture (ε_b).

flux. It can be due to the orientation and crystallization[42] of the molecules, also, due to the fiber orientation that reinforced the starch matrix. Assays without fiber that had high ε_b values (P6, M11, and M1) have also an increment in water absorption values; however, samples with fiber (M13 and P5) with increasing fiber concentration decreased ε_b values; this behavior can be due to anchorage in matrix restricting the molecular movement of starch chains. The fitness in films with fiber showed more resistance when they were tensioned using rollers in calendering process, resulting with smaller thickness (0.02–0.04 mm) as observed in sample W15, allowing an increment in WAC and decrement in ε_b values; this behavior can be due to the grade of crystallinity of the fiber interacting with the starch matrix[57] that permit a better extension of the material before their rupture[58] during processing. Recently, Pushpadass et al.[8] reported that the addition of 1% of fiber to starch-glycerol films disrupted the film-forming and sheeting characteristics of starch and it is hypothesized that the plasticizing properties of stearic acid and its interaction with starch were different from those of glycerol. Also, according to these authors, probably the presence of stearic acid decreased the film flexibility due to antiplasticizing effects as reported on wheat gluten films.[36]

The elongation at break of the GPS/CN composites decreased from 11 to 3% when the CN content was increased 5% more than the initial value,[53] and this effect was related to the present study. Da Róz et al.[55] and López et al.[59] reported values of strain at rupture (ε_b) from 10 to 47% for thermoplastic starch and from 4 to 48% for films of chemically modified starches, respectively. These values are similar to those found in this work (9.98–48.46%).

Young's modulus

The E values varied from 7.81 to 78.47 MPa (Table I). The regression analysis showed that E was affected by FM-FC interaction ($P \leq 0.1$). The prediction model for E used the following codified variables:

$$Y_{E.} = 25.39 - 0.64^{*}X_1 - 12.54^{*}X_2 + 12.0^{*}X_3 - 17.48^{*}X_1^{*}X_2$$

Using the original variables:

$$Y_{E-PS} = -286.18128 + 16.10911^{*}FM + 57.71629^{*}FC - 3.10863^{*}FM^{*}FC$$
$$Y_{E-NS} = -262.18928 + 16.10911^{*}FM + 57.71629^{*}FC - 3.10836^{*}FM^{*}FC$$

For E values, the used prediction model explained the 41.67% of the total variation ($P \leq 0.092$; Table II). The highest E values (44.05 and 68.04 MPa) were for the samples formulated with PS or NS in a range from 19.38 to 20.5% FM and from 0 to 5% FC; however, when the FC values were increased (5–10%) the E values were decreased (Fig. 3). In most of the assays, the values of E were higher in samples analyzed in longitudinal direction to the exit of the extruder, probably between of the limit of the Young's modulus, the tension and deformation is showed with high values, and this fact keeps an association with the previous results of mechanical properties (σ_r, ε_b). Potato sample with fiber (P5) showed high E value than sample without fiber (P6); this effect was attributed that during the extrusion process in where the potato starch granules showed higher water uptake improved with the incorporation of the
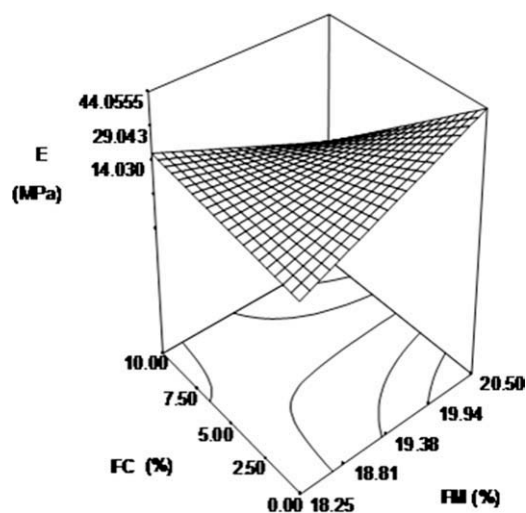
Figure 3 Effect of feed moisture-fiber content interaction on Young's Modulus (E).

plasticizing agent and the addition of fiber that resulted in a more flexible and resistant film, due mainly to the flow orientation of the fiber at the exit of the die.[60] Similar results (20–48 MPa) were found on tensile strength of tapioca starch with the addition of diverse surfactants.[47] These researchers cited that for all starch contents, the addition of glycerol significantly decreased the Young's modulus, which is indicative of a loss of rigidity in the films with an increasing concentration of plasticizer.

The technical data in films used to fabricate commercial disposable bags (PEBD, PEAD) showed values close to the values of films prepared with potato starch (P5 and P6). According to Mohd et al.[61] and Romaní et al.,[62] the mechanical properties of films can be improved with the incorporation of composites into the polymeric matrix, and with the use of long fibers.

Avérous et al.[63] reported that a significant improvement in stiffness is obtained by blending plasticized wheat starch with cellulose fibers that impart reinforcement of the materials. Young's modulus (E modulus) was increased and the modulus increases with the fiber length. Similar trends were observed for the tensile stress at rupture. Strength improvement depends both on the fiber length and content. Elongation at break decreases with the addition of fiber. Zullo and Iannace[54] reported values of E from 34 to 219 MPa in films blowing with different starches and plasticizers. These values were higher than those found in this work (7.81–78.47 MPa). Myllaärinen et al.[52] found that below 10 wt %, the plasticizer polymer interactions are weak and the materials are fragile and difficult to work with, while above 20 wt %, there is a progressive increase in the flexibility and in the elongation properties of the films.

In general, the mechanical properties showed a significant prediction model ($P \leq 0.1$).

Physicochemical analyses

Water absorption capacity (WAC) and water disintegration index (WDI)

The values of WAC varied from 66.280 to 108.647% (Table I). A regression analysis showed that the WAC was affected by FM ($P \leq 0.1$) and FC ($P \leq 0.1$). A prediction model for WAC used the codified variables:

$$Y_{WAC} = 102.27 - 15.80^*X_1 - 24.60^*X_2$$
$$-9.42^*X_3 + 17.76^*X_1^*X_3$$

Using origin variables:

$$Y_{WAC-PS} = -102.98866 - 1.74995^*FM$$
$$-56.26731^*FC - 3.15808^*FM^*FC$$
$$Y_{WAC-NS} = -102.15418 - 1.74995^*FM$$
$$+56.26731^*FC - 3.15808^*FM^*FC$$

The values of WDI varied from 9.598 to 84.977 g solids/g sample (Table I). Regression analyses showed that the WDI was affected by FM ($P \leq 0.1$), FC ($P \leq 0.1$), type of starch TS ($P \leq 0.1$), and FM-FC interaction ($P \leq 0.1$). A prediction model for WDI used the codified variables:

$$Y_{WDI} = 72.78 - 34.95^*X_1 - 17.50^*X_2$$
$$-22.76^*X_3 + 20.99^*X_1^*X_2$$

Using the coded variables:

$$Y_{WDI-PS} = -162.32901 + 12.40594^*FM$$
$$-68.81342^*FC + 3.73232^*FM^*FC$$
$$Y_{WDI-NS} = -207.84106 + 12.40594^*FM$$
$$-68.81342^*FC + 3.73232^*FM^*FC$$

A prediction model used for WCA explained 97.63% of the total variation ($P \leq 0.022$; Table II). Figure 4(a) illustrated the effect of FM-FC interaction, where the maximum values of WCA (169.84 and 151.01% for FS and NS, respectively) were attained with 20.5% FM and 10% FC; when the FM and FC decreased, WCA also decreased with values of 85.11 and 66.28% for PS and NS, respectively. For WDI, the prediction model explained 99.02% of the total variation ($P \leq 0.1$; Table II). Figure 4(b) showed the effect of the FC-FM interaction, where the maximum values for WDI were 168.98 and 123.47 for PS and NS, respectively, at high FM (20.5%) and FC (10%); however, when these values were decreased, WDI values also decreased. In the WAC, this effect is due mainly to a diffusion of the water molecules inside of the film, where starting modifications in the internal structure of the biopolymer therefore allowing the formation of the gel, the highest WAC values obtained of films indicate structural changes that can provide its degradation. Samples formulated with fiber (M13, P5, and W15) showed the highest WAC values, attributable to the hydrophilic capacity of the fiber components, and also the ramifications that they have.[64] All samples had high WDI values. These values are between the ones reported by Irissin-Mangata et al.[37] and Sebio[65] of films prepared with gluten and corn respectively, although the samples M1 and W15 showed the highest values, probably due to the type of starch that could facilitate the microorganism degradation therefore favoring their biodegradation.
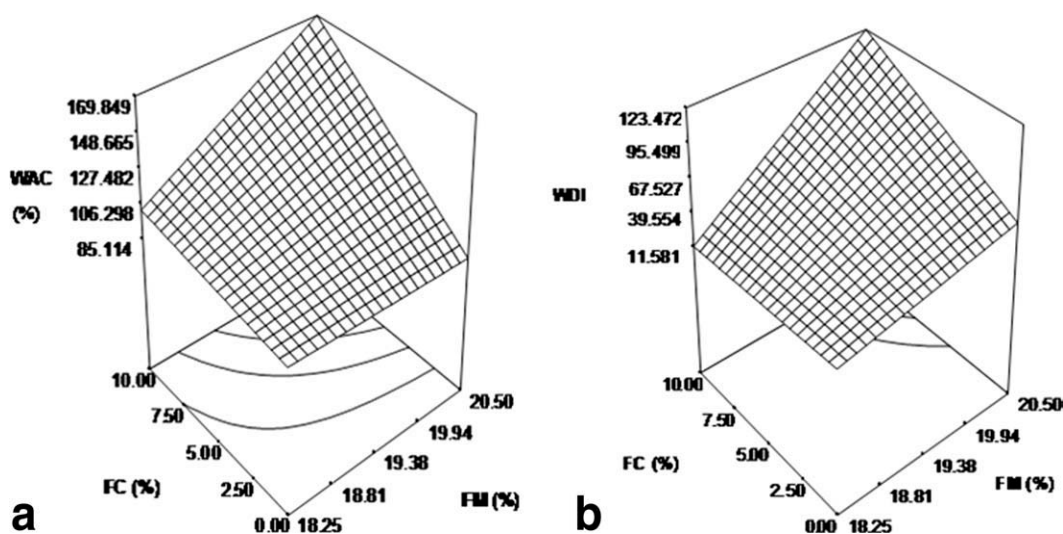
Figure 4 Effect of feed moisture-fiber content interaction in (a) Water absorption capacity (WAC) and (b) Water disintegration index (WDI).

Sitohy and Ramadan[66] evaluated the degradability of different PSs and thermoplastic films prepared from corn starch phosphomonoesters; these authors concluded that the plastic films prepared from phosphorylated corn starch showed both higher disintegration rate and a greater degradability by thermostable bacterial α-amylase than those prepared from non-PS.

Luminosity

The luminiosity (L^*) values of films varied from 45.517 to 71.327 (Table I). The regression analysis indicated that L^* was affected by a FM-FC interaction ($P \leq 0.1$). A prediction model used the codified variables:
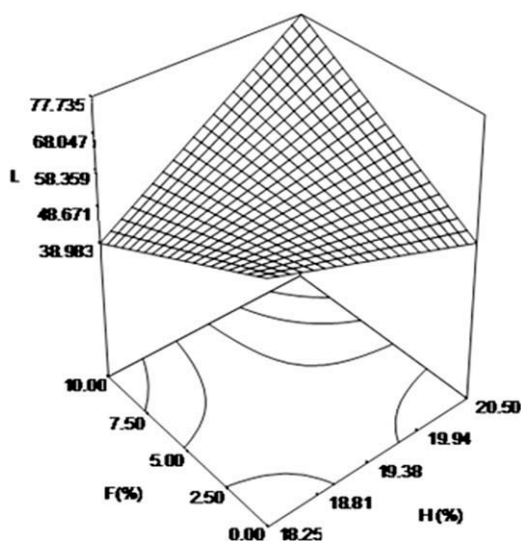

Figure 5 Effect of feed moisture-fiber content interaction in luminosity (L^*).

$$Y_{L^*} = 57.66 + 4.67^*X_1 + 1.91^*X_2 + 1.21^*X_3 + 14.70^*X_1^*X_2$$

Using origin variables:

$$Y_{L^*-\text{PS}} = 227.28790 - 8.91605^*\text{FM}$$
$$-50.26281^*\text{FC} + 2.61393^*\text{FM}^*\text{FC}$$
$$Y_{L^*-\text{NS}} = 229.70568 - 8.91605^*\text{FM}$$
$$-50.26281^*\text{FC} + 2.61393^*\text{FM}^*\text{FC}$$

Prediction model explained the 82.94% of total variation ($P \leq 0.1$) for L^* values (Table II). Figure 5 illustrates the effect of FM-FC interaction, where the maximum L^* values (77.73 and 80.15% for PS and NS, respectively), in a FM range from 18.25 to 19.38% and FC from 0 to 5%; when the FM value was increased up 20.5% and FC values were from 5 to 10%, L^* values were decreased (38.98 and 41.40 for PS and NS, respectively). Assays with fiber keep a relation with the lowest L^* values (darkness), due to lignin and sugar residues present in the fiber, resulting in a brown dark coloration; on the other hand, the addition of starch improved the L^* values. Color samples can be affected by reactions that might occur during an extrusion process, like Maillard reactions, caramelization and hydrolysis, and other nonenzymatic reactions with the pigments degradation[67]; however, the color is also an indicator of chemical changes during processing.[68] Aguilar-Palazuelos et al.[19] reported that the color of biodegradable polymers reinforced with fiber can be degraded during severe conditions of extrusion.

CONCLUSIONS

The incorporation of natural fiber with medium values (5%) provided reinforcement in films when increasing the σ_r and E (12 and 30% in potato and

corn starch films, respectively), due to existence of fiber orientation to extrusion process flow direction. The ε values increased in films without fiber (25–40% in corn and potato starch films) showed in a direct way the fiber anchorage in the matrix starch. WAC and WDI values were an indicator of modification in the internal structure of film due to high starch higroscopicity that provides its degradation in high moistures. After the extrusion-calendering process, the films showed small thickness (280–350 μm). Luminosity values were an indicative that do not exist degradation in film materials due to condition extrusion process used, the behavior in samples with fiber were due with the presence of residues present in natural fibers. Through the RSM, it was possible to know the fiber content and feed moisture effect on response variables and carry out the statistic analysis of data. The films obtained represented a potential in the development of biopolymer material in future use like packing materials.

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