Mixture design applied for the development of films based on starch, polyvinyl alcohol, and glycerol

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ABSTRACT: Starch and polyvinyl alcohol (PVA) are biodegradable materials with potentiality to replace the conventional polymers in some applications. The aim of this work was to produce biodegradable films of PVA, cassava starch, and glycerol by thermoplastic extrusion using a mixture design to evaluate the effects of each component in the blend properties. Six formulations were prepared using a twin-screw extruder coupled with a calender. All the materials were visually homogeneous and presented good processability. Mechanical properties were dependent on both the relative humidity conditioning and the formulation; higher relative humidities detracted the mechanical properties, which was associated to plasticizer effect of the water. Furthermore, the mechanical properties were better when higher concentrations of PVA were used, resulting in films with lower opacity, lower water vapor permeability, and higher thermal stability, according to TGA. Biodegradable materials based on starch, PVA, and glycerol have adequate mechanical and processing properties for commercial production. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42697.

INTRODUCTION

Plastic polymers are widely used in several areas, and they are an important industrial sector worldwide. Plastics are widely used in packaging because they are inexpensive, lightweight, durable, and easily processed into desired shapes. However, the widespread use of plastics in applications with short life cycles results in the accumulation of millions of tons of plastic waste per year, resulting in serious environmental problems.[1] Therefore, the search for substitutes for conventional plastics is increasing.

Starch was one of the first polymers used as a substitute for conventional plastics and it is still widely studied because it is inexpensive, easily renewable, and fully biodegradable. However, the use of pure starch has some problems, such as poor mechanical properties, water barrier properties, and low thermal stability and processability.[2] To overcome the problems associated with conventional plastics and starch-based plastics, one alternative is to develop novel polymeric composite materials based on starch and other polymers, that can be degraded by microorganisms in soil and water, and this area is attracting the increasing attention of researchers.[3]

There are currently many biodegradable polymers that have properties similar to those of conventional polymers, such as polyvinyl alcohol (PVA), poly(butylene adipate-co-terephthalate) (PBAT), and poly(lactic acid) (PLA), but these polymers are expensive compared to conventional polymers. Thus, one alternative to reduce the production costs of biodegradable materials is to develop starch blends, in which the starch is responsible for reducing the production costs and another polymer is responsible for reinforcing the structural integrity of the blend.

PVA is a material that has high technological potential due to its excellent optical and physical properties, and because PVA possess many hydroxyl groups in its structure, PVA is highly compatible with starch and can be used in starch blends to produce biodegradable materials as an alternative to nonbiodegradable plastics.[2,4]

The aim of this work was to develop biodegradable materials based on cassava starch, PVA, and glycerol produced by extrusion using mixture design to understand the effects of each component on the properties of the blends. Mixture design is a statistical tool that allows evaluating the influence of each component in the mixture, as well as the interactions between them, which is important in the study of polymer blends because the mathematical models obtained are predictive, allowing the optimization of the material properties as desired.

Table I. Concentration of the Components According to the Mixture Design

Formulation	Component (wt %)			Pseudocomponent[a]		
	Starch	PVA	Glycerol	Ps_1	Ps_2	Ps_3
F1	20.0	50.0	30.0	0.000	1.000	0.000
F2	40.0	30.0	30.0	1.000	0.000	0.000
F3	20.0	40.0	40.0	0.000	0.500	0.500
F4	20.0	45.0	35.0	0.000	0.750	0.250
F5	30.0	30.0	40.0	0.500	0.000	0.500
F6	32.5	32.5	35.0	0.625	0.125	0.250

[a] P_{s1} = starch; P_{s2} = PVA; P_{s3} = glycerol.

The biodegradable films of cassava starch and PVA have adequate mechanical, microstructural, and thermal properties, indicating a good miscibility between the starch and the PVA. The mechanical properties are also dependent on the relative humidity. Biodegradable materials based on starch, PVA, and glycerol blends have adequate properties and processability for commercial production.

EXPERIMENTAL

Materials

Selvol[TM] 523 PVA (degree of hydrolysis: 87.84%; viscosity of 4% aqueous solution: 24.50 cP) (Sekisui Chemical, Japan), cassava starch (Indemil, Brazil) and pure glycerol (Dinâmica, Brazil) as a plasticizer were used.

Methods

Mixture Designs. A mixture design with upper and lower limits defined by preliminary tests was used, and the independent variables of the experimental design were the concentrations of starch, PVA, and glycerol. The limits refer to the maximum and minimum concentration of each component necessary to produce the films by thermoplastic extrusion. The response variables were analyzed with STATISTICA 7.0 (Statsoft, USA) using the aforementioned mixture design. Linear [eq. (1)] and quadratic (eq. (2)) models were used because they provided the best fits to the experimental data.

Table II. Regression Coefficients for the Mechanical Properties in Different Relative Humidities

Coef[a]	Tensile strength (MPa)			Young's modulus (MPa)			Elongation at break (%)		
	33% RH	54% RH	75% RH	33% RH	54% RH	75% RH	33% RH	54% RH	75% RH
β_1	5.78	4.86	3.30	8.04	6.56	4.75	586	566	402
β_2	10.42	8.92	8.35	12.15	9.83	7.42	714	702	652
β_3	0.69	1.14	1.83	−5.70	1.76	0.51	273	227	105
β_{12}	–	ns[b]	ns	−19.57	–	–	−1725	ns	ns
β_{13}	–	ns	ns	15.95	–	–	ns	ns	474
β_{23}	–	6.39	−7.53	11.46	–	–	ns	831	ns
R^2	0.82	0.90	0.90	0.99	0.99	0.95	0.73	0.85	0.81

[a] β_1 = starch; β_2 = PVA; β_3 = glycerol; β_{12} = interaction starch : PVA; β_{13} = interaction starch : glycerol; β_{23} = interaction PVA : glycerol.
[b] ns = not significant.

Table III. Observed and Predicted Data for Tensile Strength in Different Relative Humidities

Formulation	Tensile strength (MPa)					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	11.0 ± 1.6	10.4	7.8 ± 0.9	8.9	8.7 ± 0.9	8.4
F2	6.8 ± 0.9	5.8	4.8 ± 0.5	4.9	3.3 ± 0.4	3.3
F3	6.1 ± 1.0	5.6	6.0 ± 0.8	6.6	3.5 ± 0.3	3.2
F4	9.1 ± 1.0	8.0	8.0 ± 1.0	8.2	5.2 ± 0.8	5.3
F5	3.5 ± 0.4	3.2	3.1 ± 0.4	3.0	2.6 ± 0.2	2.6
F6	4.1 ± 0.4	5.1	4.0 ± 0.3	4.6	2.9 ± 0.4	3.3

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \qquad (1)$$

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \qquad (2)$$

where y is the dependent variable, β is the regression coefficient for each component, x_1 is the percentage of starch, x_2 is the percentage of PVA, and x_3 is the percentage of glycerol.

The pseudocomponents were calculated using eq. (3).

$$Ps_x = (C_x - a_y)/(1 - \sum a_y) \qquad (3)$$

Where Ps_x is the pseudocomponent of each component, C_x is the real concentration of the component, a_y is the lower limit of the real component, and Σa_y is the sum of the lower limits of the three components in the mixture design.

Table I shows the real concentrations and the pseudocomponents of each mixture.

Film Production. Each formulation (Table I) was manually homogenized and placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 min at 85°C to incorporate the glycerol using a method adapted from Jang and Lee.[5] After this step, the blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm (L/D = 35), a screw speed of 100 RPM, and a temperature profile of 90/200/200/200/200°C from the feeder zone until the flat die zone. The feed velocity was 33 RPM, and the extruder was equipped with a six holes (2 mm) die to produce cylindrical strands. After pelletization of the strands, the pellets were extruded in the same extruder and under the same conditions cited above using a flat die with a 0.8 mm aperture and 320 mm length, and a 3-roll water-cooled calender (AX Plásticos, Brazil) to produce the films.

Mechanical Properties. The tensile strength, Young's modulus, and elongation-at-break were determined according to ASTM D882-02 method,[6] with some modifications. Ten samples from each treatment (50 mm in length and 20 mm in width) were conditioned in a desiccator with three controlled relative humidities (33 ± 2%, 53 ± 2%, and 75 ± 2%) and a temperature of 23 ± 2°C for a minimum of 72 h before analysis. The samples were then analyzed in a texture analyzer (model TA.XT2i, Stable Micro Systems, England) with an initial distance between the grips of 30 mm and a cross-head speed of 0.8 mm s^{-1}.

For puncture analysis, 10 replicates from each treatment were conditioned as described above and were then attached to a support and punctured perpendicularly with a 6.35-mm-diameter cylindrical probe at a velocity of 2.0 mm s^{-1}. The puncture strength was obtained by dividing the maximum force by the film thickness. The puncture elongation was the maximum elongation supported by the film, expressed in millimeters.

Apparent Opacity (Op). The apparent opacities of the films were measured using a colorimeter (BYK Gardner, Germany) according to the method described by Maria et al.[7] using the illuminant D65 (daylight) and a visual angle of 10°. Opacity (Op) was determined as the ratio of the opacity of the sample over a black standard Op$_b$ and the opacity over a white standard Op$_w$ being represented on an arbitrary scale (0–100%), and the analyses were performed in triplicate according to eq. (4).

Table IV. Observed and Predicted Data for Young's Modulus and Elongation at Break in Different Relative Humidities

| | Young's modulus (MPa) | | | | | | Elongation at break (%) | | | | | |
| | 33% RH | | 54% RH | | 75% RH | | 33% RH | | 54% RH | | 75% RH | |
Formulation	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	12.3±0.3	12.2	9.9±0.3	9.8	7.0±0.3	7.4	643±80	714	646±54	702	655±26	693
F2	7.9±0.5	8.0	6.2±0.4	6.56	4.7±0.3	4.8	628±64	586	543±50	566	407±40	416
F3	6.1±0.4	6.1	5.5±0.3	5.8	4.0±0.3	4.0	565±71	494	614±56	672	377±32	390
F4	9.9±0.5	9.8	8.0±0.3	7.8	5.9±0.2	5.7	649±49	604	699±72	739	514±68	506
F5	5.3±0.2	5.2	4.5±0.3	4.2	3.1±0.4	2.6	416±60	430	417±71	397	383±53	394
F6	6.2±0.3	6.4	5.4±.02	5.8	3.8±0.2	4.0	403±56	389	467±44	524	419±60	422

Table V. Regression Coefficients for the Puncture Analysis

Coefficient[a]	Puncture strength (N/mm)			Puncture elongation (mm)		
	33% RH	54% RH	75% RH	33% RH	54% RH	75% RH
β_1	180	107	80	17.18	16.92	17.67
β_2	208	152	98	19.79	23.11	23.42
β_3	10	−71	−168	23.69	16.46	24.57
β_{12}	−264	−339	−504	35.05	−20.08	–
β_{13}	ns[b]	205	355	ns	22.06	–
β_{23}	Ns	242	379	ns	17.04	–
R^2	0.98	0.98	0.95	0.66	0.97	0.70

[a] β_1 = starch; β_2 = PVA; β_3 = glycerol; β_{12} = interaction starch : PVA; β_{13} = interaction starch : glycerol; β_{23} = interaction PVA : glycerol.
[b] ns = not significant.

$$Op = (Op_b/Op_w) \times 100 \qquad (4)$$

Weight Loss in Water (WLW). The analysis of weight loss in water (WLW) was performed as described by Olivato et al.[8] The weight loss in water measurements were performed in triplicate and expressed as the percentage of the original mass (M_i) and the final mass (M_f) of the film after immersion in water for 48 h at 25°C, according to eq. (5).

$$WLW = [(M_i - M_f)/M_i] \times 100 \qquad (5)$$

Water Vapor Permeability (WVP). Water vapor permeability was determined gravimetrically according to the ASTM E96-00[9] standard. The measurements were performed in triplicate using a relative humidity gradient of 33–64%.

Scanning Electron Microscopy (SEM). Scanning electron micrographs were recorded using a scanning electron microscope (FEI Quanta 200, USA). The films were fractured in liquid nitrogen, attached to aluminum supports, and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40–50 nm in thickness) at 25°C and a pressure of 2.105 Torr for 180 s. The surface and the fracture surface of the films were analyzed.

Fourier Transform Infrared Spectroscopy (FT-IR). The samples were dried over anhydrous calcium chloride salt for 1 week and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IRPrestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000–750 cm^{-1}.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed using a TGA-50 (Shimadzu, Japan). The samples were dried over anhydrous calcium chloride salt and analyzed from 25 to 600°C with a 10°C min^{-1} heating rate under a nitrogen atmosphere (20 mL min^{-1}).

RESULTS AND DISCUSSION

All the films were uniform, visually homogeneous, and easy to handle. The average thickness of the films was 771($\pm$176) µm. The influence of the components (PVA, glycerol, and starch) on film properties was evaluated based on the modeling coefficients, considering the isolated effect of each component (β_1, β_2, and β_3) and their interactions (β_{12}, β_{13}, and β_{23}). All of the

coefficients of determination (R^2) were greater than 0.70, most of them higher than 0.90, demonstrating an adequate fit of the models to the experimental data. These R^2 values were useful to predict the influence of each component (PVA, glycerol, and starch), and their interactions, on the properties of the starch/PVA films, as can be noted considering the observed and predict results showed at Tables III, IV, VI, and VII, for all properties. For all models, the lack of fit was not significant ($p > 0.05$).

Mechanical Properties

The coefficients of the mixture design models for the mechanical properties (tensile strength, Young's modulus, and elongation-at-break) of the films under different relative humidities are shown in Table II. According to Tables III and IV, the tensile strengths ranged from 2.6 to 11.0 MPa, the Young's moduli ranged from 3.1 to 12.3 MPa, and the elongation-at-break ranged from 377% to 698% for all the formulations and relative humidities tested.

Increasing the relative humidity caused a slight decrease in the coefficients of PVA and starch (Table II), thereby reducing the tensile strength and the Young's modulus. The role of water as plasticizer was already fully studied.[2,10] Considering the plasticizer effect and the hydrophilic character of the PVA and starch, when the material is conditioned into a higher relative humidity, the presence of water in the matrix increases the molecular mobility of the polymeric chains and results in a less rigid structure, which can explain the above mentioned results.

Similar behavior was observed in casting films of PVA (completely hydrolyzed and medium size chain) and corn starch (1 : 1 wt %) plasticized with glycerol (0–50 wt %), in which increasing the relative humidity promoted a reduction in the tensile strength and Young's modulus.[11]

Mao and coworkers[12] produced extruded films of corn starch containing 9.1 wt % PVA (completely hydrolyzed to medium chain size) and plasticized with glycerol, and the tensile strengths of the films ranged from 47 (0% glycerol) to 9 MPa (35% glycerol) at 30% RH and from 12 (0% glycerol) to 2 MPa (35% glycerol) at 50% RH. Under the same conditions, the maximum elongations were 250 and 150%, respectively. These results demonstrate the plasticizing effect of the water in PVA/starch films, i.e., with increasing water content, the films

exhibited a decrease in tensile strength and an increase in elongation; the same behavior was observed with increasing glycerol content in the blends.

Ramaraj[13] produced casting films of potato starch and PVA (medium degree of hydrolysis and chain size). The tensile strengths of the films ranged from 8.02 to 13.00 MPa, the elongation at break ranged from 94 to 398%, and the Young's modulus ranged from 4 to 43 MPa depending on the starch concentration (0–50 wt %), which is in contrast to the behavior observed in this study, where the main component responsible to increase the tensile strength and Young's modulus properties was the PVA instead of starch. Also considering 33% RH (Table II), the coefficients showed a positive effect for starch and PVA in the blends ($\beta_1 = 8.04$, $\beta_2 = 12.15$) and a negative effect for glycerol ($\beta_3 = -5.70$) for Young's modulus. Based on this, higher glycerol content decreased the Young's modulus and higher starch and mainly PVA concentrations increased the rigidity of the films (greater Young's modulus). The same authors[13] attributed the increase of Young's modulus to a filler effect promoted by the addition of starch in the blends, with the starch granules acting as reinforcement.

In produced casting films of maize starch and 10–40 wt % PVA (fully hydrolyzed and chain size of 100,000–146,000) without plasticizers, the tensile strengths of the films ranged from 70 to 20 MPa and the elongation at break ranged from 7 to 48% depending on the RH (20–100%), and this RH effect was due to the water functioning as a plasticizer.[14]

Coefficients of the mixture design models for the puncture strength and puncture elongation of the films under different relative humidities are shown in Table V. The puncture strengths ranged between 40.5 and 201.4 N/mm, and the puncture elongations ranged from 17.7 to 24.7 mm (Table VI). The main component coefficients of the puncture strength model decreased with increasing moisture content and this effect was due to the plasticizing effect of water, and increasing the concentration of PVA in the blend improved the puncture properties of the materials. This behavior was similar to the mechanical properties; therefore, the same previous discussions are valid.

Weight Loss in Water

The weight loss in water of the biodegradable films ranged from 54.4 to 75.4% (Table VII), and high values of weight loss were expected because all the blend components were water soluble, and as shown in Table VIII, the PVA component (β_2) had the greatest effect on weight loss. Lee and coworkers,[11] in PVA:corn starch films plasticized with glycerol (0–50 wt %), obtained values of solubility in water from 20 to 60%, which are less than those obtained in this work; however, the methodology employed by the authors was different. A high solubility of biodegradable materials is important for accelerating the biodegradation process when the materials are disposed of in sanitary landfills, aquatic environments, or in specific agricultural uses; thus, a high solubility is a good characteristic of the material.

Table VI. Observed and Predicted Data for the Puncture Analysis

Formulation	Puncture strength (MPa)						Puncture elongation (mm)					
	33% RH		54% RH		75% RH		33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	201±20	208	156±13	152	100±9	98	19.6±1.6	19.8	21.9±2.3	23.1	22.0±2.2	23.4
F2	163±17	180	102±7	107	69±9	80	17.8±1.5	17.2	17.7±0.9	16.9	17.7±1.2	17.7
F3	105±10	109	87±12	101	64±9	60	21.6±1.4	21.7	21.9±2.1	24.0	22.1±3.7	24
F4	164±10	158	148±12	141	100±5	102	21.8±1.3	20.8	24.7±0.8	24.6	23.3±0.8	23.7
F5	94±4	95	68±5	69	40±5	44	21.6±0.9	20.4	21.2±1.6	22.2	22.0±1.4	21.1
F6	119±6	120	80±3	81	46±4	48	21.8±1.1	21.9	20.0±0.6	20.0	19.7±0.9	20.1

Table VII. Observed and Predicted Data for the Apparent Opacity, Weight Loss in Water, and Water Vapor Permeability of the Films

	Apparent opacity (%)		Weight loss in water (%)		Water vapor permeability (g m^{-1} s^{-1} kPa^{-1}) ($\times 10^{10}$)	
Formulation	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	42.4 ± 6.9	38.6	75.4 ± 8.9	80.6	2.1 ± 0.2	2.1
F2	40.4 ± 7.1	40.4	69.1 ± 1.6	69.1	2.8 ± 0.9	2.7
F3	23.8 ± 2.6	22.4	54.4 ± 0.2	54.7	4.7 ± 0.2	4.4
F4	42.9 ± 7.4	42.9	63.4 ± 4.1	63.2	3.0 ± 0.2	3.3
F5	28.6 ± 2.7	28.6	67.1 ± 5.0	67.1	4.5 ± 0.7	4.7
F6	28.2 ± 4.0	28.2	62.0 ± 2.0	62.0	3.7 ± 0.2	3.6

Water Vapor Permeability

The water vapor permeability (WVP) of the films ranged from 2.14 to 4.74 $\times$ 10^{-10} g m^{-1} s^{-1} kPa^{-1} (Table VII), and the glycerol component (β_3) showed the greatest effect on increasing the permeabilities of the films (Table VIII). Limpan and coworkers[15,16] produced casting films with fish myofibrillar protein and different types and proportions of PVA plasticized with glycerol (50 wt %), and the WVP ranged from 8 to 12 $\times$ 10^{-10} g m^{-1} s^{-1} kPa^{-1}, higher than those obtained in the present study. Xianda and coworkers[17] produced PVA casting films, nonplasticized and plasticized with 30% of glycerol, and the WVP were 3.80 and 15.8 $\times$ 10^{-11} g m^{-1} s^{-1} kPa^{-1}, respectively. Higher glycerol concentration increases the WVP because glycerol enhances the film hygroscopicity and consequently the WVP.[18]

Scanning Electron Microscopy (SEM)

As shown in Figure 1, the surfaces and fracture surfaces of the films were both homogeneous, without the presence of domains, visible pores or cracks, demonstrating that starch and the PVA had a good compatibility.

Similar results were obtained with wheat starch + PVA films produced by extrusion,[19] with corn starch + PVA + glycerol films,[20] and with PVA + pea starch films obtained by casting.[21] All the authors obtained good miscibility between the polymers, and they observed a trend in which the surface became rougher with increasing starch concentration; this behavior was also observed in this study, as shown by the scanning electron micrograph of film F2, which had the highest starch concentration.

Apparent Opacity

Apparent opacities of the films ranged from 23.8 to 42.9% (Table VII). Considering the most significant effects showed at Table VIII, it was observed positive effects for the coefficients of the interactions starch:glycerol ($\beta_{13} = 220.04$) and PVA:glycerol ($\beta_{23} = 198.66$), which resulted in higher opacities. A negative effect was observed for the starch:PVA ($\beta_{12} = -245.06$) interaction that led to more translucent materials (lower apparent opacity).

The increasing opacity can be attributed to the good adhesion between the polymeric phases that difficult the light to pass through the matrix,[22] as discussed in SEM analysis (Figure 1).

Fourier Transformed Infrared Spectroscopy (FT-IR)

Because the formulations are composed of polymers that have various common functional groups, their spectra were very similar (Figure 2). There was a large absorption band at 3400 cm^{-1} due to the stretching of hydroxyls present in the three components of the blend, and the region of 3000–2850 cm^{-1} showed bands for the stretching of —CH groups. These data are consistent with those observed by another authors.[21,23]

The absorption band at 1730 cm^{-1} was attributed to the stretching of carbonyl groups present in the residual acetate groups of the PVA molecule,[24] the absorption band at 1275 cm^{-1} was attributed to secondary alcohol presents in PVA

Table VIII. Regression Coefficients for the Apparent Opacity, Weight Loss in Water, and Water Vapor Permeability of the Films

Coefficient[a]	Apparent opacity (%)	Weight loss in water (%)	Water vapor permeability (g m^{-1} s^{-1} kPa^{-1}) ($\times 10^{10}$)
β_1	40.41	69.09	2.73
β_2	38.56	80.65	2.13
β_3	−93.19	65.03	6.62
β_{12}	−245.06	−66.60	–
β_{13}	220.04	ns[b]	–
β_{23}	198.66	−72.39	–
R^2	0.77	0.89	0.77

[a] β_1 = starch; β_2 = PVA; β_3 = glycerol; β_{12} = interaction starch : PVA; β_{13} = interaction starch : glycerol; β_{23} = interaction PVA : glycerol.
[b] ns = not significant.

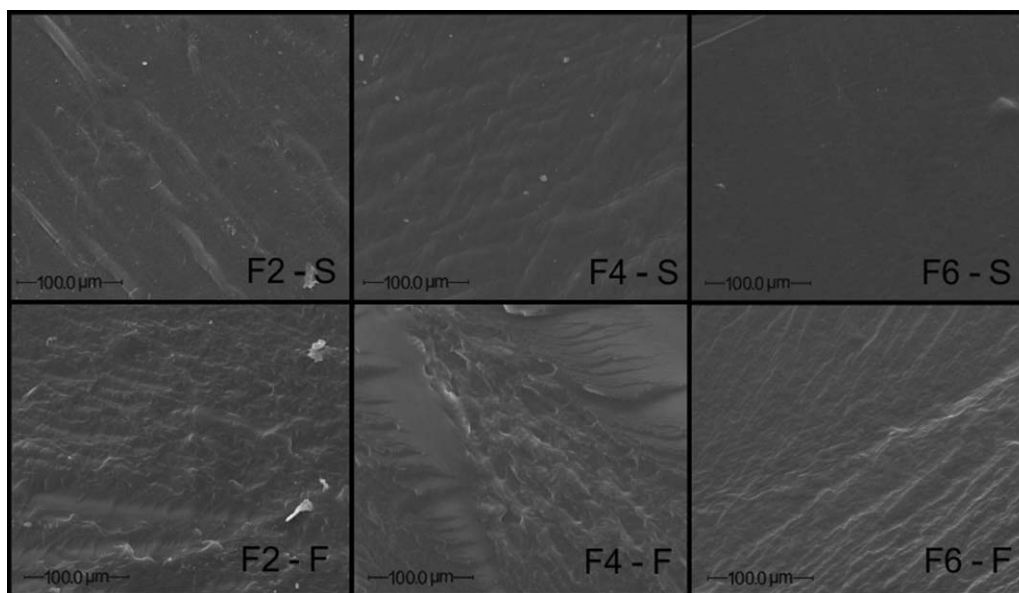**Figure 1.** Scanning electron microscopy micrographs of the fracture surfaces (F) and unaltered surfaces (S) with magnification at 800×.

molecules. Both absorption bands exhibited good correlation with the percentage of PVA present in the blend.

Thermogravimetric Analysis (TGA)

Figure 3 shows the weight loss versus temperature curves of the films, and the mass loss at 300°C was primarily related to the glycerol concentration, ranging from 48.98% (formulation F3—glycerol content of 40%) to 68.64% (formulation F2—glycerol content of 30%).

Thermal degradation occurred between 150 and 450°C, which is the same range observed with corn starch + PVA (average degree of hydrolysis) films plasticized with glycerol and urea.[25]

According to the DTG analysis (Figure 4), the films showed two or three pronounced steps. Films F2, F5, and F6 showed only two steps, most likely because the missing step (~250°C) is related to the initial degradation of the PVA, which had a lower concentration in the above formulations.

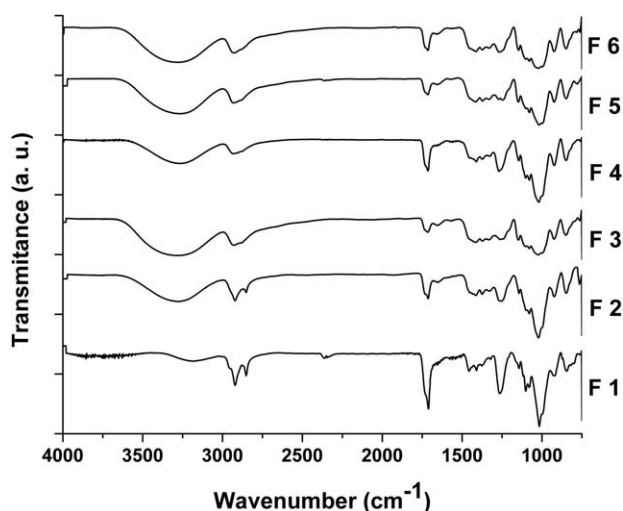Ray and coworkers,[26] in starch + PVA casting films plasticized with glycerol, observed that the degradation rates decreased compared with the pure components and that the position of the highest degradation peak shifted to higher temperatures, mainly at higher PVA concentrations. Similar behavior was observed in our study, in which the formulations containing the highest PVA concentrations showed degradation peaks at higher temperatures. The hydrogen bonds between the components of the blend increase the thermal stability of the material.[26]

Was observed similar behavior in films of PVA + corn starch plasticized with glycerol, with three distinct onset regions; the first was due to the loss of volatiles, such as water and glycerol; the second degradation region was attributed to either starch and PVA; and the third region was due to carbonization of the material.[20]

In produced casting films with cassava starch + PVA (fully hydrolyzed), and the mass loss curves also showed three stages (stage 1—below 200°C; stage 2—between 200 and 500°C; and stage 3—above 500°C). The authors observed that PVA

Figure 2. FT-IR analysis of the mixture designed films.
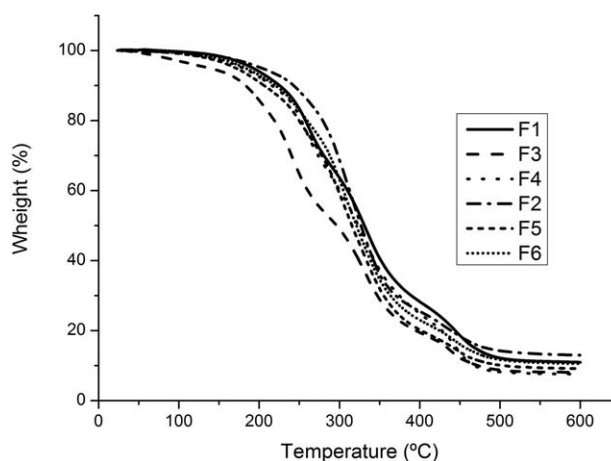

Figure 3. TGA analysis of the mixture designed films.
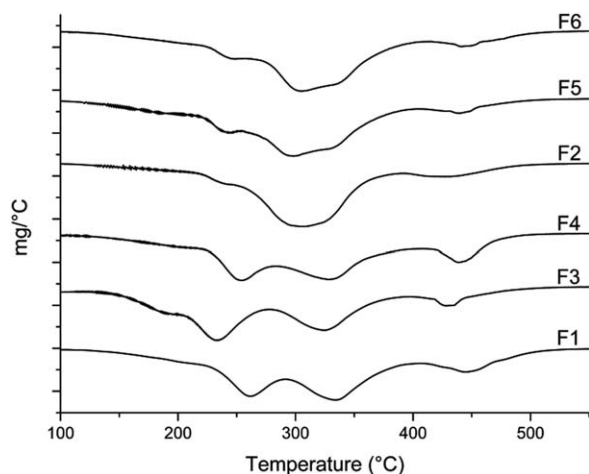
Figure 4. DTGA analysis of the mixture designed films.

decomposed faster than the starch and that the PVA had two stages of degradation: at ~200 and ~450°C.[27] The intensities of the thermogravimetric steps observed at ~450°C correlated with the concentration of PVA present in the blends, which is consistent with the result obtained in this work.

CONCLUSIONS

The biodegradable films of cassava starch and PVA has adequate mechanical, microstructural, and thermal properties, indicating a good miscibility between the starch and the PVA. All the formulations exhibited good processability and extrudability, and the materials were visually homogeneous. The mechanical properties are influenced by formulation and relative humidity of conditioning.

In general, a higher PVA concentration in the blend improves the mechanical and barrier properties of the biodegradable films. In contrast, a higher glycerol concentration and a higher relative humidity decrease the mechanical and barrier properties of the materials.

Biodegradable materials based on starch, PVA, and glycerol blends has adequate properties and processability when compared with previous works.

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