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Mechanical properties and water vapor transmission in some blends of cassava starch edible films

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Abstract

The continuous increase of consumer interest in quality, convenience and food quality has encouraged further research into edible films and coatings from natural polymers, such as polysaccharides. Ecoefficient products are the new generation of biobased products prepared with sustainable materials, that agree with ecological and economic requirements including environmentally acceptable disposal of post-user waste. The numerous potential applications of natural polymers such as polysaccharides stimulated the study with edible films based on cassava starch. Blends of glycerol (GLY) and polyethylene glycol (PEG) as plasticizers, and glutaraldehyde (GLU) as crosslinking agent were prepared in order to determine the mechanical properties and water vapor transmission of those films. A response surface methodology was applied on the results to identify the blend with the best mechanical properties and lowest water vapor transmission. The crosslinking effect of glutaraldehyde in the films can be observed. The plasticizing action of polyethylene glycol was restrained by more than 0.5 g of glutataraldehyde. The use of glycerol was less evident for this property even after 284 h of contact time with water vapor.
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1. Introduction

Nowadays, about 150 million tons of plastics are produced annually all over the world, and the production and consumption continue to increase. Most of these plastics are crude oil based, and an increase in their production results in an increase of oil use and causes serious environmental pollution, due to wasted and undegraded polymers. One of the strategies to solve the difficult questions related to fossil resources and global environment is thorough recycling wasted polymeric materials. The recycling of wasted plastics is limited, whether materials recycling or chemical recycling consumes a considerable amount of thermal energy, and plastics cannot be recycled forever, that is, wasted plastics are eventually destined to be burnt or buried in landfills.

Biological recycling of polymers must then be considered as an alternative to more traditional recycling procedures and this has stimulated researchers to synthesize new polymers that can be returned to the biological cycle after use. Therefore, the use of agricultural biopolymers that are easily biodegradable not only would solve these problems, but would also provide a potential new use for surplus farm production (Okada, 2002; Pavlath & Robertson, 1999; Scott, 2000).

The ecological impact of raw material resources used in manufacturing products and its ultimate disposal are relevant considerations in its design. Products designated, as ecoefficient products are the new generation of biobased products made from sustainable materials that conform to ecological and economic requirements (Narayan, 1994, 1998).

Biodegradable polymers from renewable resources have their importance based on the control or reduction of CO_2 emissions and sustainable development of carbon based polymeric materials. However, the concept of biopolymers

only is valid if the oil utilization life-cycle is shorter for biopolymers than for synthetic polymers (Scott, 2000).

Biodegradable polymers based on natural polysaccharides, particularly starch, can be produced at low cost and at large scale. As polysaccharides themselves do not have plasticity, they are often used after chemical modifications and/or a blend with a biodegradable synthetic polymer (Okada, 2002). According to Narayan (2001) starch based materials reduce nonrenewable resources use and environmental impact associated with increasing emissions as CO_2 and other products.

Life-cycle assessment (LCA) of materials provides a useful comparison of the ecological impact between products. According to Narayan (2003), low-density polyethylene (LDPE) when incinerated produces five times more CO_2 and two and a half times more ozone precursors (estimated in grams of ethylene equivalent) when compared to starch pellets.

Calculation of cradle-to-factory gate fossil energy requirements indicated the sum (process energy and feedstock energy in GJ/ton plastic) of 25 for thermoplastic starch pellets and 80 for high-density polyethylene (HDPE) or 77 for polyethylene terephtalate (PET bottle grade).

The continuous increase of consumer interest in convenience and food quality also has encouraged further research in edible films and biopolymers coatings. The reinvention of 'edible films' was due mainly to their numerous applications, such as sausage coatings, chocolate coatings for nuts, fruits and vegetables (Arvanitoyannis, Psomiadou, & Nakayama, 1998; Psomiadou, Arvanitoyannis, & Yamamoto, 1996).

Several materials from agricultural sources have been used to produce renewable biodegradable and edible packaging, frequently called agricultural or agro packaging materials, such as protein and polysaccharides (Cuq, Gontard, & Guilbert, 1998).

Since the pioneer research of Bradbury and Martin (1952) on the use of gelatin in packaging, coating and film fabrication, a great deal of work has been accomplished in this field (Azeredo, Faria, & Azeredo, 2000; Cuq et al., 1998).

Polysaccharides (starch and others) are often used in industrial foods. They produce films with good mechanical properties and coverings that are efficient barriers against low polarity compounds. However, they do not offer good barrier against humidity (Azeredo et al., 2000; Kester & Fennema, 1986). Proteins (egg albumin, keratin, casein, gelatin and others) are better barriers than polysaccharides. Protein films are usually transparent, flexible, water resistant and impervious to oxygen (Azeredo et al., 2000; Bradbury & Martin, 1952; Chiellini, Cinelli, Corti, & Kenawy, 2001; Cuq, Aymard, Cuq, & Guilbert, 1995; Grouber, 1983; Guilbert, 1988; Hebert & Holloway, 1992; Monteiro & Airoldi, 1999). Biodegradable protein and polysaccharide films with satisfactory mechanical properties and good appearance are potential and ecological alternatives for substituting synthetic packaging in

pharmaceutical and food applications. Pavlath and Robertson (1999) describe physicochemical property improvements that are comparative to commercial nonbiodegradable films, through chemical modification.

A major component of edible films are the plasticizer, as well as, the film-forming polymer. The addition of a plasticizer agent to edible films is required to overcome film brittleness, caused by high intermolecular forces. Plasticizers reduce these forces and increase the mobility of polymer chains, thereby improving flexibility and extensibility of the film. On the other hand, plasticizers generally decrease gas, water vapor and solute permeability of the film and can decrease elasticity and cohesion (Gontard, Guilbert, & Cuq, 1993; Sobral, Menegalli, Hunbinger, & Roques, 2001).

Many researchers have studied thermal and mechanical properties of edible films as a function of plasticizing. Arvanitoyannis, Psomiadou, Nakayama, Aiba, and Yamamoto (1997) reported a decrease of Tg (glass transition temperature) and tensile strength with increasing water or polyol concentrations in gelatin and soluble starch blends. Chiellini et al. (2001) reported the effect of a cross-linking agent, such as glutaraldehyde on thermal properties and degradation rate of gelatin and poly (vinyl alcohol) (PVA) blends, by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). The results reported by the authors demonstrated a complete and very fast biodegradability of these films. Sobral, Monterrey, and Habitante (2002) determined the Tg of Nile tilapia myofibrilar protein based films plasticized with glycerol and water, by DSC and reported a phase separation of the protein and the plasticizer, where the plasticizer Tg is displaced by influence of the water.

Cassava, *Manihot esculenta Crantz*, one of the main sources of industrial starch, is cultivated throughout the Brazilian territory and other tropical countries; therefore, cassava is an abundant and cheap agricultural source of starch (Matsui et al., 2004).

The aim of this study was to manufacture edible films based on cassava starch and blends of glycerol (GLY) and polyethylene glycol (PEG) as plasticizers, and glutaraldehyde (GLU) as a cross-linking agent, in order to determine the mechanical properties and water vapor transmission (WVT) of these films. A response surface methodology was applied to the results to determine the blend that presents better mechanical properties and lowest WVT. Studies of gas permeability concerning these edible films are in progress and will be addressed in future works.

2. Materials and methods

2.1. Materials

Cassava starch was supplied by Fadel Ind and Com. Ltda. SP, Brazil, with 98% of starch. Glycerol and glutaraldehyde

were supplied by Polyorganic and PEG additive 300 USP was supplied by Oxiteno S/A, Brazil.

2.2. Edible films preparation

Edible films were prepared using a casting process, which consists of dehydrating a filmogenic solution applied on a support The filmogenic solutions were prepared at pH 9.0 and 70 °C, from cassava starch (1 g of starch/100 ml of water) and additives according to the experimental design as shown on Table 1. The solutions were prepared by addition of starch and additives in a beaker with water at ambient temperature. After that, the solutions were kept at 70.0 ± 0.5 °C, in a controlled temperature water bath for 15 min (Fisatom). Addition of GLY, GLU or PEG was carried out under stirring for 15 min at 70.0 °C.

2.3. Mechanical tests

Tensile strength and percentage elongation were measured according to ASTM-D D412-98a (ASTM, 1998) using a Mechanical Universal Testing Machine Instron 4400R, with a 50 N load cell and at a velocity of 1.0 mm/s. Test samples were cut in dumb-bell Die F dimensions according to the ASTM standard method. The results are the average of five samples.

2.4. Water vapor transmission

The WVT was determined according to ASTM E96-80 (ASTM, 1989), modified by Gontard et al. (1993). A container with silica gel was closed with a sample of edible film firmly fixed on top. Then, the container was placed in a desiccator with distilled water at a temperature of 25.0 °C. The films were weighed daily on a Mettler analytical balance for 10 days. The WVT was calculated according to Eq. (1):

$$WVT = \frac{w \times x}{A} \qquad (1)$$

where WVT is Water Vapor Transmission (g H_2O mm cm^{-2}), x is the average thickness of the film (0.048 ± 0.012 mm) and A is the permeation area (12.57 cm^2).

The Water Vapor Transmission rate (WVTR) was calculated according to Eq. (2):

$$WVTR = \frac{w \times x}{t \times A} \qquad (2)$$

where WVTR is Water Vapor Transmission Rate (g H_2O mm h^{-1} cm^{-2}), and the term x/t was calculated by linear regression from the points of weight gain and time, during constant rate period. The tests were carried out in triplicate.

2.5. Statistical analysis

ANOVA and regression analysis were performed in all results using a statistical program Statgraphics for Windows v4.0, at a confidence interval of 95%.

3. Results and discussion

The films from cassava starch produced from blends with glycerol and PEG were transparent, homogeneous and flexible (see Fig. 1). However, those with glutaraldehyde became slightly opaque. The average thickness of the films was 0.048 ± 0.012 mm.

3.1. Mechanical properties

The tensile strength and percentage elongation of cassava starch films are given on Table 2. An ANOVA was applied to the results and indicated that the additives glycerol and glutaraldehyde have a statistically significant effect on tensile strength, at a 95.0% confidence level. The ANOVA

Table 1
Quantities of glycerol, glutaraldehyde and polyethylene glycol used in the elaboration of blends of cassava starch edible films

Blends	Glycerol (GLY) (g)	Glutaraldehyde (GLU) (g)	Polyethylene glycol (PEG) (g)
1	1.0	1.0	0.0
2	1.0	0.0	0.0
3	2.0	0.2	0.0
4	1.0	0.5	0.0
5	1.0	0.1	0.0
6	1.0	0.0	0.1
7	1.0	0.0	0.3
8	2.0	0.0	0.2
9	2.0	0.0	0.3
10	3.0	0.0	0.3
11	1.0	0.2	0.2
12	1.0	0.3	0.3

Fig. 1. Illustrative picture of cassava starch edible film (blend of 1.0 g of glycerol; 0.3 g of glutaraldehyde; 0.3 g of polyethylene glycol).

Table 2
Tensile strength and percentage elongation according to the quantities of glycerol, glutaraldehyde and polyethylene glycol used in the elaboration of the blends of cassava starch edible films

Blends	Glycerol (GLY) (g)	Glutaraldehyde (GLU) (g)	Polyethylene glycol (PEG) (g)	Tensile strength (MPa)	Elongation (%)
1	0.0	0.0	0.0	0.069 ± 0.050	11.10 ± 0.45
2	1.0	0.0	0.0	0.357 ± 0.018	11.00 ± 0.47
3	1.0	0.1	0.0	0.299 ± 0.018	9.86 ± 0.44
4	1.0	0.5	0.0	0.381 ± 0.022	10.1 ± 1.31
5	1.0	1.0	0.0	0.421 ± 0.020	12.1 ± 1.35
6	2.0	0.2	0.0	0.288 ± 0.019	15.90 ± 0.84
7	1.0	0.0	0.1	0.444 ± 0.022	15.60 ± 1.19
8	1.0	0.0	0.3	0.473 ± 0.024	27.60 ± 1.33
9	2.0	0.0	0.2	0.238 ± 0.009	21.60 ± 1.19
10	2.0	0.0	0.3	0.058 ± 0.003	52.10 ± 2.22
11	3.0	0.0	0.3	0.083 ± 0.005	72.90 ± 2.98
12	1.0	0.2	0.2	0.399 ± 0.018	11.16 ± 0.64
13	1.0	0.3	0.3	0.352 ± 0.018	10.92 ± 0.54

also indicated that all three additives significantly influenced elongation of the films. As can be observed in Fig. 2, an increase of glutaraldehyde caused an increase in film tensile strength, whereas the mechanical properties only increased at the level of 1 g of glycerol. The films manufactured with more than 1 g of glycerol presented lower values of tensile strength. Therefore, at levels above 1 g of glycerol, this additive acts as a plasticizer agent, changing film mechanical behavior.
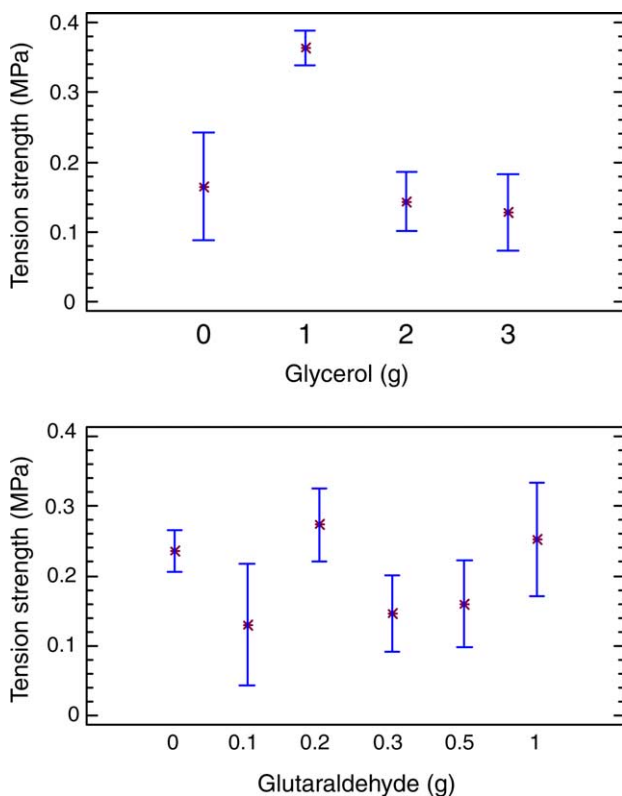

Fig. 2. Tensile strength (MPa) of cassava starch films as a function of glycerol and glutaraldehyde addition (g).
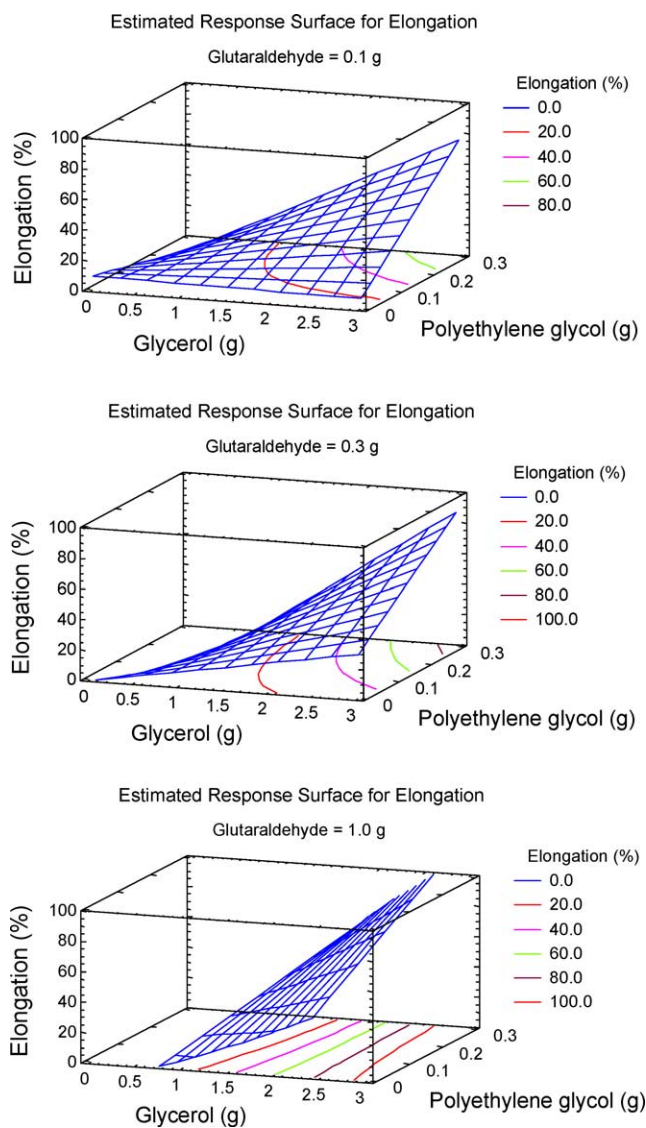

Fig. 3. Elongation (%) of cassava starch films as a function of glycerol and polyethylene glycol addition (g), at 0.1, 0.3 and 1.0 g of glutaraldehyde.

Table 3
Coefficients and significance of regression models to tensile strength (MPa), elongation (%) and Water Vapor Transmission Rate (WVTR) according to the quantities of glycerol, glutaraldehyde and polyethylene glycol used in the elaboration of the blends of cassava starch edible films

Term	Tensile strength (MPa)	Elongation (%)	WVT (g H_2O mm cm^{-2})
Constant	0.2200	14.0700	1.5244×10^{-4}
Glycerol	0.0870*	-6.1882*	3.6574×10^{-5}
Glutaraldehyde	0.6798*	-48.6154*	-9.2749×10^{-5}*
Polyethylene glycol	1.5144*	-37.0144	1.7383×10^{-3}*
Time			7.2358×10^{-7}*
Glycerol $\times$ Glutaraldehyde	-0.6008*	53.4405*	-4.1130×10^{-5}
Glycerol $\times$ Polyethylene glycol	-1.0534*	95.6542*	8.8099×10^{5}
Glycerol $\times$ Time			-1.0238×10^{-8}
Glutaraldehyde $\times$ Polyethylene glycol	-1.4530*	-178.3760*	-6.9664×10^{-3}*
Glutaraldehyde $\times$ Time			-1.6708×10^{-7}
Polyethylene glycol $\times$ Time			1.9086×10^{-6}*
s	0.0689	3.7988	6.1392×10^{-5}
R^2	70.5204	95.0733	96.5616

*$p < 0.05$.

Table 4
Water Vapor Transmission Rate (WVTR) according to the quantities of glycerol, glutaraldehyde and polyethylene glycol used in the elaboration of the blends of cassava starch edible films

Blends	Glycerol (GLY) (g)	Glutaraldehyde (GLU) (g)	Polyethylene glycol (PEG) (g)	Water Vapor Transmission Rate (WVTR) (g H_2O mm h^{-1} cm^{-2})	R^2
1	0.0	0.0	0.0	7.19×10^{-7}	0.9581
2	1.0	0.0	0.0	6.89×10^{-7}	0.9649
3	1.0	0.1	0.0	6.23×10^{-7}	0.9603
4	1.0	0.5	0.0	5.05×10^{-7}	0.9373
5	1.0	1.0	0.0	5.93×10^{-7}	0.9112
6	2.0	0.2	0.0	7.04×10^{-7}	0.9744
7	1.0	0.0	0.1	7.69×10^{-7}	0.9450
8	1.0	0.0	0.3	1.55×10^{-6}	0.9877
9	2.0	0.0	0.2	9.03×10^{-7}	0.9796
10	2.0	0.0	0.3	1.68×10^{-6}	0.9778
11	3.0	0.0	0.3	8.38×10^{-7}	0.8812
12	1.0	0.2	0.2	7.39×10^{-7}	0.7818
13	1.0	0.3	0.3	5.80×10^{-7}	0.8369

To predict the relationship between the additives and film mechanical properties, regression analysis was performed using the response surface methodology. Only the elongation data were well correlated with this model ($p < 0.05$), with R^2 value $> 95.0\%$ (Table 3). As can be observed in Fig. 3, an increase of PEG increased drastically the elongation of the films, and levels above 1 g of glycerol confirmed the plasticizing affect on the films.

3.2. Water vapor transmission

The film WVTR was calculated according to Eq. (2) and the results are shown on Table 4. The ANOVA indicated that an increase in glycerol decreased WVTR, whereas increase in PEG increased this property. In this paper, glycerol and PEG were used as plasticizing agents, to reduce the intermolecular interactions and increase mobility of

Table 5
Analysis of variance for Water Vapor Transmission (WVT) according to the quantities of glycerol, glutaraldehyde and polyethylene glycol used in the elaboration of the blends of cassava starch edible films

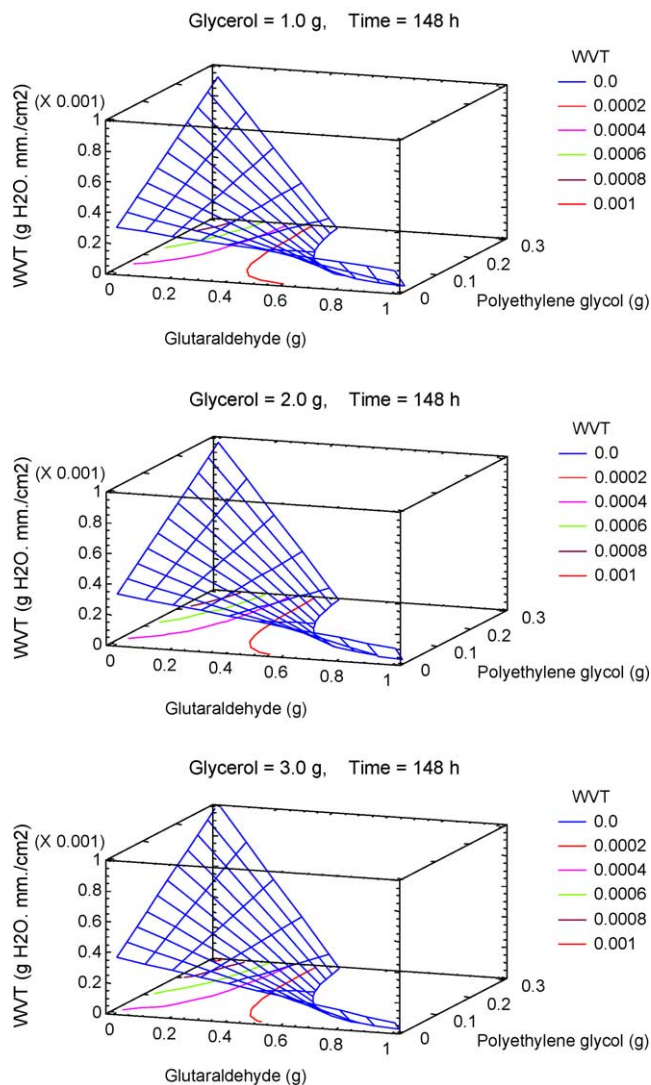| Source	Sum of squares	Df	Mean square	F-ratio	P-value
Main effects					
Glycerol	2.0920×10^{-7}	3	6.9734×10^{-8}	9.71	0.0000
Glutaraldehyde	1.6453×10^{-6}	5	3.2907×10^{-7}	45.81	0.0000
PEG	2.5791×10^{-6}	3	8.5969×10^{-7}	119.67	0.0000
Time	7.5304×10^{-7}	13	5.7926×10^{-8}	8.06	0.0000
Residual	7.3993×10^{-7}	103	7.1838×10^{-9}		
Total (corrected)	1.2692×10^{-6}	127			

Fig. 4. Water Vapor Transmission (WVT) according to the quantities of glycerol, glutaraldehyde and polyethylene glycol at the time of 148 h, used in the elaboration of the blends of cassava starch edible films.
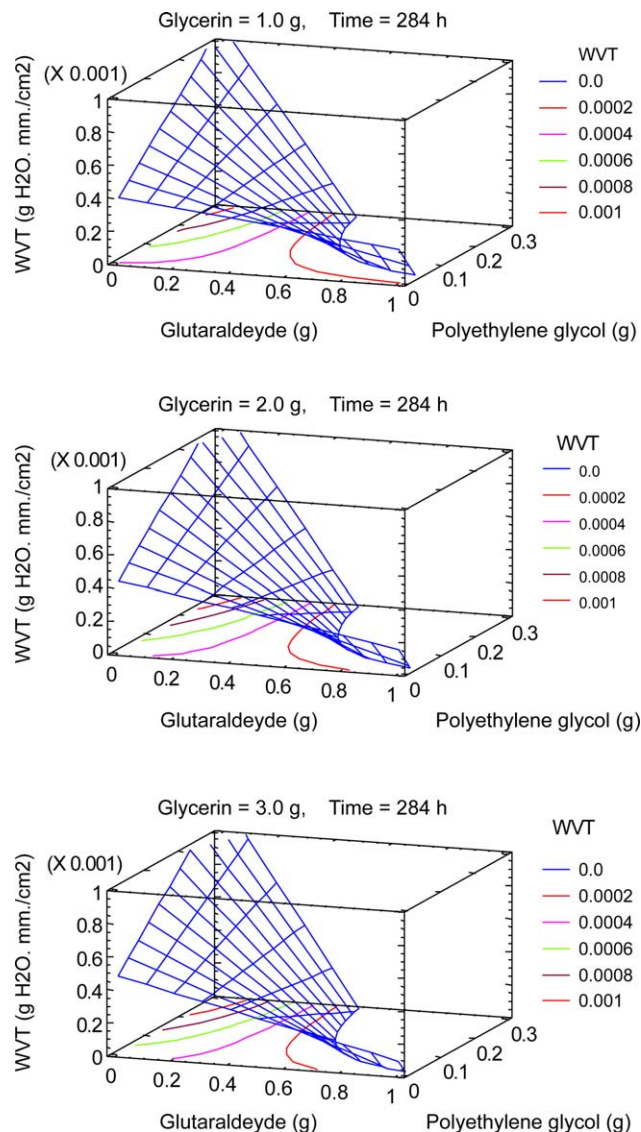

Fig. 5. Water Vapor Transmission (WVT) according to the quantities of glycerol, glutaraldehyde and polyethylene glycol at the time of 284 h, used in the elaboration of the blends of cassava starch edible films.

the macromolecules. Consequently, water permeability increased, mainly due to the high hydrophilic nature of PEG.

An ANOVA was applied to the results of WVT and indicated that all additives and test time significantly influenced the results, at a 95.0% confidence interval. Table 5 presents a summary of the ANOVA analysis for WVT. To verify how these factors affected WVT of the films, regression analysis was performed. This analysis indicated that the results were well fitted by the predicted model with a correlation factor R^2 of 96.5838% (Table 3).

Figs. 4 and 5 show the variation of WVT of the blends of cassava starch films and compare the results between 148 and 284 h of contact. The cross linking effect of glutaraldehyde in the films can be observed. More than 0.5 g of this additive restrained the plasticizing action of PEG. The use of glycerol was less evident for this property even after 284 h of contact time.

4. Conclusions

A response surface methodology was applied to the results obtained in this paper to understand the behavior of the blend in terms of better mechanical properties and lower water vapor transmission. Predictive models indicated that blends formulated with PEG up to 0.3 g exhibited good elongation. This behavior is adequate for films that require flexibility. However, levels above 1 g of glycerol increased WVTR, reducing the applicability of these films in wet environments. Films made with levels up to 0.5 g of glutaraldehyde presented lower water permeability due the crosslinking effect.

Films from starch cassava formulated with the blends studied in this paper had good performance of flexibility

and low water permeability, indicating potential application as edible films.

Acknowledgements

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