

## RESEARCH ARTICLE

# Mechanical properties of pea starch films associated with xanthan gum and glycerol

Manoel Divino da Matta Jr.<sup>1</sup>, Silene Bruder Silveira Sarmento<sup>1</sup>, Léa Mariza de Oliveira<sup>2</sup> and Silvio Sandoval Zocchi<sup>1</sup>

<sup>1</sup> Luiz de Queiroz College of Agriculture, University of Sao Paulo, Piracicaba, Sao Paulo, Brazil

<sup>2</sup> Food Technology Institute, Campinas, Sao Paulo, Brazil

The aim of this study was to evaluate the effect of the addition of xanthan gum and glycerol to the starch of green pea with high content of AM (cv. Utrillo) in the preparation of films and their physical characteristics. Filmogenic solution (FS) with different levels of pea starch (3, 4, and 5%), xanthan gum (0, 0.05, and 0.1%), and glycerol (glycerol–starch ratio of 1:5 w/w) were studied. The FS was obtained by boiling (5 min), followed by autoclaving for 1 h at 120°C. The films were prepared by casting. Films prepared only with pea starch were mechanically resistant when compared to other films, prepared with corn, cassava, rice, and even other pea cultivars (yellow, commercial). The tensile strength of these films is comparable to synthetic films prepared with high-density polyethylene and linear low-density polyethylene. However, they are films of low elasticity when compared to other films, such as rice starch films, and especially when compared to polyethylene films. The increased concentration of starch in the solution increased the puncture force. The increased concentration of glycerol slightly decreased the film crystallinity and interfered in the mechanical properties of the films, causing reduction of the maximum values of tensile strength, strain at break, and puncture force. The plasticizer also caused an increase of elongation at break. Xanthan gum was important to formation of films; however, it did not affect their mechanical properties.

Received: July 19, 2010  
Revised: December 28, 2010  
Accepted: December 30, 2010

**Keywords:**

Biofilms / Gum / *Pisum sativum* / Plasticizer / Starch

## 1 Introduction

The packaging industry has shown increasing interest in replacing synthetic polymers with materials of faster degradation in the environment. In this context, starches from several sources have been studied for the production of films. These films have good mechanical properties and oxygen barrier; however, a number of limitations are

observed with respect to their hydrophilic characteristics and permeability to water vapor.

The mechanism of starch film formation depends on the concentration of solids and AM contents. The preparation occurs through aggregation and packing of the swollen starch granules of a dispersion with relatively high concentration of solids. The transition from coil to helix and the aggregation of double helices also play a role in the formation of films from dilute starch solutions [1]. Furthermore, the AM content shows significant effects in time and extent to which the double helices are formed and aggregate. The AM solution results in greater formation of helicoids and aggregation. In short, the formation of films from dilute starch solutions follows the formation order of helicoids, aggregation or gelification and reorganization of aggregates, and the beginning is primarily driven by cooling, followed by dehydration [1].

---

**Correspondence:** Dr. Silene Bruder Silveira Sarmento, Departamento de Agroindústria, Alimentos e Nutrição, Escola Superior de Agricultura Luiz de Queiroz, Universidade de São Paulo, Av. Pádua Dias, 9. CEP 13418-900- Piracicaba, São Paulo, Brazil

**E-mail:** sbssarme@usp.br

**Abbreviation:** FS, filmogenic solution; LLDPE, linear low-density polyethylene; RS, rice starch; YPS, yellow pea starch.

By showing higher AM contents, pea starch may be a good source for obtaining films. In literature, however, studies about films from pea starch [2–5] assess only commercial starches of yellow varieties, as cv. Miranda, with AM contents between 30 and 40%. According to these authors, these starches produce films with better characteristics of physical integrity, gas barriers, mechanical properties, but with high permeability to water vapor.

The AM content can reach 76% in the starch of some pea varieties [6]. These varieties, however, were not evaluated for film production. According to Matta Júnior [7], the pea starch cultivar Utrillo presents high AM amounts.

In the search of new formulations and associations of components in order to obtain better characteristics for edible films, starch/hydrocolloid associations have also been studied. These latter may interfere with the gelatinization and retrogradation of starches [8–10], which may affect the characteristics of films. Two explanations can be proposed for the understanding of these interactions: association with swollen starch or with AM chains leached in the paste, and the competition with starch for water. These associations are highly dependent on the gum structure [11].

The literature shows examples of hydrocolloids associated with starches, changing the thermal or mechanical characteristics or barrier properties of films. The combination of gum xanthan (0 to 0.1% w/w)/cassava starch (3–5%) was studied by Santos et al. [12] to obtain films. The addition of gum xanthan to the filmogenic solution (FS) had no significant impact on the mechanical properties or on the water absorption kinetics of films when compared to control (5% of cassava starch).

Associations of pea starch hydroxypropylated with  $\kappa$ -carrageenan were also studied [13], with increased viscosity of the hot paste, improvement in the gelling properties and in the film drying and formation, without changes in its properties. In a study by Chen et al. [14], the association of yellow pea starch/Konjac increased the strain at break and the elongation of the films obtained.

The interactions between AM and AP molecules contribute to the film formation, but when they are very intense, the starch films become Bt and stiff. The presence of plasticizers in starch films helps to stop the formation of double helix of AM with AP fragments, thus reducing the interaction between AM and AP molecules, forming a flexible film [3].

In previous work [7] films produced with wrinkled pea starch, cv Utrillo, with or without xanthan gum, and glycerol showed better barrier to oxygen and water vapor and low solubility in water if compared with films of yellow pea starch and other starch sources founded in the literature. So, this study had the objective of evaluate mechanical properties of edible films made from wrinkled pea starch of high AM content associated with gum xanthan and glycerol.

## 2 Material and methods

### 2.1 Material

The starch was extracted from green pea (*Pisum sativum* L.), wrinkled-type cultivar Utrillo. The fresh peas were purchased directly from the producer. The gum xanthan used was a courtesy from CPKelco (Keltrol<sup>®</sup> RD), food grade.

### 2.2 Methods

#### 2.2.1 Starch macromolecular composition

The AM content was determined according to ISO 6647 [15].

#### 2.2.2 Film preparation

The films were prepared according to the casting technique. FS were obtained by heating the suspension (5 min) at boiling temperature and autoclaving (1 h at 121°C and 1 atm). The FS (30 g) were placed in Plexiglas plates (15 cm diameter) and dried in oven (37°C for 3 h), followed by drying at room temperature (2 h).

#### 2.2.3 Film characterization

##### 2.2.3.1 Mechanical properties

The tests were performed at 23°C ± 2°C and 50 ± 3% RH, after conditioning the samples for a period of 48 h at 25°C and 75% RH.

The average thickness of the films was determined with a flat-end digital micrometer Mitutoyo MDC 25 SB and calculated as the arithmetic mean of 12 random measurements of the film.

The tensile properties were determined according to ASTM D882-02: Standard test method for tensile properties of thin plastic sheeting [16]. The samples (15 mm wide) were tensioned in an universal testing machine, INSTRON, model 5500R, operating with a load cell of 100 N at a speed of 500 mm/min. The initial distance between grips was 50 mm. The test was conducted with five replications. The thickness of each sample was given in three points, using flat-end digital micrometer label Starret with resolution of 1 μm. The average thickness of each sample was used to calculate the stress and the tensile strength of each repetition.

The puncture force was determined according to ASTM F 1306-90, Standard test method for slow rate puncture force of flexible barrier films and laminate [17], on universal testing machine, Instron model 5500R, using a load cell of 100 N. Samples with 35 mm diameter were drilled with a

ballpoint metal tip with 3.2 mm diameter at a speed of 25 mm/min.

### 2.2.3.2 XRD

The XRD was evaluated in samples that presented the extremes values of mechanical properties and also in the media point of surface response.

XRD analysis of films stored a week at 20°C and 70% relative humidity were carried out using an X-ray diffractometer (Rigaku Miniflex II, Tokyo, Japan) equipped with Cu K $\alpha$  radiation. It was used 30 kV and 15 mA, with counter monochromator. Divergent slit 1.25 and receiving slit 0.3. Step scan: 0.05 (2 $\theta$ ) degrees, 1 (2 $\theta$ ) degrees per minute. Scan from 3 to 40 (2  $\theta$ ) degrees. The samples were analyzed in duplicate.

From the scattering spectrum, the relative crystallinity of films was determined according to Nara and Komiya [18] using the software Origin 7.5 (Microcal Inc., Northampton, MA, USA) as the ratio of the integrated crystalline intensity to the total intensity.

### 2.2.4 Experimental design

The complete 2<sup>3</sup> factorial design was adopted to study the influence of the three explanatory variables: starch concentration ( $x_1$ ), gum concentration ( $x_2$ ), and glycerol concentration ( $x_3$ ) on properties (response variables  $y$ ) of films. The complete design, as shown in Table 1, consists of 13 experimental points, including five replicates of the central point ( $x_1 = 0$ ,  $x_2 = 0$  and  $x_3 = 0$ ) that were included in order to estimate the pure error and to evaluate the lack of adjustment of the proposed models.

The model adjustment and simplification were carried out using the stepwise procedure and the REG procedure of the SAS software, version 9.1 [19]. The resulting plots of significant mathematical models were obtained by Maplesoft, Maple version 9.5 [20].

## 3 Results and discussion

### 3.1 Starch composition

This pea starch cultivar presented an AM content of 61% and it can be considered high. According to Themeier et al. [21], this plant species can present from 20.7 to 70.6% of AM.

### 3.2 Film formation

Only treatment 5 (FS with 5% starch) did not allow the formation of film, probably due to the absence of plasticizer and to the strong interactions between starch polymers,

**Table 1.** Independent variables (coded and real values)

Treatment	$x_1$	$x_2$	$x_3$
1	−1 (3)	−1 (0)	−1 (0)
2	−1 (3)	−1 (0)	1 (20)
3	−1 (3)	1 (0.10)	−1 (0)
4	−1 (3)	1 (0.10)	1 (20)
5	1 (5)	−1 (0)	−1 (0)
6	1 (5)	−1 (0)	1 (20)
7	1 (5)	1 (0.10)	−1 (0)
8	1 (5)	1 (0.10)	1 (20)
9	0 (4)	0 (0.05)	0 (10)
10	0 (4)	0 (0.05)	0 (10)
11	0 (4)	0 (0.05)	0 (10)
12	0 (4)	0 (0.05)	0 (10)
13	0 (4)	0 (0.05)	0 (10)

$x_1$  = starch,  $x_2$  = xanthan gum e,  $x_3$  = glycerol.

making the film Bt and stiff. The presence of xanthan gum in the FS, however, was important allowing to get films in the treatment 7 (with 5% starch and 0.1% gum).

### 3.3 Statistical analysis

The analysis of variance (ANOVA) of the film properties in function of the FS composition is presented in Table 2. The mathematical models for the parameters thickness, tensile strength, and puncture force were significant at 1% ( $p < 0.01$ ) and for the elongation at rupture it was significant at 5% ( $p < 0.05$ ).

The starch content in the FS influenced thickness, rupture factor and puncture force, and the coefficients of these regression models were significant at 1% level.

The glycerol concentration affected the maximum tensile strength, stress at break, rupture factor and puncture force, being the regression coefficients models significant at 1% level. For elongation at rupture, the coefficient was significant at 5% level.

### 3.4 Thickness

The film thickness was influenced by the starch and glycerol contents in the FS, according to the response surface plot (Fig. 1). The higher the starch and glycerol content, the higher the thickness of the films.

The parameter that most influenced thickness was the starch content, probably by increasing the amount of solids in the FS. The effect of the starch content in the film thickness was also observed by other authors such as Wang et al. [22], who obtained films with thickness of 0.044 mm for FS with 2% of potato starch and 0.069 mm for FS with 3% of this starch, both being added of glycerol (1:2 w/w starch/glycerol).

**Table 2.** Regression coefficients for dependent variables and analysis of variance of the polynomial models

Dependent variables (y)	Coefficients of the regression models							$R^2$	Model (p)	CV (%)	Lack of fit significance (p)
	$B_0$	$\beta_1$	$\beta_2$	$\beta_3$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$				
Thickness	0.077	0.011***		0.007*				0.66	0.0074	11.1	0.3765
Maximum values of tensile strength	31.374			-15.446***				0.95	0.0001	10.0	0.1947
Elongation at break	8.163			4.943**				0.40	0.0261	58.1	0.0547
Strain at break	30.487			-15.242***				0.96	0.0001	9.0	0.4702
Puncture force	9.961	1.911***		-2.158***				0.79	0.0009	12.5	0.5366
Deformation at break	2.252			0.716***				0.78	0.0001	13.7	0.0033

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + e$$

$y$  = dependent variable,  $x_1$  = starch concentration,  $x_2$  = gum concentration and  $x_3$  = glycerol concentration. \*, \*\*, and \*\*\* = significant at  $p \leq 0.10$ ,  $p \leq 0.05$  and  $p \leq 0.01$ , respectively. CV = Coefficient of variation;  $R^2$  = Coefficient of determination.

Another factor contributing to the film thickness is the shrinkage degree of the FS during the drying process, *i.e.*, the evaporation of the solvent and/or aging of the gel. According to Phan The et al. [23], shrinkage is an important factor in establishing the thickness of films obtained by casting technique and it is mainly caused by the retrogradation and syneresis of the polymer. So, the shrinkage percentage is related to the reorganization of polymer chains during drying. These authors observed that shrinkage seemed to be insignificant in the presence of branched chains, since their structures prevent molecular associations.

The pea starch used in this study should provide a considerable shrinkage, since this starch has AM content (linear fraction) of 61%, and therefore a high tendency to

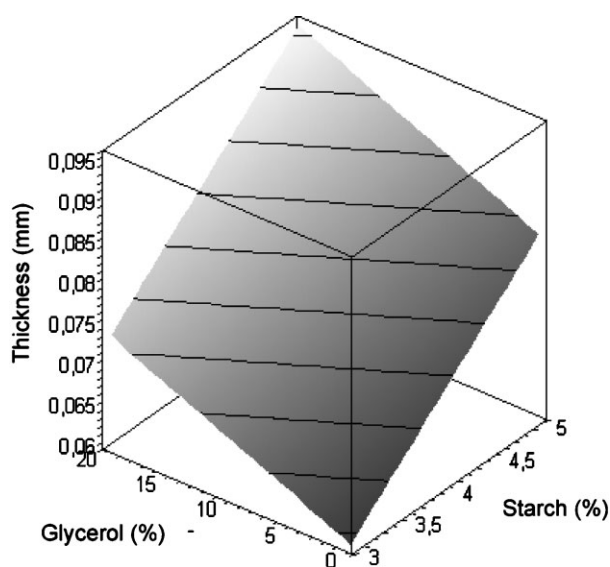
retrogradation. The addition of plasticizer, however, disrupts the formation of double helices of AM with AP fragments, thus reducing the interaction between these molecules [3].

Laohakunjit and Noomhorm [24] studied the effect of glycerol on the rice starch film thickness. Those not added of glycerol showed thickness of 0.100 mm and those added of the plasticizer in proportions of 20, 25, 30, and 35%, generated thicknesses of 0.108, 0.105, 0.106, and 0.109 mm, respectively. Leyva et al. [25] also observed a significant increase in the thickness of wheat starch films with the addition of glycerol from 25 to 40%.

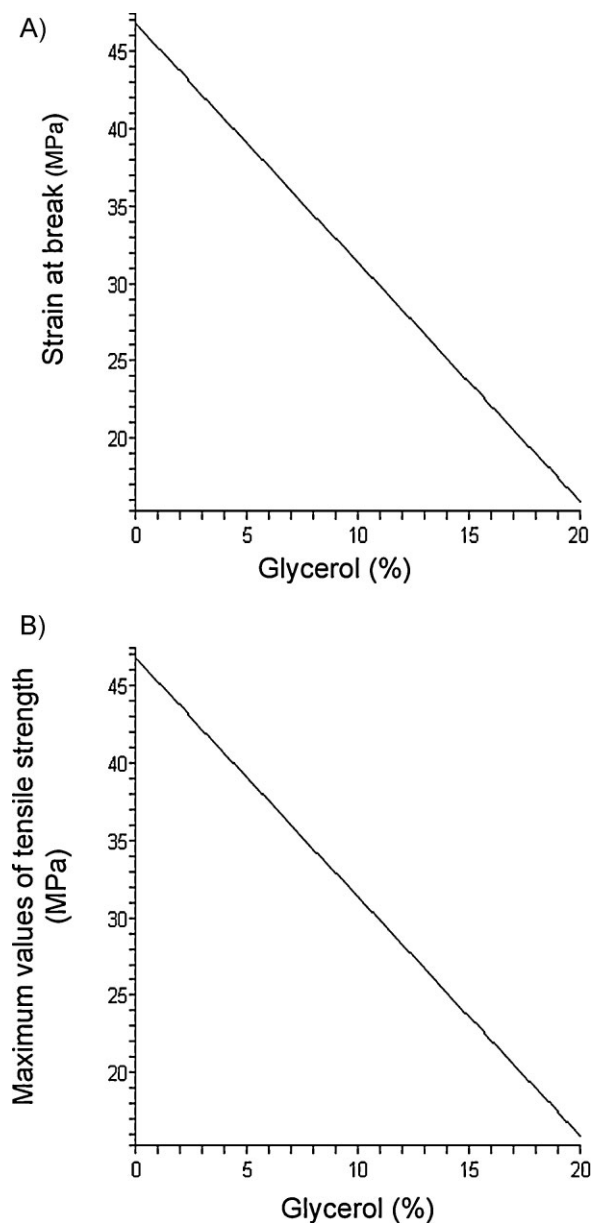
### 3.5 Tensile properties

The maximum tensile strength and strain at break of films were similar and varied in inverse proportion to the glycerol contents as shown in Fig. 2. The maximum strength ranged from 11.4 MPa for treatment 2, containing 3% of starch and 20% of glycerol to 47.3 MPa for treatment 7, with 5% of starch, 0.1% of gum. In the central point (treatment 9), the value was 32.7 MPa. The strain at break of pea starch films ranged from 11.1 for treatment 2 to 46.2 MPa for treatment 7. The central point value (treatment 9) was 17.3 MPa.

Comparing this pea starch film obtained by casting with those films from other peas obtained by extrusion as in the study by Liu [26], the maximum tensile strength (conditioned at 23°C and 50% RH) of the latter were very low, because they ranged from 2.65 to 4.32 MPa. Besides the source of the starch, the lower relative humidity in the conditioning (50 versus 75%) may have contributed to the decreased resistance of these films in relation to those under study. The water in the conditioning environment is absorbed by the starch film and acts as a plasticizer, reducing the interaction between polymer chains.



**Figure 1.** Effect of starch and glycerol concentration on the thickness of pea starch film.



**Figure 2.** Effect of glycerol concentration on the strain at break (A) and on the maximum value of tensile strength (B) of the pea starch films.

The results concerning the influence of the glycerol content on the maximum tensile strength are in agreement with those found in literature. Lohakunjit and Noormhorm [24] reported that even a small increase in the glycerol content results in a large reduction in the tensile properties. Other studies have reported that the addition of plasticizer reduces the direct interactions of the film-forming polymer [27, 28, 4], thus reducing the compression of the network that forms the film and hence, its mechanical strength. Li et al. [29] also suggest that the increased aggregation of film-forming molecules (more compact

molecular structure) provided by reducing the plasticizer concentration increases the maximum tensile strength.

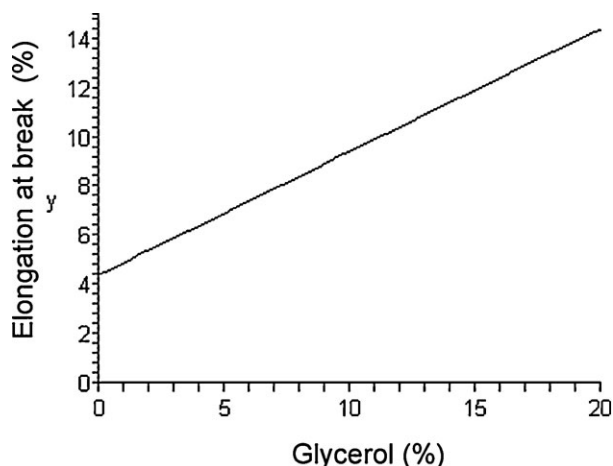
Yellow pea starch films (3%) added of glycerol in the ratio of 20/50 (w/w glycerol/starch) and conditioned for 72 h at 25°C and 50% RH were studied by Zhang and Han [4]. The maximum tensile strength of these films was 5.8 MPa, at 50% RH and 25°C. However, yellow pea starch films (3%) added of glycerol in the ratio of 40/60 (w/w glycerol/starch) studied by Han et al. [5] showed maximum tensile strength of 2.3 MPa when conditioned for 48 h at 50% RH and 25°C.

Mehyar and Han [2] studied rice (RS) and yellow pea (YPS) starch films made with 3% of starch and glycerol (1:2 (w/w) glycerol:starch) and stored for 3 days under two different RH (51 and 90%). The RS films added of glycerol and stored at 51% RH showed maximum tensile strength of 3.2 MPa and YPS films of 4.2 MPa. When stored at 90% RH, the values were 1.9 (RS) and 2.8 MPa (YPS) in films with glycerol. Films without glycerol (only starch) at 90% RH showed 12.1 (RS) and 3.0 MPa (YPS). The value showed by RS film (12.1MPa) is similar to some values found in this study, such as in treatments 8 (12.2 MPa) and 2 (11.4 MPa), although in this work, conditioning has been done at 75% RH.

The xanthan gum concentrations (0 to 0.1% starch) used in this study did not influence the tensile properties of pea starch films with high AM content. However, studies in literature have reported that the addition of this hydrocolloid may limit the mobility of starch chains due to its rigid structure. The elasticity and deformability of gels composed of mixed systems of potato soluble starch and gum xanthan were studied and were lower than the system made of pure starch. The elasticity of pure starch gels was twice that of gels prepared with 0.1% xanthan and three times higher than those containing 0.3% of xanthan [30].

The lowest strain at break values at rupture in this study can be compared to synthetic films made of low-density polyethylene (LDPE) with up to 100  $\mu\text{m}$  in thickness, whose pattern of strain at break ranges from 8.3 to 11.7 MPa (ASTM D 4635). In turn, films of high-density polyethylene (HDPE) and those of linear low-density polyethylene (LLDPE) have strain at break of about 30 to 40 MPa [31], compatible with some of the formulations studied. Polyethylene films, especially LLDPE, are used to give mechanical strength to monolayer or multilayer sacks.

The elongation of the films at rupture increased with glycerol content (Fig. 3) ranging from 4.91% in treatment 1 (3% starch) to 28.6% in treatment 8 (5% starch, 0.1% xanthan and 20% glycerol), and the central point value was 6.66%. These values are much lower than those of Han et al. [5] for yellow pea starch films added of glycerol in the ratio of 60/40 w/w and conditioned for 48 h at 50% RH, which was 51.4%. This value is probably due to the higher



**Figure 3.** Effect of glycerol concentration on the elongation at break of the pea starch films.

glycerol proportion (60% versus a maximum of 20% in this study).

Similar values were obtained for the average elongation of the films at the point of maximum tensile strength value (Table 3), which ranged from 4.75% in treatment 1 (3% starch) to 25.8% in treatment 8 (5% starch, 0.1% gum and 20% glycerol). The central point value was 4.99%. The same treatments showed maximum and minimum elongation values at the point of maximum resistance and break; however, there was a mathematical model to explain the behavior of the films in relation to the elongation at maximum tensile strength.

The results of this experiment were expected and are consistent with those obtained for parameters resistance and stress, since increasing the glycerol concentration, which acts as a plasticizer, reduces the proximity and direct interactions between starch chains and facilitates their mobility [28] *i.e.*, the resistance decreases and the elongation increases. In other words, the material becomes more ductile, *i.e.*, with greater capacity for deformation and lower tensile strength [25].

Liu [26] worked with extrusion in obtaining pea starch films added of 50% of glycerol and conditioned at 23°C and 50% RH and reported elongation values at rupture ranging from 16.1 to 26.3%. This maximum value was close to the 25.8% found for the film of treatment 8 (5% starch, 0.1% gum, and 20% glycerol) conditioned at 23°C and 75% RH. The results were similar probably because the glycerol

content used by those authors was higher than 20% and the conditioning in the present study was at lower RH.

Leyva et al. [25] reported elongation values at maximum tensile strength in wheat starch films ranging from 1.42 to 1.73% when added of 25% of glycerol. When the glycerol concentration increased to 40%, however, the values of this parameter increased to 24.6–38.9%. The authors of this paper classified films made with wheat starch as resistant, however, with little ductility. In the present study (pea cultivar Utrillo with 20% glycerol), the elongation at maximum tensile strength was greater than that of Leyva et al. [25] for films with 25% glycerol.

The effect of plasticizer in rice starch films was studied by Laohakunjit and Noomhorm [24], who found that the increase from 20 to 30% of glycerol caused a significant increase of elongation. According to them, a small increase in glycerol content in FS results in a significant decrease in the stress and an increase in elongation of films.

The literature and the data from this study indicate a relationship between the elasticity and the stress in films, and the increase of one of these parameters is always followed by a decrease of the other. This behavior was also evidenced in literature [24, 28, 4, 32, 33, 34] in films of rice, yam, yellow peas, chemically modified corn, cassava, and potato starches, respectively.

Generally, when the structure of the film becomes less rigid, the properties related to resistance/tensile characteristics are reduced and the elongation increases. A greater elongation indicates that the film is capable of withstanding a deformation before rupture. When this increased elongation is associated with strength, the material shows a greater ability to withstand tensile forces and compression. In the case of films, this may be associated with improved performance in packaging machines and during handling and transport.

Xantham gum did not change these properties in the present study. In tapioca starch film [35] produced by extrusion, however, this gum produced a reinforcing effect raising the ultimate tensile strength and elastic modulus and lowering the strain at break values.

The films of this experiment showed elongation values lower than those of synthetic films. According to ASTM D 4635 [36], the standard elongation of LDPE films ranges from 225 to 350% depending on the direction of the material. In practice, values above these can also be found.

**Table 3.** Maximum elongation values for tensile strength of the pea starch films

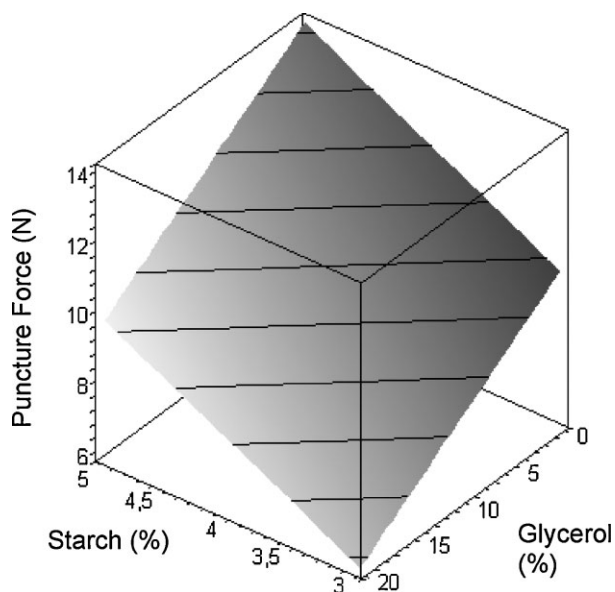
	T1	T2	T3	T4	T5	T6	T7	T8	T9
Maximum elongation values of tensile strength (%)	4.75	11.1	5.68	10.7	–	12.8	7.18	25.8	4.99

### 3.6 Puncture force

The puncture force ranged from 6.26 N for treatment 2 (3% starch and 20% glycerol) to 14.9 N for treatment 7 (5% starch and 0.1% gum xanthan), with central point treatment showing value of 11.58 N. Thus, high starch content in the absence of glycerol resulted in higher puncture force and higher glycerol contents associated with lower starch contents resulted in the opposite. This can be evidenced by the response surface plots (Fig. 4).

The increase of starch concentration associated with reduced glycerol content tends to result in an increased puncture force, as occurred with the maximum tensile strength and the strain at break. As already mentioned, this behavior should be correlated with the ease compaction of the film-forming network in the presence of low plasticizer levels.

Similar behavior was observed by Mali et al. [28] in yam starch films added of glycerol, where high starch concentrations combined with low glycerol concentrations or high thickness promoted the formation of films with high puncture force.



**Figure 4.** Effect of starch and glycerol concentration on the puncture force of the pea starch films.

**Table 4.** Puncture deformation of the pea starch films

	T1	T2	T3	T4	T5	T6	T7	T8	T9
Puncture deformation (mm)	1.66	3.37	1.74	2.80	–	3.45	1.89	2.92	1.58

Puncture forces like those obtained in this study are consistent with LDPE and HDPE synthetic films with thickness ranging from 35 to 60  $\mu\text{m}$ .

The average deformation of the films at the puncture time according to the treatments used is shown in Table 4.

The average deformation in the puncture ranged from 1.66 mm for treatment 1 (3% starch) to 3.45 mm for treatment 6 (5% starch and 20% glycerol). There was no adjustment of models to explain the behavior of this parameter in function of the composition of FS. A greater deformation of films with higher glycerol content was expected due to its plasticizing action, as that observed in the tensile properties.

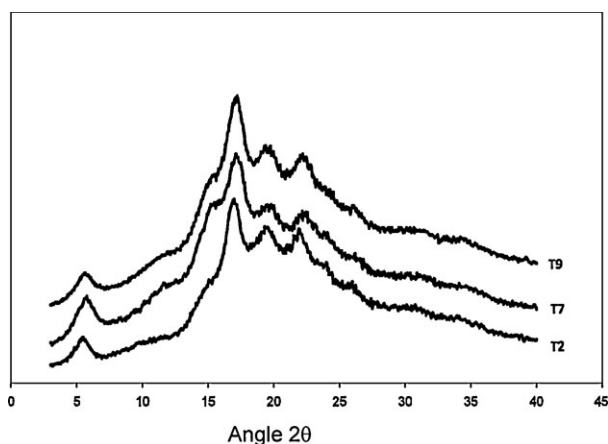
Both strength and deformation in the puncture were not affected by the gum concentration in the range employed.

Yam starch films added of glycerol and reported that only the glycerol concentration influenced in the film deformation during puncture. The authors also justified this fact by the plasticizer action of glycerol, which changes the starch network structure, making the films less dense and facilitating the mobility of polymer chains [28].

Both strength and deformation in the puncture were not affected by the gum concentration in the range employed.

### 3.7 Crystallinity

The XRD patterns of the films in the treatments T2 (3% starch and 20% glycerol), T7 (5% starch and 0.1% xanthan), and T9 (4% starch, 0.05% xanthan and 10% glycerol) are showed in Fig. 5.



**Figure 5.** XRD patterns of the pea starch films.

X-ray pattern of the film with more starch (5%) and 0.1% xanthan (T7) could be assigned to a B-type starch. The same pattern was found by Polesi [37] in pea native starch of the same cv. (Utrillo). The composition of the other two films (T2 and T9) did not change the presence of characteristics peaks showed by T7 film.

The relative crystallinity of the films was  $T7 = 25.7$  and  $T9 = 25.4$ , very close, and both were slightly higher than  $T2$  film = 23.0, that had less starch and more plasticizer. Plasticizer addition also decreased crystallinity of corn and amylo maize starch films as compared to films without plasticizer [38].

## 4 Conclusions

The formation of films with only 5% of starch in the FS was not possible, however, the addition of xanthan gum made it possible. In spite of this, the increased gum xanthan concentration in the solution did not interfere with physical and mechanical properties of the films.

The increased glycerol concentration decreased film crystallinity and affected the mechanical properties of films, reducing the maximum tensile strength, strain at break and puncture force and increasing the elongation and deformation. The glycerol acts as a plasticizer, reducing the direct interactions between polymer chains. Films prepared only with pea starch, cultivar Utrillo, at the concentrations studied (3 and 5%) were mechanically resistant when compared to other films, prepared with corn, cassava, rice, and even other pea cultivars (yellow, commercial). The tensile strength of these films is comparable to synthetic films prepared with high-density polyethylene and linear low density polyethylene. However, they are films of low elasticity when compared to other films, such as rice starch films, and especially when compared to polyethylene films.

The properties of films prepared with green pea cultivar Utrillo distinguished from those of other starch sources or pea starch from other varieties. The most prominent property was the high tensile strength. However, this feature is associated with low elasticity.

*The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support.*

*The authors have declared no conflict of interest.*

## 5 References

[1] Liu, Z., Han, J. H., Film-forming characteristics of starch. *J. Food Sci.* 2005, 70, 31–36.  
 [2] Mehvar, G. F., Han, J. H., Physical and mechanical properties of high-amylose rice and pea starch films as affected by

relative humidity and plasticizer. *J. Food Sci.* 2004, 69, 449–454.  
 [3] Zhang, Y., Han, J. H., Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *J. Food Sci.* 2006, 71, 109–118.  
 [4] Zhang, Y., Han, J. H., Plasticization of pea starch films with monosaccharides and polyols. *J. Food Sci.* 2006, 71, 253–261.  
 [5] Han, J. H., Seo, G. H., Park, I. M., Kim, G. M., Lee, D. S., Physical and mechanical properties of pea starch edible films containing Beeswax emulsions. *J. Food Sci.* 2006, 71, 290–296.  
 [6] Ratnayake, W. S., Hoover, R., Warkentin, T., Pea starch: Composition, structure and properties - a review. *Starch/Stärke* 2002, 54, 217–234.  
 [7] Matta, M. D., Junior Sarmiento, S. B. S., Sarantópoulos, C. G. L., Zocchi, S. S., Propriedades de barreira e solubilidade de filmes de amido de ervilha associado com goma xantana e glicerol. *Polímeros* 2011, 21(1), 1–6.  
 [8] Liu, Z., Eskin, N. A. M., Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatin. *Food Hydrocolloids* 1998, 12, 37–41.  
 [9] Rojas, J. A., Rosell, C. M., Barber, C. B., Pasting properties of different wheat flour-hydrocolloid systems. *Food Hydrocolloids* 1999, 13, 27–33.  
 [10] Chaisawang, M., Suphantharika, M., Pasting and rheological properties of native and anionic tapioca starches as modified by guar gum and xanthan gum. *Food Hydrocolloids* 2006, 20, 641–649.  
 [11] Lee, M. H., Baek, M. H., Cha, D. S., Park, H. J., Lin, S. T., Freeze-thaw stabilization of sweet potato starch gel by polysaccharide gums. *Food Hydrocolloids* 2002, 16, 345–352.  
 [12] Santos, P. V., Suzuki, M. P., Cereda, M. P., Scamparini, A. R. P., Microstructure and color of starch-gum films: Effects of gum deacetylation and additives. Part 2. *Food Hydrocolloids* 2005, 19, 1064–1073.  
 [13] Lafargue, D., Lourdin, D., Doublier, J. L., Film-forming properties of a modified starch/ $\kappa$ -carrageenan mixture in relation to its rheological behaviour. *Carbohydr. Polym.* 2007, 70, 101–111.  
 [14] Chen, Y., Cao, X., Chang, P. R., Huneault, M. A., A Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. *Carbohydr. Polym.* 2008, 73, 8–17.  
 [15] International Organization for Standardization. Norme internationale: Riz-détermination de la teneur en amylose 1987, ISO 6647  
 [16] ASTM International. D 882-02: standard test method for tensile properties of thin plastic sheeting. Philadelphia 2002.  
 [17] ASTM International. F 1306-90 (Reapproved 2008): standard test method for slow rate penetration resistance of flexible barrier films and laminates. Philadelphia 1990.  
 [18] Nara, S., Komiya, T., Studies on the relationship between water saturated state and crystallinity by the diffraction method for moistened potato starch. *Starch/Stärke* 1983, 35, 407–410.  
 [19] *Statistical Analysis System*, Procedures guide: version 6, 3rd edn., SAS Institute, Cary, NC 1990.  
 [20] Maplesoft. Maple 9.5 getting started guide. Maple soft, Waterloo, Ontario, Canada 2004.



- [21] Themeier, H., Hollmann, J., Neese, U., Lindhauer, M. G., Structural and morphological factors influencing the quantification of resistant starch II in starches of different botanical origin. *Carbohydr. Polym.* 2005, 61, 72–79.
- [22] Wang, L., Liu, L. I., Holmes, J., Kerry, J. F., Kerry, J. P., Assessment of film-forming potential and properties of protein and polysaccharide-based biopolymer films. *Int. J. Food Sci. Technol.* 2007, 42, 1128–1138.
- [23] Phan The, D., Debeaufort, F., Voilley, A., Luu, D., Biopolymer interactions affect the functional properties of film based on gar, cassava starch and arabinoxylan blends. *J. Food Eng.* 2009, 90, 548–558.
- [24] Laohakunjit, N., Noomhorm, A., Effect of plasticizers on mechanical and barrier properties of rice starch film. *Starch/Stärke* 2004, 56, 348–56.
- [25] Leyva, M. B., Chávez, P. T., Wong, B. R., Jatomea, M. P., Bojórquez, F. B., Physical and mechanical properties of durum wheat (*Triticum durum*) starch films prepared with a- and b- type granules. *Starch/Stärke* 2008, 60, 559–567.
- [26] Liu, L., Kerry, J. F., Kerry, J. P., Selection of optimum extrusion technology parameters in the manufacture of edible/biodegradable packaging films derived from food-based polymers. *J. Food, Agric. Environ.* 2005, 3, 51–58.
- [27] Mali, S., Grossman, M. V. E., Effects of yam starch films on storability and quality of fresh strawberries. *J. Agric. Food Chem.* 2003, 24, 7055–7011.
- [28] Mali, S., Grossman, M. V. E., Garcia, M. A., Mertino, M. N., Zaritzky, N. E., Mechanical and thermal properties of yam starch film. *Food Hydrocolloids* 2005, 19, 157–164.
- [29] Li, Y., Shoemaker, C. F., Ma, J., Shen, X., Zhong, F., Paste viscosity of rice starches of different amylose content and carboxymethylcellulose formed by dry heating and the physical properties of their films. *Food Chem.* 2008, 109, 616–623.
- [30] Mandala, I. G., Palogou, E. D., Kostaropoulos, A. E., Influence of preparation and storage conditions on texture of xanthan-starch mixtures. *J. Food Eng.* 2002, 53, 27–28.
- [31] Pengilly, B. W., Hill, J. W., *Modern Plastic Encyclopedia*, McGraw-Hill, New York 1990.
- [32] López, O. V., Garcia, M. A., Zaritzky, N. E., Film forming capacity of chemically modified corn starches. *Carbohydr. Polym.* 2008, 73, 573–581.
- [33] Bergo, P. V. A., Carvalho, R. A., Sobral P. J. A., Santos, R. M. C., et al. Physical properties of edible films based on cassava starch as affected by the plasticizer concentration. *Packag. Technol. Sci.* 2002, 21, 85–89.
- [34] Talja, R. A., Helén, H., Ross, Y. H., Jouppila, K., Effect of type and content of binary polyol mixtures on physical and mechanical properties of starch-based edible films. *Carbohydr. Polym.* 2008, 71, 269–276.
- [35] Flores, S. K., Costa, D., Yamashita, f., Gerschenson, L. N., Grossmann, M. V. E., Mixture design for evaluation of potassium sorbate and xanthan gum effect on properties of tapioca starch films obtained by extrusion. *Mater. Sci. Eng.* 2010, 30, 196–202.
- [36] ASTM D 4635-08 Standard specification for polyethylene films made from low density polyethylene for general use and packaging applications.
- [37] Polesi, L. F., Amido resistente obtido a partir de amido de leguminosas e de seus hidrolisados. 2009, Master dissertation. Piracicaba, Universidade de São Paulo.
- [38] Garcia, M. A., Martino, M. N., Zaritzky, N. E., Plata, L., Microstructural characterization of plasticized starch-based films. *Starch/Stärke* 2000, 52, 118–124.