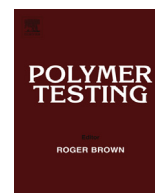


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Material properties

Effect of cooling and coating on thermoplastic starch/poly(lactic acid) blend sheets

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ABSTRACT

The influence of the processing conditions (cooling rate) and coating on the physicochemical properties of thermoplastic starch/poly(lactic acid) blend sheets was studied. Two cooling rates were used: fast and slow, and in the latter case the sheets were both non-coated and coated with cross-linked chitosan. The physicochemical properties investigated were crystallinity, morphology, water affinity (moisture sorption isotherm, water vapor permeability, water solubility and contact angle) and mechanical properties. In general, the sheets cooled at the slow rate were more crystalline, less permeable and less soluble in water than those cooled at the fast rate. They also produced a more homogeneous morphology. The coated sheets were less soluble in water and mechanically stronger than uncoated sheets cooled at the slow rate. The concentration of plasticizer in the TPS affected only the sorption isotherm and contact angle since a higher plasticizer content caused a greater affinity for water.

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1. Introduction

Research has been focused on biodegradable and natural polymers in order to replace synthetic polymeric materials. Thermoplastic starch (TPS) is a low cost material of high availability, which can be processed using equipment for conventional plastics. However, its mechanical properties are dependent on the relative humidity, limiting its application as food packaging.

To decrease the affinity between TPS and water, starch modification and the formation of composites and blends have been studied. Several blends of TPS/biodegradable polymers, such as polycaprolactone [1], polyhydroxybutyrate [2], poly(butylene adipate-co-terephthalate) [3] and poly(lactic acid) [4], are notable for their ability to maintain the biodegradability of the final product.

Poly(lactic acid) (PLA) is a commercial polymer with biodegradable and hydrophobic characteristics, and it presents equivalent properties as those of conventional materials. However, its application is limited by its high cost. In this regard, the use of TPS/PLA blends is one option to improve the cost-benefit and obtain a material with better performance.

Besides the raw materials used to obtain the blends, the processing parameters can influence the final properties of the material obtained [5]. For example, the cooling rate during the specimen molding can alter the degree of crystallinity, which in turn can affect the physical, mechanical and barrier properties [6]. Sarasua et al. [7] studied sheets of PLLA/PDLA blends with different component compositions and varied the cooling rates in order to evaluate the relationship between the crystallinity and the mechanical properties. They found that the crystallinity ranged from 7 to 50%, according to the composition. The sheets that were cooled at lower rates achieved higher crystallinity values (40–50%). On the other hand, the sheets cooled in water, had

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7% crystallinity. In general, with a higher degree of crystallinity there was an increase in the Young's modulus and a decrease in the elongation-at-break.

Another way to control the blend properties is by applying a coating of another biodegradable polymer on the sheet surface. Hoagland and Parris [8] produced chitosan laminates coated with pectin, which had higher storage and loss moduli than uncoated laminates. Bangyekan, Aht-Ong and Srikulkit [9] coated starch films with chitosan. The mechanical properties of the films were modified on increasing the chitosan concentration of the coating, and the water uptake decreased due to the hydrophobic characteristic of the chitosan.

In this study, different approaches to improving the properties of TPS/PLA blend sheets were evaluated. The molded sheets were cooled from 150 °C at room temperature applying slow and fast cooling rates and then coated with a biodegradable cross-linked polymer prior to evaluating the physicochemical properties.

2. Materials and methods

2.1. Materials

Native cassava starch (amylose 20.8 ± 0.6 wt%) was supplied by Indemil (Brazil), poly(lactic acid) by Cargill (Natureworks LLC, USA) and chitosan (medium molecular weight, 75–85% deacetylated) by Sigma–Aldrich (USA). Glycerol and glutaraldehyde were supplied by Dinâmica (Brazil) and Nuclear (Brazil), respectively. All chemicals were used without further purification.

2.2. PLA/TPS blends

Previously prepared thermoplastic starch pellets with 0.25 g or 0.30 g of glycerol per gram of starch were extruded with PLA at a constant TPS/PLA ratio of 70/30 (w/w), denoted by B25 and B30 (the numbers 25 and 30 relating to the glycerol content of the thermoplastic starch).

The blends were extruded in a single-screw extruder (BGM, model EL-25, Brazil) with a screw diameter of 25 mm and L/D of 30, at 150 °C (in all three zones) and a screw speed of 35 rpm. These extrusion parameters were the same as those applied in a previous study by Soares et al. [10].

2.3. Sheet molding

The blend pellets were thermopressed in a hydraulic press (Schulz, model PHS, Brazil) at 150 °C and 2.6 MPa, and the specimens were cooled at room temperature applying two procedures: the molded sheet was (i) kept in and (ii) removed from the heating system. The cooling procedure (i) took 3 h and procedure (ii) took only 20 min, and these are referred to herein as slow and fast cooling, respectively.

The temperature decrease as a function of time for each cooling procedure is illustrated in Fig. 1. In order to represent the sheet cooling process, the temperature was adimensionalized and the experimental data were fitted according to Equation 1.

$$\frac{T_{(t)} - T_{\infty}}{T_0 - T_{\infty}} = J e^{-kt} \quad (1)$$

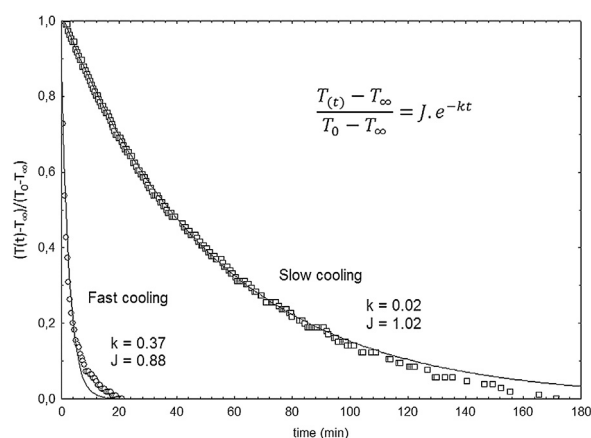


Fig. 1. Temperature decrease as a function of time for fast and slow cooling process.

where $T_{(t)}$ is the center temperature of the sheet at time t ; T_{∞} is the final temperature; T_0 is the initial center temperature of the sheet, t is time and J and k are model parameters.

The fitting of the model to the experimental data was carried out using non-linear regression and Statistica 8.0 software (Statsoft, USA).

2.4. Coating

The procedure to coat the sheets involved a spray method, as described in a previous report by Soares et al. [10]. The two sides of the TPS/PLA sheets were coated with chitosan solution (0.1% of chitosan dissolved in aqueous acetic acid solution of 0.1% v/v) and subsequently with an aqueous glutaraldehyde solution of 0.5% v/v, in order to cross-link the chitosan.

2.5. Characterization of the sheets

2.5.1. X-ray diffraction

X-ray patterns of the specimens were obtained on a Philips X'Pert diffractometer (Netherlands), with Cu ($K\alpha$) radiation ($\lambda = 1.5418$ Å), operating at room temperature, 30 mA and 40 kV. The scanned region ranged from $2\theta = 2$ – 60° , and the pitch was $0.05^\circ \text{ s}^{-1}$. The relative crystallinity index was evaluated from the relative areas of the crystalline and amorphous regions.

2.5.2. Morphological analysis

The specimens were fractured under liquid nitrogen. The fractured samples were subjected to different treatments: one part was placed in a desiccator while another part was placed in a test tube and sufficient chloroform was added to cover the specimen which was then left to stand for 24 h. The specimens were coated with gold and analyzed using a scanning electron microscope (Philips XL-30).

2.5.3. Moisture sorption isotherms

The moisture sorption isotherms were determined through the static method, using saturated saline solutions

to obtain different relative humidity conditions [11]. The Guggenheim-Anderson-de Boer (GAB) model was used to represent the experimental equilibrium data, and the model parameters were determined by non-linear regression using Statistica Software 8.0 (Statsoft, USA).

The GAB isotherm model is expressed as Equation 2.

$$X_W = \frac{m_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (2)$$

where X_W is the equilibrium moisture content on a dry basis (g water/g dry mass); m_0 is the monolayer moisture content; C is the Guggenheim constant; K is the factor correcting property of the multilayer molecules corresponding to the bulk liquid and a_w is the water activity.

2.5.4. Contact angle measurement

The contact angle was measured using a contact angle meter (Data Physics OCA-15, Germany) and the analysis of the images, captured using a high-resolution camera, was performed with Image Tool software. Sheet samples (40 mm × 20 mm) were fixed in a glass plate and placed at the base of the unit, and a drop of distilled water (5 μ L) was placed on the sheet surface using a syringe. The measurements were performed at room temperature, and the contact angle was calculated as the average of five measurements after the drop stabilized.

2.5.5. Water vapor permeability

The water vapor permeability was determined in appropriate cells using a relative humidity gradient of 2% (silica) to 75% (NaCl saturated solution) at 25 °C (ASTM E96-00). All tests were conducted in triplicate.

2.5.6. Water solubility

The solubility of the sheets in water was defined as the dry matter content that was solubilized after 24 h of immersion in water at 25 °C. Measurements were carried out on three replicates using the methodology described by Irissin-Mangata et al. [12] with some modifications.

2.5.7. Mechanical properties

The mechanical properties were determined using an EMIC DL 2000 analyzer (Brazil), according to the methodology established by ASTM D882-02. The maximum tensile strength, elongation-at-break and elastic modulus were calculated from the stress-strain curves considering the results of at least ten tests for each sample.

2.5.8. Statistical analysis

Analysis of variance (ANOVA) and the Tukey test for comparison of means were applied in the experimental data analysis. The significance level considered was $p \leq 0.05$. Statistica Software (Statsoft, USA) version 8.0 was used for all statistical analysis.

3. Results and discussion

3.1. X-ray diffraction (Crystallinity)

The sheets with a lower percentage of glycerol had a crystallinity index (CI) of 39% and 32% after slow and fast

cooling, respectively. For a higher percentage of plasticizer, the corresponding values were 40% and 31%. These values suggest that the glycerol composition had no effect on the degree of crystallinity. However, as expected, the cooling procedure did influence the crystallinity since the slow cooling rate favored a conformational reorganization of the macromolecules to achieve a crystalline state.

Sarasua et al. [7] observed similar behavior for PLA sheets. The authors used three different methods to cool the sheets after compression molding: water quenching, air annealing or annealing in the mold. In the case of water quenching the crystallinity was 7% while with the annealing in the mold it was possible to achieve 40–50% of crystallinity.

Fig. 2 shows the X-ray diffractograms associated with the different experimental conditions used to obtain the sheets, with a well-defined and intense peak at 17° corresponding to PLA. In the pattern of slowly cooled sheets, less intense peaks can be observed close to the intense peak, which are associated with starch which has peaks at 18°, 19° and 22° [13]. According to van Soest et al. [13], after processing, the thermoplastic starch can present residual and/or processing-induced crystallinity. The residual crystallinity occurs when the processing is not sufficient to destroy the starch granule structure. In this study, microscopy images showed that none of the structures were granular, suggesting no residual crystallinity in the sheets evaluated. The processing-induced crystallinity can be of the type V_H , V_A or E_H , depending on the hydration of the amylose unit cell. The type may also be associated with bulky complexing agents (isopropanol, lipids, free fatty acids, etc.). The peaks at 19° and 22° refer to the V_H type (materials containing more than 10% of water). The peak at 18° is associated with the intermediate form between V_H crystallinity (hydrated lattice) and V_A crystallinity (anhydrous lattice) according to Zobel, French and Hinkle [14].

3.2. Morphological analysis

Fig. 3 shows the micrographs of the transversal fracture of the sheets with a lower plasticizer content. Only the sheets cooled at the fast rate (Fig. 3(b)) showed some voids, probably because water and/or air were entrapped in the sheet matrix during the molding due to the fast cooling.

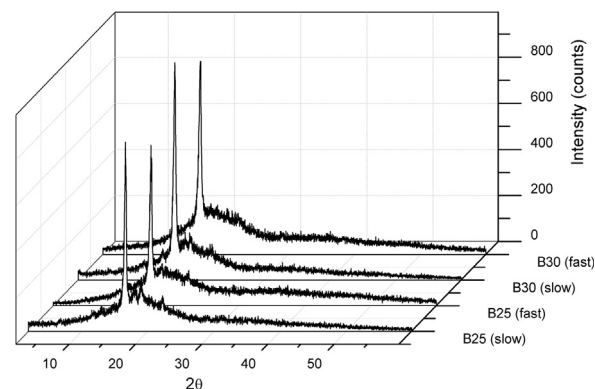


Fig. 2. X-ray diffractogram of B25 and B30 blends for fast and slow cooling process.

Fig. 3(c) and (d) show the morphology of sheet fracture after immersion in chloroform, which is a PLA solvent. The sheet cooled at the slow rate, Fig. 3(c), presented smaller PLA domains and a better distribution of these domains when compared with the sheet cooled at the fast rate, Fig. 3(d).

Müller, Pires and Yamashita [4] evaluated the morphology of TPS/PLA blends, using etching with chloroform to highlight the PLA regions. Gaps appeared in areas which were occupied by the PLA phase. The characteristics of the interface between the domains of the blend may be related to the interfacial tension between the hydrophilic surface of the matrix and the hydrophobic surface of the PLA.

3.3. Moisture sorption isotherms

Fig. 4 shows the moisture sorption isotherms of uncoated sheets, cooled at the fast and slow rates. In both processes, the isotherms exhibited a sigmoidal shape, which may be associated with hygroscopic materials and was observed in starch-based materials [11].

The cooling process did not affect the sorbed water content of the sheet, but the plasticizer concentration influenced the equilibrium moisture values. The sheets with higher glycerol concentration sorbed more water than the other sheets due to the hydrophilic characteristic of the plasticizer [15].

The GAB model was chosen because it is the model most commonly used to study processes of water sorption in biodegradable films. In addition, the model showed a good fit for all materials ($r^2 > 0.99$). The calculated GAB parameters are displayed in Table 1.

Regarding the parameter m_0 , the cooling rate had no significant influence. However, the materials with higher

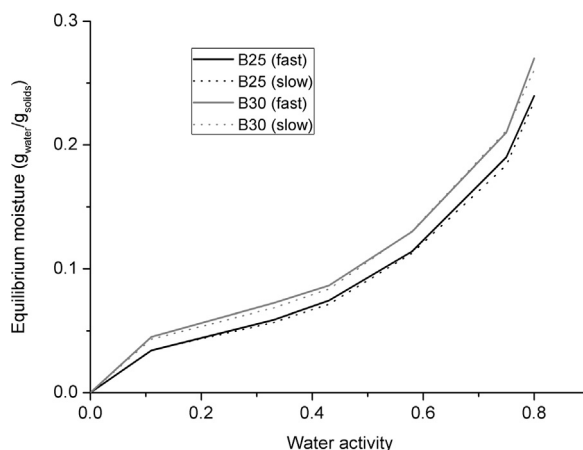


Fig. 4. Sorption isotherms of B25 and B30 blends obtained by fast and slow cooling processes.

concentrations of glycerol showed higher values of m_0 , indicating that a higher amount of glycerol increased the hydrophilicity of the sheets [16]. These values are similar to those obtained in other studies on starch films [15].

3.4. Contact angle measurement

The sheets with higher glycerol concentration presented lower contact angles when compared to samples with lower glycerol concentration (Table 2). This behavior may be associated with the more hydrophilic character of blends with higher plasticizer concentration.

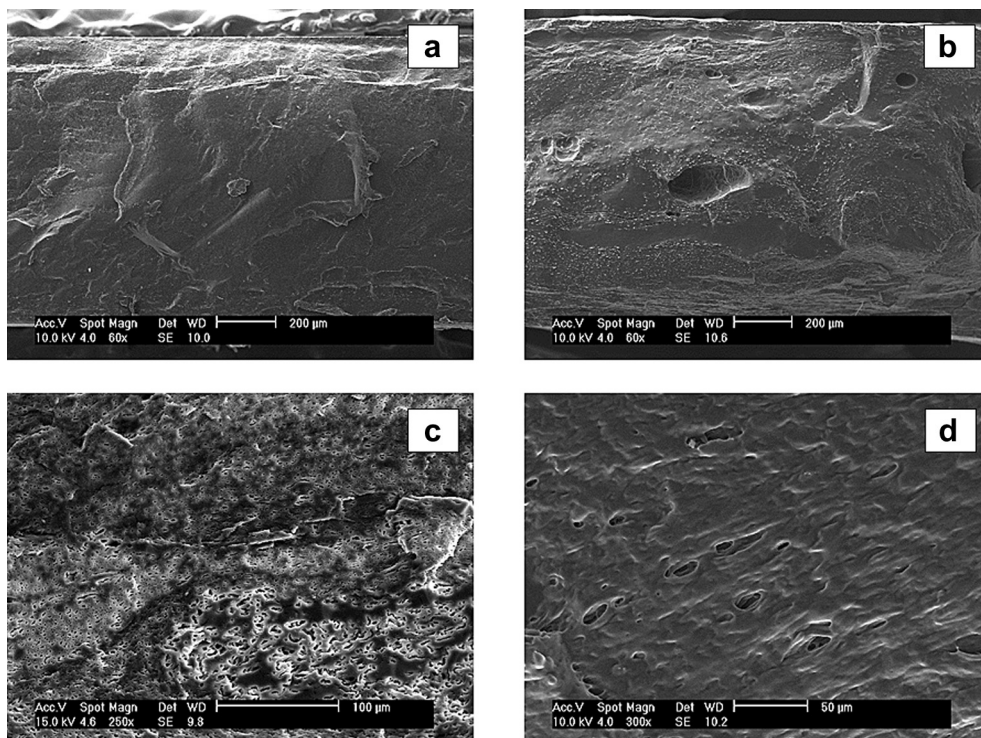


Fig. 3. Fracture micrographs of B25 cooled at (a) slow and (b) fast rates and previously immersed in chloroform cooled at (c) slow and (d) fast rates.

Table 1

GAB model parameters of B25 and B30 blends for fast and slow cooling processes.

Sample	Cooling	k	C	m_0	r^2
B25	Fast	1.00 ± 0.01^a	11.71 ± 4.23^a	$0.049 \pm 0.003^{a,b}$	0.99
	Slow	1.00 ± 0.00^a	12.79 ± 3.20^a	0.047 ± 0.001^a	0.99
B30	Fast	1.00 ± 0.01^a	22.80 ± 4.27^b	$0.054 \pm 0.002^{b,c}$	0.99
	Slow	0.99 ± 0.02^a	$15.02 \pm 1.99^{a,b}$	0.056 ± 0.003^c	0.99

Note: In the same column, different lower case letters designate significant difference ($p \leq 0.05$) between the means, according to the Tukey test.

There was no significant difference between coated and uncoated sheets with the same glycerol concentration. It is possibly that the surface roughness (observed in microscopy images in a previous study [10]) of coated sheets influences the interfacial interaction between the water and the sheets and consequently the contact angles. The heterogeneity of the surface (for instance, surface roughness) causes the distortion of the contact line between the solid-liquid interfaces.

3.5. Water vapor permeability and water solubility

After verifying the effect of the cooling and coating of the sheets on the water vapor permeability (WVP), it was observed that there was no significant difference between the sheets with different plasticizer content (Table 3).

The slow cooling significantly reduced the WVP when compared with the fast cooling, for both glycerol contents. However, the coating did not significantly improve the water barrier of the sheets cooled at a slow rate.

The fast cooling process produced less crystalline sheets with some voids, which enhances the permeability of the samples according to Sarantópoulos et al. [17], who reported that the permeability preferably occurs in non-crystalline regions. According to Tsuji et al. [18], the WVP of PLA films decreased 43% when the crystallinity index increased from 0 to 20%.

The plasticizer content did not influence the water solubility of the sheets, as can be seen from the data shown in Table 3. However, when the cooling rate was increased, the solubility of the sheets cooled at a slow rate was lower due to a higher degree of crystallinity.

The coating decreased the solubility of the sheets by approximately 48%. The cross-linking of the chitosan formed a physical barrier which is more hydrophobic than the blend (TPS/PLA), thereby hindering the passage of water and thus reducing the solubility.

Ryu et al. [19] observed similar behavior for starch films coated with zein because, as zein is more hydrophobic than

Table 2

Contact angle measurements of coated and uncoated B25 and B30 blends.

Sample	Cooling	Coating	Contact angle
B25	Fast	–	$56 \pm 8^{a,b}$
	Slow	–	63 ± 8^b
	Slow	Yes	72 ± 7^b
B30	Fast	–	41 ± 9^a
	Slow	–	42 ± 2^a
	Slow	Yes	47 ± 5^a

Note: In the same column, different lower case letters designate significant difference ($p \leq 0.05$) between the means, according to the Tukey test.

Table 3

Water solubility and water vapor permeability of TPS/PLA sheets obtained under different cooling and coating conditions.

Sample	Cooling	Coating	Permeability	Solubility
B25	Fast*	–	1.82 ± 0.18^b	$33.65 \pm 1.26^{b,c}$
	Slow	–	0.90 ± 0.16^a	$32.80 \pm 1.83^{b,c}$
B30	Slow	Yes	0.73 ± 0.02^a	16.99 ± 0.79^a
	Fast*	–	1.81 ± 0.13^b	35.24 ± 0.71^c
B30	Slow	–	0.94 ± 0.32^a	32.00 ± 0.16^b
	Slow	Yes	0.90 ± 0.09^a	16.89 ± 0.71^a

Note: Water solubility in % and water vapor permeability in 10^6 ($\text{m.g.h}^{-1}.\text{Pa}^{-1}.\text{m}^{-2}$).

In the same column, different lower case letters designate significant difference ($p \leq 0.05$) between the means, according to the Tukey test.

*Values obtained by Soares et al. [10].

starch, the coating hindered the solubilization of the starch in water.

3.6. Mechanical properties

The plasticizer concentration and cooling rate had practically no effect on the mechanical properties of the uncoated sheets (Table 4). However, the coating significantly changed these properties, since the coated sheets were stronger and more rigid than the uncoated ones, and the elongation-at-break decreased. This modification was more notable for the coated sheets with higher plasticizer concentration (B30); their tensile strength increased by 350% and there was an approximately 12-fold increase in the elastic modulus compared to sheets cooled at a fast rate. This behavior may be associated with the cross-linking of the coating layer, because the macromolecules of chitosan bonded covalently, increasing the strength and decreasing the flexibility [20]. A further noteworthy fact is the compatibility of the chitosan coating with the TPS/PLA sheet surface despite the differences in these materials in terms of their hydrophobicity/hydrophilicity.

4. Conclusions

The cooling rate affects the crystallinity and the morphology of TPS/PLA sheets and, to obtain materials with greater crystallinity and homogeneity, and consequently less permeability and solubility, it is necessary to use slower cooling rates.

The cross-linked chitosan coating reduces the solubility and mechanically reinforces the TPS/PLA sheets due to its hydrophobic characteristic and excellent compatibility with the material surface.

Table 4

Tensile strength (σ), elongation-at-break (ϵ) and elastic modulus (E) of TPS/PLA sheets obtained under different cooling and coating conditions.

Sample	Cooling	Coating	σ (MPa)	ϵ (%)	E (MPa)
B25	Fast*	–	$1.7 \pm 0.1^{a,b}$	19.2 ± 2.2^d	60 ± 9^a
	Slow	–	2.7 ± 0.4^b	9.8 ± 1.6^b	131 ± 20^a
	Slow	Yes	6.0 ± 1.5^d	1.9 ± 0.4^a	382 ± 126^b
B30	Fast*	–	1.0 ± 0.1^a	$17.2 \pm 6.1^{c,d}$	32 ± 7^a
	Slow	–	$1.5 \pm 0.3^{a,b}$	$14.1 \pm 4.2^{b,c}$	50 ± 18^a
	Slow	Yes	4.5 ± 0.9^c	2.1 ± 0.5^a	380 ± 82^b

Note: In the same column, different lower case letters designate significant difference ($p \leq 0.05$) between the means, according to the Tukey test.

*Values for sheets cooled at slow rate obtained by Soares et al. [10].

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References

- [1] H.-T. Liao, C.-S. Wu, Preparation and characterization of ternary blends composed of polylactide, poly(ϵ -caprolactone) and starch, *Materials Science and Engineering A* 515 (1–2) (2009) 207.
- [2] K.C. Reis, J. Pereira, A.C. Smith, C.W.P. Carvalho, N. Wellner, I. Yakimets, Characterization of polyhydroxybutyrate-hydroxyvalerate (PHB-HV)/maize starch blend films, *Journal of Food Engineering* 89 (4) (2008) 361.
- [3] A.P. Bilck, M.V.E. Grossmann, F. Yamashita, Biodegradable mulch films for strawberry production, *Polymer Testing* 29 (4) (2010) 471.
- [4] C.M.O. Müller, A.T.N. Pires, F. Yamashita, Characterization of thermoplastic starch/poly(lactic acid) blends obtained by extrusion and thermopressing, *Journal of Brazilian Chemical Society* 23 (3) (2012) 426.
- [5] D. Henrist, J.P. Remon, Influence of the process parameters on the characteristics of starch based hot stage extrudates, *International Journal of Pharmaceutics* 189 (1) (1999) 7.
- [6] L.-T. Lim, R. Auras, M. Rubino, Processing technologies for poly(lactic acid), *Progress in Polymer Science* 33 (8) (2008) 820.
- [7] J.R. Sarasua, A.L. Arraiza, P. Balerdi, I. Maiza, Crystallinity and mechanical properties of optically pure polylactides and their blends, *Polymer Engineering and Science* 45 (5) (2005) 745.
- [8] P.D. Hoagland, N. Parris, Chitosan/pectin laminated films, *Journal of Agricultural and Food Chemistry* 44 (7) (1996) 1915.
- [9] C. Bangyekan, D. Aht-Ong, K. Srikulkit, Preparation and properties evaluation of chitosan-coated cassava starch films, *Carbohydrate Polymers* 63 (1) (2006) 61.
- [10] F.C. Soares, F. Yamashita, C.M.O. Müller, A.T.N. Pires, Thermoplastic starch/poly(lactic acid) sheets coated with cross-linked chitosan, *Polymer Testing* 32 (1) (2013) 94.
- [11] T.D. Labuza, L.N. Bell, *Moisture Sorption: Practical Aspects of Isotherm Measurement and Use*, second ed., American Association of Cereal Chemists, 2000.
- [12] J. Irissin-Mangata, G. Bauduin, B. Boutevin, N. Gontard, New plasticizers for wheat gluten films, *European Polymer Journal* 37 (8) (2001) 1533.
- [13] J.J. van Soest, S.H.D. Hulleman, D. Wit, J.F.G. Vliegthart, Crystallinity in starch bioplastics, *Industrial Crops and Products* 5 (1) (1996) 11.
- [14] H.F. Zobel, A.D. French, M.E. Hinkle, X-Ray diffraction of oriented amylose fibers. II. Structure of V amyloses, *Biopolymers* 5 (9) (1967) 837.
- [15] S. Mali, L.S. Sakanaka, F. Yamashita, M.V.E. Grossmann, Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect, *Carbohydrate Polymers* 60 (3) (2005) 283.
- [16] C.M.O. Müller, F. Yamashita, J.B. Laurindo, Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach, *Carbohydrate Polymers* 72 (1) (2008) 82.
- [17] C.I.G.L. Sarantópoulos, L.M. de Oliveira, M. Padula, L. Coltro, R.M.V. Alves, E.E.C. Garcia, *Embalagens plásticas flexíveis: Principais polímeros e avaliação de propriedades*, CETEA/ITAL, 2002.
- [18] H. Tsuji, R. Okino, H. Daimon, K. Fujie, Water vapor permeability of poly(lactide)s: effects of molecular characteristics and crystallinity, *Journal of Applied Polymer Science* 99 (5) (2006) 2245.
- [19] S.Y. Ryu, J.W. Rhim, H.J. Roh, S.S. Kim, Preparation and physical properties of zein-coated high-amylose corn starch film, *LWT – Food Science and Technology* 35 (8) (2002) 680.
- [20] M.M. Beppu, E.J. Arruda, C.C. Santana, Síntese e caracterização de estruturas densas e porosas de quitosana, *Polímeros: Ciência e Tecnologia* 9 (4) (1999) 163.