

# Using glycerol produced from biodiesel as a plasticiser in extruded biodegradable films

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## Abstract

The demand for renewably sourced biodegradable materials has increased the need to produce materials that combine appropriate functional properties at competitive costs. Thermoplastic starch and polyester blends are an interesting alternative to current materials due to the low cost of starch and the functional properties and processability of the resulting blends. Producing thermoplastic starch (TPS) requires using a plasticiser at concentrations between 20 and 30%wt (in relation to starch). Glycerol is the most common plasticiser due to its high plasticising capacity and thermal stability at processing temperatures. The objective of this study was to evaluate glycerol waste from the biodiesel industry, with different degrees of purification, as plasticisers for TPS / poly (butylene adipate-*co*-terephthalate) (PBAT) blends. Different purities of glycerol produced films with similar mechanical, optical and barrier properties to those made with purified glycerol (99.7%). Therefore, crude glycerol is a renewable alternative plasticiser that reduces the cost of plasticisation by 6-fold.

**Keywords:** *cassava starch, poly (butylene adipate-*co*-terephthalate), biopolymers, extrusion, biodegradable packaging.*

## 1. Introduction

The search for renewable energy sources that will ensure sustainable development has resulted in using biodiesel as an alternative fuel in the Brazilian energy matrix. Glycerol is the main by-product of biodiesel production and corresponds to approximately 10% of the total biodiesel production<sup>[1]</sup>. Brazil produced 1.2 billion litres of biodiesel in 2008 to supplement plain diesel at a 2% ratio, as required by law, resulting in the production of over 100 million litres of glycerol<sup>[2]</sup>. The crude glycerol obtained by the transesterification of triglycerides with alcohol has a low aggregate value due to the presence of impurities, such as water, methanol residues, sodium hydroxide, free fatty acids, fatty acid salts, esters, sulphur compounds, proteins and minerals<sup>[3]</sup>.

The estimated glycerol production for 2013 is 488 million litres, and there are no current prospects to convert it into products with a greater aggregate value. The price of glycerol is related to its degree of refinement, ranging from US\$167/ton for crude glycerol to US\$267/ton for technical grade glycerine and US\$1000/ton for bi-distilled glycerol. The industrial use of glycerol is essential for the economic sustainability of the biodiesel industry in Brazil.

Glycerol is used as a plasticiser to produce starch-based biodegradable films. Starch and glycerol melt and flow at temperatures between 90 °C and 180 °C and under shear stress, producing thermoplastic starch that, allowing their use injection, extrusion and blowing equipment. Plasticisers create greater flexibility in the polymer structure by reducing the intermolecular forces and the glass transition temperature of the material, which increases the mobility of the polymer chains in the starch films. The required

proportion of starch and glycerol depends on the type of starch used. According to the literature<sup>[4-8]</sup> approximately 20-25 kg of glycerol are necessary to produce 100 kg of thermoplastic starch. The interactions between glycerol, starch and PBAT are mostly related to hydrogen bonds and the role of glycerol as plasticiser was already fully discussed by other researchers<sup>[6,9]</sup>.

Thermoplastic starch materials have some drawbacks, such as poor water resistance and comparatively poor mechanical properties. However, these materials can be blended with synthetic co-polyester biodegradable polymers to help improve these shortcomings. Several researches were developed using thermoplastic starch and poly (butylene adipate-*co*-terephthalate) (PBAT) to produce biodegradable blends<sup>[10-12]</sup>. According several authors<sup>[13,14]</sup> is possible to obtain starch/PBAT films with good mechanical and barrier properties using around 40%wt of PBAT in the formulation.

The objective of this work was to test three grades of glycerol from biodiesel production to develop biodegradable films based in cassava starch/PBAT, obtained by blow extrusion.

## 2. Materials and Methods

### 2.1 Materials

Three different grades of glycerol were obtained as by-products from biodiesel production (Meridional TCS Ind. e Com. de Oleos S.A, Brazil): crude glycerol (CG), technical grade glycerine (TGG) and bi-distilled glycerine

(BDG) (Table 1 and Figure 1) and were used as starch plasticisers. The biodegradable polymers tested were native cassava starch (Indemil, Brazil) and poly (butylene adipate-*co*-terephthalate) (PBAT) from Basf (Germany), traded as Ecoflex® 7011.

## 2.2 Film production

The film was produced by blow extrusion using a pilot extruder (BGM EL-25 (São Paulo, Brazil)), which is made up of a 25 mm diameter screw, a 10-HP motor drive, four heating zones and an external cooling air ring with a 300- to 350-mm diameter.

The film was manufactured using a formulation based in our previous results<sup>[13-15]</sup> by mixing 40.0%wt PBAT, 46.6%wt cassava starch and 13.4%wt glycerol of three different types (Table 1). This mixture was extruded, pelleted and the resulting blend pellets were extruded twice and then processed to form a film by blow extrusion. The formulations were named according the glycerol used as CG (crude glycerol), TGG (technical grade glycerine) and BDG (bi-distilled glycerine).

## 2.3 Film characterisation

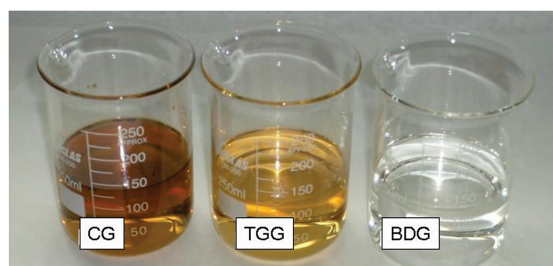
### 2.3.1 Mechanical properties of the films

The mechanical properties of the films were obtained in a Stable Micro Systems texture analyser, model TA.TX2 *plus* (Stable Micro Systems, Surrey-England), according to the methodology established by the American Society for Testing and Material ASTM D882-00<sup>[16]</sup>. Ten repetitions of each film direction (transverse and longitudinal) were tested.

**Table 1.** Chemical composition of different glycerol from biodiesel production.

Composition	CG	TGG	BDG
Glycerol content (%)	80.71	81.90	> 99.7
Moisture (%)	10.83	11.50	< 0.3
Methanol content (%)	0.014	0.024	*
Ashes (%)	5.62	5.90	*
pH	6.0	6.0	*
Density (g/mL)	1.25	1.26	*
CIE-Lab Colour Parameters			
L	34.8	42.7	46.6
a*	2.7	-0.3	-0.1
b*	15.9	10	1.0

CG = crude glycerol, TGG = technical grade glycerine, BDG = bi-distilled glycerine. \*Data not provided by the manufacturer.



**Figure 1.** Crude glycerol (CG), technical grade glycerine (TGG) and bi-distilled glycerine (BDG) from biodiesel production.

The maximum tensile strength (MPa), elongation at break (%) and Young's or elasticity modulus (MPa) were assessed.

### 2.3.2 Water vapour permeability (WVP)

The tests were conducted using the ASTM method E-96-00<sup>[17]</sup>, with some modifications. The film was previously conditioned at 53% RH and 25 °C for 48 hours, and each film sample was fixed in a circular opening of a permeation cell with a diameter of 60 mm<sup>2</sup> sealed with silicone grease. The interior of the cell was filled with a saturated magnesium chloride solution (33% RH) and was stored at 25 °C in a desiccator containing a saturated sodium nitrite solution to provide 64% RH.

### 2.3.3 Optical properties

The films' opacity was determined using a BYK Gardner colorimeter (D<sub>65</sub> illuminant and visual angle of 10°). Sample opacity (Y) was calculated as the ratio between the opacity of the sample placed under a black pattern (Y<sub>b</sub>) and the opacity of the sample placed under a white pattern (Y<sub>w</sub>), according to the equation:  $Y = (Y_b / Y_w) \times 100$ . Five samples of each formulation were tested.

### 2.3.4 Contact angle measurement

The contact angle was measured using a contact angle meter (Data Physics OCA-15, Germany). Images were captured through a high-resolution camera and were analysed using the Image Tool software. Film samples (40 mm × 20 mm) were fixed in a glass plate and placed at the base of the unit. A distilled water drop (5 µL) was placed on the film surface using a syringe. The measurements were performed at room temperature, and the contact angle was calculated as the average of five measurements after drop stabilisation. The contact angle hysteresis was calculated by measuring the difference between the advancing and receding angles.

### 2.3.5 Statistical analysis

The results of the mechanical and WVP tests were analysed using STATISTICA 7.0 software (Statsoft, Oklahoma), with analysis of variance (ANOVA) and Tukey's test at a 5% significance level.

## 3. Results and Discussion

### 3.1 Mechanical properties

The mechanical properties of the films produced with cassava starch, PBAT and the different types of glycerol are presented in Table 2.

The tensile strength of the films ranged from  $4.9 \pm 0.3$  MPa to  $6.4 \pm 0.7$  MPa, and there were no significant differences among the films produced with crude glycerol (CG), technical grade glycerine (TGG) and bi-distilled glycerine (BDG) in both longitudinal and transverse tensile tests. These results showed that the presence of some impurities in the crude glycerol did not influence the tensile strength of the films.

On the other hand, for the same formulation, the longitudinal tensile strength was significantly higher than the transverse tensile strength by approximately 11 to 24%, most likely due to the direction of the polymer chains' alignment during the extrusion process. This anisotropic

**Table 2.** Mechanical properties of the films.

Sample	Tensile strength (MPa)		Elongation at break (%)		Young's Modulus (MPa)	
	L	T	L	T	L	T
CG	5.9 <sup>aA</sup> (±0.4)	5.3 <sup>bA</sup> (±0.3)	182.6 <sup>aA</sup> (±91)	71.7 <sup>bA</sup> (±26)	82.3 <sup>bAB</sup> (±36)	122.1 <sup>aA</sup> (±13)
TGG	6.4 <sup>aA</sup> (±0.7)	5.0 <sup>bA</sup> (±0.5)	171.4 <sup>aA</sup> (±23)	52.9 <sup>bB</sup> (±12)	114.5 <sup>aA</sup> (±28)	126.2 <sup>aA</sup> (±26)
BDG	6.1 <sup>aA</sup> (±0.6)	4.9 <sup>bA</sup> (±0.3)	250.6 <sup>aA</sup> (±51)	81.1 <sup>bA</sup> (±21)	48.5 <sup>bB</sup> (±12)	101.6 <sup>aA</sup> (±27)

<sup>a,b</sup> Means with different letters in the same row indicate differences at the 0.05 level by Tukey's test. <sup>A,B</sup> Means with different letters in the same column indicate differences at the 0.05 level by Tukey's test. L = Longitudinal direction; T = Transverse direction.

behaviour for blown-films is well-known and already studied in thermoplastic starch films<sup>[18]</sup>. Santana and Manrich<sup>[19]</sup> observed the same anisotropic behaviour for polypropylene/polystyrene blown films. According to the authors, the tensile properties were influenced by the composition of the materials and process conditions.

Considering the elongation at break results, the samples were more extensible in the longitudinal direction than in the transverse direction (~3×) and were not significantly affected by the glycerol grade. This fact shows that the purity grade of the glycerol did not influence the plasticisation of the film, which can be explained by the different composition of the crude and distilled glycerol. Considering that crude glycerol has a lower concentration of the glycerine, due the presence of impurities, the composition of the impurities includes fatty acids as a result of the glycerol production from biodiesel. The fatty acids also acted as plasticisers<sup>[20]</sup> resulted in films with similar elongation at break than those with TGG and BDG. Similar results were observed by Nobrega et al.<sup>[21]</sup>.

The Young's modulus showed that the samples were significantly more rigid in the transverse direction than in the longitudinal direction, varying between 10 and 90% difference.

Based in the mechanical properties, it is possible to observe that the crude glycerol (CG) can be used to produce starch/PBAT films with similar properties to those produced with BDG and TGG, without additional steps of purification. This represents an important way to save resources and to promote the utilisation of a by-product of biodiesel industry.

### 3.2 Water vapour permeability (WVP)

Considering the results presented at Table 3, the water vapour permeability of plasticised films did not differ significantly for CG, TGG and BDG glycerol; the permeability value varied from  $2.13 \times 10^{-6}$  to  $3.49 \times 10^{-6}$  g / m.Pa.day (Table 3). Based on these results, is possible to observe that the different types of glycerol did not interfere in the molecular mobility of the polymeric chains, i. e., the plasticiser effect was the same for all the samples, which is in according with the results of the mechanical properties. In addition, the results showed that the impurities of the crude glycerol (CG) did not change the WVP of the films.

Previous researches<sup>[5,9]</sup> also evaluated the effect of the plasticisers, particularly glycerol, on the films and observed that greater proportions of glycerol contributed to the increase in WVP because it causes structural modifications in the polymeric network and increases the molecular mobility, which facilitates the diffusivity of water. In this work, however, no changes in WVP were recorded.

**Table 3.** Water vapour permeability (WVP) of the films.

Sample	Water vapour permeability (x10 <sup>6</sup> )
	(g/m.Pa.day)
CG	2.47 <sup>a</sup> (±0.62)
TGG	2.13 <sup>a</sup> (±0.12)
BDG	3.49 <sup>a</sup> (±0.55)

<sup>a,b</sup> Means with different letters indicate differences at the 0.05 level by Tukey's test.

Other authors that studied blends of PBAT and thermoplastic starch, even with different proportions between these components, found similar results to those presented in this work. Bilck et al.<sup>[22]</sup> found WVP values of  $4.22 \times 10^{-6}$  g / m.Pa.day and Nobrega et al.<sup>[15]</sup> found  $8.07 \times 10^{-6}$  g / m.Pa.day, using a 33%-64% RH gradient across the film. Also Olivato et al.<sup>[23]</sup> evaluated the WVP in films of starch/PBAT (50:50) using 0-75% as RH gradient and reported values of  $5.4 \times 10^{-6}$  g /m.Pa.day for WVP.

### 3.3 Opacity

The opacity ranged from 48.64% (TGG films) to 50.60% (BDG films) (Table 4). Despite the colour difference among the three different grades of glycerol (Table 1, Figure 1), there were no significant differences in the opacity among the films, which is an interesting result when the objective is the application of the film as food packaging.

The presented results (Table 4) agreed with the results reported by other authors, which obtained an opacity value around 50%, for thermoplastic starch film<sup>[24,25]</sup>, and 34% for PBAT film<sup>[24]</sup>. Is important to point out that the results of this work for the blends starch/PBAT was intermediary when compared to the pure polymers, which were already expected.

### 3.4 Contact angle

Table 5 shows the contact angle results and the Figure 2 shows photographs of the drop deposition on the surface of the films.

The CG and TGG films showed no significant differences in contact angle, indicating that these materials have similar smoothness. However, the BDG film had a contact angle lower than CG and TGG films, indicating a difference in surface energy. This behaviour could be associated with the glycerol composition; the BDG had approximately 25% more glycerol than the others (Table 1), and, consequently, had proportionally more plasticiser that created its higher hygroscopic surface. Other researchers reported that starch-based films had increased hygroscopic characteristics with increased glycerol concentrations and associated this process with an increase in hydroxyl groups available to make hydrogen bonds with water<sup>[4,13-15]</sup>.

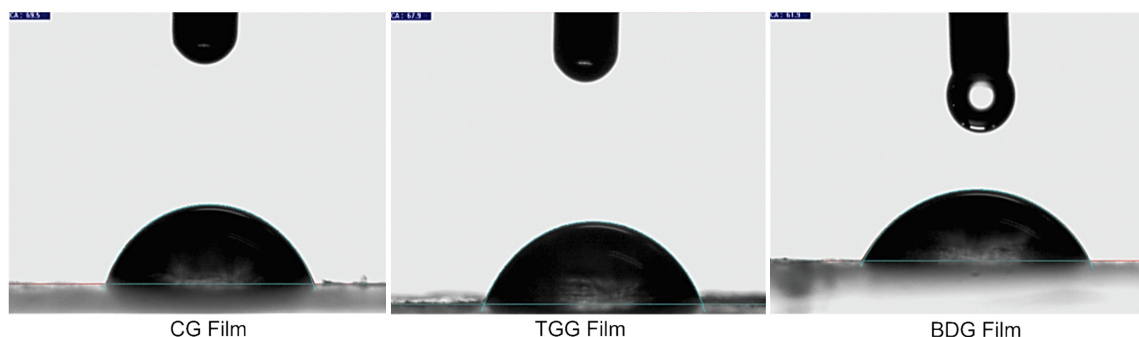


Figure 2. Images of the drop on the film surface.

Table 4. Opacity of the sample placed under a black pattern ( $Y_b$ ), under a white pattern ( $Y_w$ ) and opacity (%) of the films.

Film	$Y_w$	$Y_b$	Opacity (%)
CG	91.34 <sup>a</sup> ( $\pm$ 0.44)	46.16 <sup>a</sup> ( $\pm$ 0.97)	50.53 <sup>a</sup> ( $\pm$ 1.29)
TGG	91.82 <sup>a</sup> ( $\pm$ 0.28)	44.65 <sup>a</sup> ( $\pm$ 2.13)	48.64 <sup>a</sup> ( $\pm$ 2.44)
BDG	91.30 <sup>a</sup> ( $\pm$ 0.28)	46.19 <sup>a</sup> ( $\pm$ 1.14)	50.60 <sup>a</sup> ( $\pm$ 1.30)

<sup>a,b</sup> Means with different letters in the same column indicate differences at the 0.05 level by Tukey's test.

Table 5. Contact angle and hysteresis of the films.

Sample	Contact angle	Advancing angle	Receding angle	Hysteresis
CG	70.9 ( $\pm$ 2.5) <sup>b</sup>	79.2 ( $\pm$ 3.4)	43.9 ( $\pm$ 3.1)	35.3 <sup>b</sup>
TGG	68.4 ( $\pm$ 1.5) <sup>ab</sup>	79.0 ( $\pm$ 1.6)	43.6 ( $\pm$ 1.7)	35.4 <sup>b</sup>
BDG	60.6 ( $\pm$ 3.7) <sup>a</sup>	70.0 ( $\pm$ 2.4)	44.1 ( $\pm$ 1.2)	25.9 <sup>a</sup>

<sup>a,b</sup> Means with different letters in the same column indicate differences at the 0.05 level by Tukey's test.

Białopiotrowicz<sup>[26]</sup> examined the contact angle in corn and potato starch films at different concentrations (2, 4, 6, 8, 10 and 12%wt) for different liquids (water, glycerol, formamide, ethylene glycol and diiodomethane poly(methyl methacrylate)) and reported that the contact angles decreased linearly with increasing starch concentration. According to the author, an increasing in starch concentration increased the water bound to the starch chains, thereby reducing the amount of water available at the surface.

Other researchers working with starch blends reported similar contact angle values to those found in this work. Veiga-Santos et al.<sup>[27]</sup> reported contact angle values between 38.2° and 80.1° for cassava starch and xanthan gum blends. Demirgöz et al.<sup>[28]</sup> used blends of corn starch with other polymers (ethylene-vinyl alcohol, cellulose acetate and  $\epsilon$ -caprolactone) and observed contact angles between 39.9° and 73.6°.

#### 4. Conclusion

Different purities of glycerol from biodiesel production did not affect the mechanical and barrier properties when used to plasticise starch-based films. Therefore, crude glycerol could be used as an alternative plasticiser to reduce the cost of producing these polymer films.

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#### 6. References

- Chi, Z., Pyle, D., Wen, Z., Frear, C., & Chen, S. (2007). A laboratory study of producing docosahexaenoic acid from biodiesel-waste glycerol by microalgal fermentation. *Process Biochemistry*, 42(11), 1537-1545. <http://dx.doi.org/10.1016/j.procbio.2007.08.008>.
- Freitas, S. M., & Nachiluk, K. (2009). Desempenho da Produção Brasileira de Biodiesel em 2008. *Análises e Indicadores do Agronegócio*, 4(2), 1-4. Retrieved in 09 June 09 2014, from <http://www.iea.sp.gov.br/out/LerTexto.php?codTexto=10115>
- Thompson, J. C., & He, B. B. (2006). Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Applied Engineering in Agriculture*, 22(2), 261-265. <http://dx.doi.org/10.13031/2013.20272>.
- Müller, C. M. O., Yamashita, F., & Laurindo, J. B. (2008). 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), 82-87. <http://dx.doi.org/10.1016/j.carbpol.2007.07.026>.
- Galdeano, M. C., Mali, S., Grossmann, M. V. E., Yamashita, F., & Garcia, M. A. (2009). Effects of plasticizers on the properties of oat starch films. *Materials Science and Engineering C*, 29(2), 532-538. <http://dx.doi.org/10.1016/j.msec.2008.09.034>.
- Müller, C. M. O., Laurindo, J. B., & Yamashita, F. (2009). Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values. *Carbohydrate Polymers*, 77(2), 293-299. <http://dx.doi.org/10.1016/j.carbpol.2008.12.030>.
- Müller, C. M. O., Laurindo, J. B., & Yamashita, F. (2009). Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. *Food Hydrocolloids*, 23(5), 1328-1333. <http://dx.doi.org/10.1016/j.foodhyd.2008.09.002>.
- Pelissari, F. M., Grossmann, M. V. E., Yamashita, F., & Pineda, E. A. G. (2009). Antimicrobial, mechanical, and barrier properties of cassava starch-chitosan films incorporated with oregano essential oil. *Journal of Agricultural and Food Chemistry*, 57(16), 7499-7504. <http://dx.doi.org/10.1021/jf9002363>. PMID:19627142.
- Alves, V. D., Mali, S., Beleia, A. P., & Grossmann, M. V. E. (2007). Effect of glycerol and amylose enrichment on cassava starch film properties. *Journal of Food Engineering*, 78(3), 941-946. <http://dx.doi.org/10.1016/j.jfoodeng.2005.12.007>.
- Kijchavengkul, T., Auras, R., Rubino, M., Ngouajio, M., & Fernandez, R. T. (2008). Assessment of aliphatic-aromatic



- copolyester biodegradable mulch films. Part I: field study. *Chemosphere*, 71(5), 942-953. <http://dx.doi.org/10.1016/j.chemosphere.2007.10.074>. PMID:18262221.
11. Brandelero, R. H. H., Yamashita, F., & Grossmann, M. V. E. (2010). The effect of surfactant Tween 80 on the hydrophilicity, water vapor permeation, and the mechanical properties of cassava starch and poly(butylene adipate-co-terephthalate) (PBAT) blend films. *Carbohydrate Polymers*, 82(4), 1102-1109. <http://dx.doi.org/10.1016/j.carbpol.2010.06.034>.
  12. Bilck, A. P., Roberto, S. R., Grossmann, M. V. E., & Yamashita, F. (2011). Efficacy of some biodegradable films as pre-harvest covering material for guava. *Scientia Horticulturae*, 130(1), 341-343. <http://dx.doi.org/10.1016/j.scienta.2011.06.011>.
  13. Olivato, J. B., Grossmann, M. V. E., Yamashita, F., Eiras, D., & Pessan, L. A. (2012). Citric acid and maleic anhydride as compatibilizers in starch/poly(butylene adipate-co-terephthalate) blends by one-step reactive extrusion. *Carbohydrate Polymers*, 87(4), 2614-2618. <http://dx.doi.org/10.1016/j.carbpol.2011.11.035>.
  14. Olivato, J. B., Grossmann, M. V. E., Bilck, A. P., & Yamashita, F. (2012). Effect of organic acids as additives on the performance of thermoplastic starch/polyester blown films. *Carbohydrate Polymers*, 90(1), 159-164. <http://dx.doi.org/10.1016/j.carbpol.2012.05.009>. PMID:24751025.
  15. Nobrega, M. M., Olivato, J. B., Müller, C. M. O., & Yamashita, F. (2012). Biodegradable starch-based films containing saturated fatty acids: Thermal, infrared and Raman spectroscopic characterization. *Polímeros: Ciência e Tecnologia*, 22(5), 475-480. <http://dx.doi.org/10.1590/S0104-14282012005000068>.
  16. American Standard Testing Methods. (2002). *D-882-02: standard test methods for tensile properties of thin plastic sheeting*. Philadelphia: ASTM. Annual book.
  17. American Standard Testing Methods. (2000). *E-96-00: standard test methods for water vapor transmission of material*. Philadelphia: ASTM. Annual book.
  18. Thunwall, M., Kuthanová, V., Boldizar, A., & Rigdahl, M. (2008). Film blowing of thermoplastic starch. *Carbohydrate Polymers*, 71(4), 583-590. <http://dx.doi.org/10.1016/j.carbpol.2007.07.001>.
  19. Santana, R. M. C., & Manrich, S. (2005). Filmes tubulares de compósitos de termoplásticos pós-consumo: Análise térmica e mecânica. *Polímeros: Ciência e Tecnologia*, 15(3), 163-170. <http://dx.doi.org/10.1590/S0104-14282005000300005>.
  20. Nobrega, M. M., Olivato, J. B., Grossmann, M. V. E., Bona, E., & Yamashita, F. (2012). Effects of the incorporation of saturated fatty acids on the mechanical and barrier properties of biodegradable films. *Journal of Applied Polymer Science*, 124(5), 3695-3703. <http://dx.doi.org/10.1002/app.35250>.
  21. Nobrega, M. M., Olivato, J. B., Bilck, A. P., Grossmann, M. V. E., & Yamashita, F. (2012). Glycerol with different purity grades derived from biodiesel: Effect on the mechanical and viscoelastic properties of biodegradable strands and films. *Materials Science and Engineering C*, 32(8), 2220-2222. <http://dx.doi.org/10.1016/j.msec.2012.06.005>.
  22. Bilck, A. P., Grossmann, M. V. E., & Yamashita, F. (2010). Biodegradable mulch films for strawberry production. *Polymer Testing*, 29(4), 471-476. <http://dx.doi.org/10.1016/j.polymeresting.2010.02.007>.
  23. Olivato, J. B., Grossmann, M. V. E., Yamashita, F., Nobrega, M. M., Scapin, M. R. S., Eiras, D., & Pessan, L. (2011). Compatibilisation of starch/poly(butylene adipate co-terephthalate) blends in blown films. *International Journal of Food Science & Technology*, 46(9), 1934-1939. <http://dx.doi.org/10.1111/j.1365-2621.2011.02704.x>.
  24. Costa, D. L. M. G. (2008). *Produção por extrusão de filmes de alto teor de amido termoplástico de mandioca com poli(butileno adipato co-terefalato) (PBAT)* (Masters dissertation). Universidade Estadual de Londrina, Londrina.
  25. Melo, C., Garcia, P. S., Grossmann, M. V. E., Yamashita, F., Dall'Antônia, L. H., & Mali, S. (2011). Properties of extruded xanthan-starch-clay nanocomposite films. *Brazilian Archives of Biology and Technology*, 54(6), 1223-1233. <http://dx.doi.org/10.1590/S1516-89132011000600019>.
  26. Bialopiotrowicz, T. (2003). Wettability of starch gel films. *Food Hydrocolloids*, 17(2), 141-147. [http://dx.doi.org/10.1016/S0268-005X\(02\)00046-2](http://dx.doi.org/10.1016/S0268-005X(02)00046-2).
  27. Veiga-Santos, P., Oliveira, L. M., Cereda, M. P., Alves, J., & Scamparini, A. R. P. (2005). Mechanical properties, hydrophilicity and water activity of starch-gum films: Effect of additives and deacetylated xanthan gum. *Food Hydrocolloids*, 19(2), 341-349. <http://dx.doi.org/10.1016/j.foodhyd.2004.07.006>.
  28. Demirgöz, D., Elvira, C., Mano, J. F., Cunha, A. M., Piskin, E., & Reis, R. L. (2000). Chemical modification of starch based on biodegradable polymeric blends: effects on water uptake, degradation behavior and mechanical properties. *Polymer Degradation & Stability*, 70(2), 161-170. [http://dx.doi.org/10.1016/S0141-3910\(00\)00102-6](http://dx.doi.org/10.1016/S0141-3910(00)00102-6).

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