Polymeric films of protein extracted from chromed leather wastes and cornstarch: effect of different plasticizers on the mechanical and solubility properties.

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Abstract

It is common knowledge that the discard, mainly the inappropriate discard, of non-biodegradable polymers is extremely harmful to the environment since these materials take centuries to break down. Therefore, over the past years biodegradable polymers, mainly the ones from renewable sources, have attracted the attention not only of researchers, but also of the industry and of the society. Polymers from renewable sources, however, still need to be studied to have their properties improved for future wider use. The same environmental concern makes it every time more common and necessary the reuse of solid wastes or fractions of them as raw materials. Taken all of it into account, the objective of this work was to evaluate the properties of polymeric films produced with protein extracted from chromed leather waste (reuse of solid wastes) and cornstarch (a renewable source) when varying the type and quantity of plasticizer employed in the material. Even though the elongation at break of the films produced in this work (values of up to 133.8%) is lower than the ones presented by commercial films, their tensile strength (values of up to 29.6 MPa) is similar to the one of commercial films. Solubility of the films varied from 17.3 to 25.9%. The use of sorbitol as plasticizer led to the production of more resistant films when compared to the use of glycerol as plasticizer. Higher quantities of plasticizer led to the production of less resistant, but also less brittle, films.

Key words: Polymer. Film. Properties. Starch. Protein. Leather Wastes.

Theme Area: Clean Technologies

1 Introduction

According to the Brazilian Association of the Plastic Industry (ABIPLAST, 2015), 6.71 million tons of plastic were produced and 7.24 millions tons were consumed in Brazil in 2014. In the world, according to PlasticEurope (2015), 311 million tonnes of plastic were produced in 2014. This production/consumption profile is characteristic of the modern society and concerns researchers worldwide due to the amount of non-biodegradable plastic wastes discarded in the environment.

Plastic represents 13.5% of the wastes produced in Brazil. From all the Brazilian urban solid waste, 80.3% is collected by trucks and taken to dumps, landfills or recycling facilities. However, in only 15% of the Brazilian cities the selective collection is carried out, which means that most of the plastic waste ends up not being recycled (ABIPLAST, 2015).

Data like these ones encourage researchers to study the production of materials that degrade more easily than petroleum-based polymers. Polymeric materials produced from renewable sources such as lignin, cellulose, chitosan, proteins and starch are of special interest (GANDINI & LACERDA, 2015).

When it comes to polymers, the petroleum based ones are still the best economical alternative. However, it has been proved that polymers obtained from renewable sources, such as starch, have a better environmental performance (RIBEIRO *et al.*, 2013). Thermoplastic starch, for example, requires 68% less energy for its production than petroleum based polymers, emits lower rates of CO_2 to the atmosphere and results in an biodegradable polymer (ÁLVAREZ-CHÁVEZ *et al.*, 2012).

Studies need to be performed in order to improve the characteristics of polymers obtained from renewable raw materials. Combining different materials in their production has shown good results in properties improvement (GÓMEZ-GUILLÉN *et al.*, 2009). One of the studied combinations is of starch and protein (gelatin) (AL-HASSAN & NORZIAH, 2012; ARVANITOYANNIS *et al.*, 1997; FAKHOURY *et al.*, 2012).

Gelatin is usually obtained from animal bones, skin and cartilages. However, when not used for feeding purposes, gelatin – which is a protein partially hydrolyzed from collagen - may be obtained from wastes, such as chromed leather wastes (CLW). CLW hydrolysis for protein extraction, when conducted under alkaline conditions, generates a product with low chromium content (DETTMER *et al.*, 2014).

In this work, protein extracted from CLW, cornstarch, and plasticizers (glycerol or sorbitol) were used for polymeric films production. These films may be an alternative to the petroleum based ones.

2 Materials and Methods

2.1 Materials

Protein used for film production was extracted from CLW provided by Peles Pampa tannery (Portão – RS – Brazil). The extraction was carried out employing magnesium oxide analytical degree (Vetec - Brazil). Commercial cornstarch (Yoki – Brazil), analytical grade glycerol (Cinética – Brazil) and sorbitol (Cinética – Brazil) were also used for film production.

2.2 Methods

2.2.1 Protein extraction

Protein was extracted from CLW through alkaline hydrolysis. For that, 50 g of CLW were mixed with 250 ml of water and 2 g of magnesium oxide. The mixture was agitated in an orbital shaker (MA 832, Marconi, Brazil) for 6 h, at 70°C and 180 rpm. The solid cake and the protein obtained in aqueous media were separated through vacuum filtration. The protein was stored at approximately 4°C up to film production.

2.2.2 Film production

For film production, 200 ml of protein extracted from CLW in aqueous media were previously heated to 25 ± 5°C. It was then added to it 9.6 g of cornstarch and, when appropriate, 0.96 or 1.92 g plasticizer (glycerol or sorbitol). The mass of plasticizer added represents, respectively, 10 and 20% of the total mass of cornstarch added to the film. The solution formed is called filmogenic solution. The film formulations tested in this work are presented in Table 1. Each film was produced in duplicates.

Table 1 – Composition of the filmogenc solution used for polymeric films production.

Film[a]	Plasticizer	Mass of plasticizer (g/100 cornstarch)
SP	--	--
SPS10	Sorbitol	10
SPS20	Sorbitol	20
SPG10	Glycerol	10
SPG20	Glycerol	20

[a] All the films were produced with 200 ml of protein extracted from CLW in aqueous media and 9.6 g of cornstarch.

The filmogenic solution was heated under constant magnetic stirring at starch gelatinization temperature. This temperature, 85°C, was previously determined by differential scanning calorimetry, as described by Scopel et al. (2015).

After that, the filmogenic solution was cooled to 25 ± 5°C and spread onto a 30 x 30 cm glass plate covered with a polytetrafluoroethylene layer with an initial thickness of 2 mm. The films were dried under room temperature (20 ± 5°C) for 48 h.

2.2.3 Protein and film characterization

Protein extracted from CLW was characterized for its Total Kjeldahl Nitrogen (TKN) content according to Standard Methods for Examination of Water and Wastewater (SMEWW) Method 4500N_{org}-B. Chromium content was determined according to SMEWW Method 3111-B in an atomic absorption spectroscope (Analyst 200, Perkin Helmer, USA).

The films were characterized for their solubility and mechanical properties (tensile strength and elongation at break).

Solubility was determined in triplicates for each film sample according to the method proposed by Fakhoury *et al.* (2012). Samples of 2 x 2 cm were oven dried (A35ED, DeLeo, Brazil) at 105°C until sample mass was constant for initial dry mass determination. Then, the samples were immersed into 50 ml of deionized water and agitated in a thermostatic bath (501/1D, Nova Era, Brazil) at 80 rpm and 25°C for 24 h. The samples were dried again at 105°C until constant mass for final dry mass determination. Percentage of mass loss was determined and represented the solubility of the films. All mass measurements were performed with an analytical balance (AUY220, Shimadzu, Japan).

Tensile strength and elongation at break of the films were determined according to American Society for Testing and Materials (ASTM) Method D882-2012. For each film produced, five specimens measuring 2 x 10 cm were stored at 23°C ± 2°C and air humidity of 50 ± 10% for at least 48 h. They were then subjected to 25 $mm.min^{-1}$ rate of grip separation in a universal testing machine (DL200, Emic, Brazil).

Statistical analysis of the experiments was performed through analysis of variance (ANOVA) with the software Statistica 12 (StatSoft Inc.). It was used to determine statistical significance of the factors studied in a confidence interval of 95% and confidence level of $P < 0.05$.

3 Results and Discussion

The protein extracted from CLW presented TKN content of 2.2 g/L^{-1} and chromium concentration under 0.04 $mg.L^{-1}$.

Statistical analysis indicated that the differences found in the solubility of the films when the two types of plasticizer (sorbitol and glycerol) and their two different percentages (10 and 20%) were compared were not significant (P-value > 0.05). The differences, however, were statistically significant when it was compared the presence or absence of plasticizer.

Still according to statistical analysis, the differences found in the elongation at break and in the tensile strength of the films are statistically significant (P-value < 0.05) for both factors studied: type of plasticizer and its percentage.

The solubility results are shown in Figure 1. Solubility ranged from 17.3% (for films with no plasticizer) to 28.0% (for films with a sorbitol mass equal to 20% of the starch mass). The presence of plasticizers increases the interaction of the films with water (DÍAZ *et al.*, 2011) and, therefore, it also increases films solubility, as can be seen in Figure 1. Values for solubility ranging from 20.8 to 39.5%, were obtained by Fakhoury *et al*. (2012), who studied films of starch, gelatin, glycerol and sorbitol

Figure 1 - Solubility and its standard deviation of the starch/protein films plasticized with: SP – no plasticizer; SPS10 – 10% (of the starch mass) of sorbitol; SPS20 - 20% (of the starch mass) of sorbitol; SPG10 10% (of the starch mass) of glycerol; SPG20 20% (of the starch mass) of glycerol.

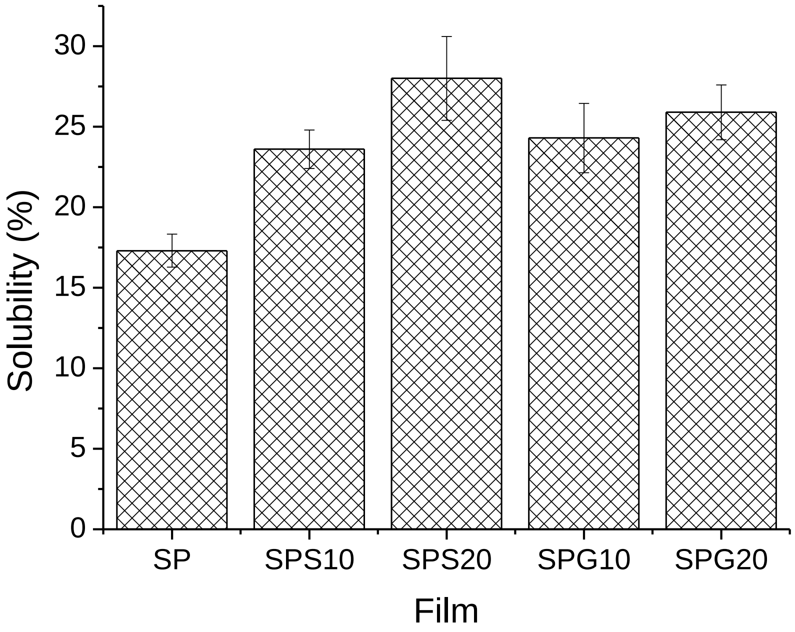


Figure 2 presents the tensile strength of the films produced in this work and Figure 3 presents the elongation at break of the material.

Figure 2 - Tensile strength and its standard deviation of the starch/protein films plasticized with: SP – no plasticizer; SPS10 – 10% (of the starch mass) of sorbitol; SPS20 - 20% (of the starch mass) of sorbitol; SPG10 10% (of the starch mass) of glycerol; SPG20 20% (of the starch mass) of glycerol.

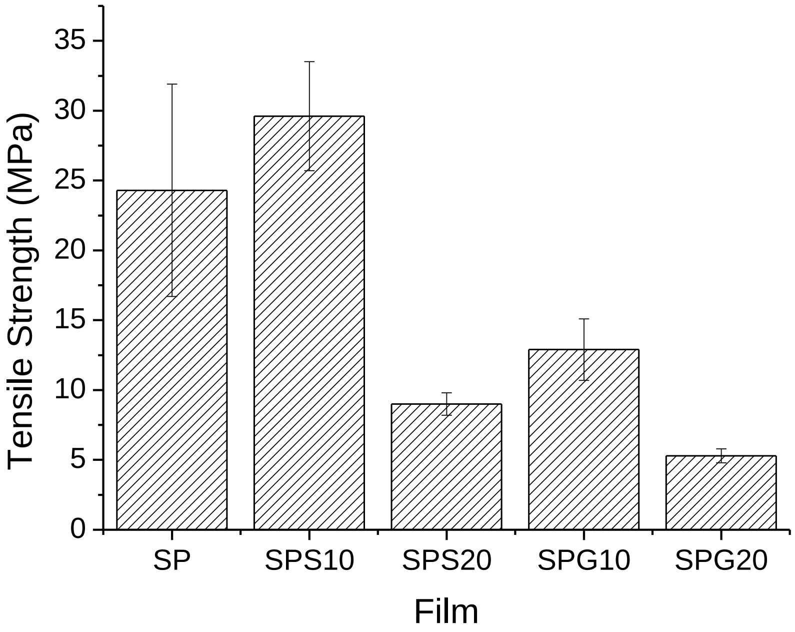
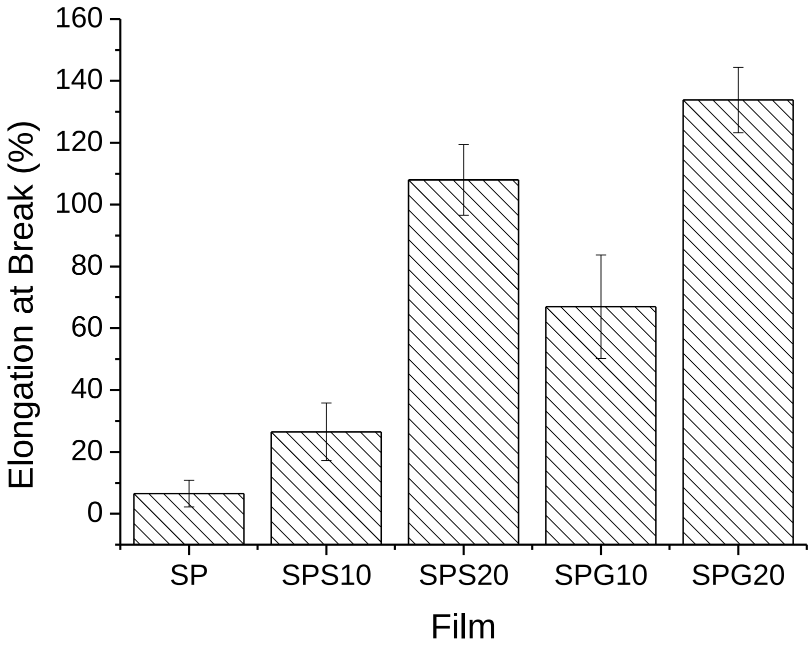


Figure 3 – Elongation at break and its standard deviation of the starch/protein films plasticized with: SP – no plasticizer; SPS10 – 10% (of the starch mass) of sorbitol; SPS20 - 20% (of the starch mass) of sorbitol; SPG10 10% (of the starch mass) of glycerol; SPG20 20% (of the starch mass) of glycerol.



The use of sorbitol as plasticizer increased tensile strength and decreased elongation at break when compared to the use of glycerol. The number of hydroxyl groups present in the sorbitol chain is twice the number of hydroxyl groups in the glycerol chain. The hydroxyl groups of the plasticizers interact with the starch and protein carboxyl groups. As a result, the mobility of the chains decreases with the use of sorbitol in comparison with the use of glycerol. Sorbitol is also less hygroscopic than glycerol, which reduces the interaction of sorbitol films with water. Water is the natural plasticizer of starch/protein films (FAKHOURY *et al.*, 2012).

Table 2 presents the mechanical properties of commercial biodegradable films and conventional polyethylene films.

Table 2 – Mechanical properties of commercial biodegradable films and of polyethylene films (adapted from (ANDRADE, 2011))

	Biomind	**Mater-Bi®**	**Polyethilene**
Type of film	Biodegradable	Biodegradable	Conventional
Producer	Cabopol	Silvex	Cabopol
Tensile strength (MPa)	18.0	23.6	18.0
Elongation at break (%)	450	335	375

Even though the films produced of cornstarch and protein extracted from CLW presented lower elongation at break, the tensile strength of the cornstarch/protein films are comparable or even higher than the ones of commercial films.

It is so confirmed that the films produced in this work are not only environmentally less aggressive by employing renewable raw-materials and substances extracted from wastes, but also present properties comparable to the ones of commercially available films.

4 Conclusion

It was concluded from this work that the use of cornstarch (a renewable raw material) and protein extracted from chromed leather waste is not only environmentally but also technically feasible. The use of sorbitol as plasticizer produced more resistant, but more brittle, films when compared to the use of glycerol as plasticizer. Higher amounts of plasticizer led to the production of less brittle, less resistant and more soluble films.

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