Agricultural mulch films produced from cornstarch and protein extracted from chromed leather wastes: thickness, water vapor transmission, nitrogen and chromium content

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Abstract

Plastic films are used as agricultural mulch films worldwide. They allow higher production and less use of herbicides and pesticides by covering the soil, controlling weed, maintaining temperature, and avoiding water evaporation. The most used plastics films in agriculture are made of polyethylene. During usage, however, most part of these polyethylene films are partially disintegrated and small parts of them remain in the soil. Since this is not a biodegradable material, an environmental issue is so created due to plastic accumulation in the environment. An alternative for it is the use of biodegradable mulch films such as the ones produced from starch, or starch combined with other compounds like proteins. In this work, chromed leather wastes (CLW) were hydrolyzed in alkaline media to extract protein. Cornstarch and glycerol were mixed with this protein (in aqueous solution) for the production of polymeric films latter applied as agricultural mulches. The films were tested for their thickness, water vapor transmission, nitrogen and chromium content. Water vapor transmission of the films was from 3.6 to 4.6 times lower the water vapor transmission with no barrier. It indicates the films would reduce water evaporation and, consequently, the amount of water needed for irrigation. The amount of chromium (prevenient from the CLW extracted protein) is in accordance to international standards for chromium in fertilizers. After use, the films may be mixed to the soil, where they may degrade and release nitrogen and carbon, which are nutrients for the soil.

Key words: Mulch. Film. Agriculture. Starch. Protein. Chromed leather wastes.

Theme Area: Clean Technologies

1 Introduction

The agricultural practice called mulching is used in crop production for conservation of soil moisture, temperature regulation and weed control (TOUCHALEAUME *et al.*, 2015). Plastic mulches have been used since the middle of the 20^{th} century. Increase in crop production and less dependence on herbicides and pesticides are some of the results obtained from this practice (BRIASSOULIS, 2007).

According to Agriculture, Plastics and Environment Europe (APE, 2015), low density polyethylene (LDPE) represents 502,000 tonnes, approximately 60%, of the total agricultural plastic used. Only 43% of the agricultural plastics used in Europe are recovered, and only half of it is recycled. Since LDPE is not a biodegradable material, it can be expected substantial amounts of plastic accumulated in the environment.

In this context, biodegradable plastic films are a desirable alternative to the LDPE ones. Polylactic acid, co-polyester-starch blends, poly(butylene adipate-coterephthlate), and polypropylene carbonate are some of the biodegradable materials used for film production (LI *et al.*, 2014; TOUCHALEAUME *et al.*, 2015).

Not only the creation of alternatives to conventional non-biodegradable polymers production is an environmental issue to be widely discussed. Even though leather and leather products are responsible for an estimated global trade value of nearly US$ 100 billion a year (UNIDO, 2010), leather industries generate about 4 million tonnes of wastes per year worldwide (KONG *et al.*, 2013). From 80% to 85% of tanneries apply chromium based processes to turn hides and skins into leather by means of chromium III salts (UNIDO, 2010). Each 1,000 kg of hides or skins produce about 250 kg of chromed leather waste (CLW) (MATYASOVSKY *et al.*, 2011) and at least 500 kg of total solid waste (HU *et al.*, 2011).

Protein recovered from CLW through hydrolysis can be combined with starch to produce polymeric films. In the presented context, this would allow a raw-material recovery from wastes (protein from CLW) and the application of a renewable source raw material (starch) in the production of an alternative to petroleum based polymers. Extraction of protein must be carefully performed so that less chromium is carried over to the protein phase. Alkaline extraction is helpful since in high pH values chromium tends to precipitate and does not solubilizes in high quantities in the aqueous protein phase (DETTMER *et al.*, 2014). In low concentrations (as a trace metal), chromium is an important micronutrient. According to the Micronutient Information Center from the Oregon State University (MIC, 2015), trivalent chromium (which is the one present in CLW) may play a role in normal insulin function.

In this context, protein extracted from CLW was mixed with cornstarch to produce polymeric films. The films were plasticized with glycerol, which may be obtained as a by-product of biodiesel production. These films can be used as agricultural mulch films.

2 Materials and Methods

2.1 Materials

CLW used for protein extraction was provided by Peles Pampa tannery (Portão – RS – Brazil). Magnesium oxide analytical degree (Vetec - Brazil) was employed in protein extraction. Commercial cornstarch (Yoki – Brazil) and analytical grade glycerol (Cinética – Brazil) were used for film production.

2.2 Methods

2.2.1 Protein extraction

Alkaline hydrolysis was used to extract protein from CLW. The extraction was carried out in an orbital shaker (MA 832, Marconi, Brazil) for 6 h, at 70°C and 180 rpm using a proportion of 50 g of CLW, 250 ml of water, and 2 g of magnesium oxide. The protein in aqueous media was separated from the cake of the process through vacuum filtration.

2.2.2 Film production

Film production started by obtaining a filmogenic solution, which was later dried for film forming. For the filmogenic solution production, 200 ml of protein extracted from CLW in aqueous media were previously heated to 25 ± 5°C. Starch (6.4 or 8.0 g) and, in some samples, the plasticizer glycerol (in a proportion of 20 g for each 100 g of cornstarch) were added to the protein. The filmogenic solution was heated under constant magnetic stirring at starch gelatinization temperature (85°C) 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. Table 1 presents the composition of the films tested in this work. For each of them, a duplicate was produced.

Table 1 – Composition of the filmogenic solution used for polymeric film production.

Film[a]	**Mass of Starch (g)**	**Mass of Glycerol (g/100 cornstarch)**
6.4S0G	6.4	0
6.4S20G	6.4	20
8.0S0G	8.0	0
8.0S20G	8.0	20

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

2.2.3 Protein and film characterization

Protein extracted from CLW was characterized according to its Total Kjeldahl Nitrogen (TKN) content via Standard Methods for Examination of Water and Wastewater (SMEWW) Method 4500N_{org}-B (SMEWW, 2012a).

For chromium content determination, a 5 g aliquot of the films was digested using nitric acid according to American Society for Testing and Materials (ASTM) method D5198-09 (ASTM, 2009). After digestion, the sample was diluted to 100 ml and chromium content was determined according to SMEWW- Method 3111-B (SMEWW, 2012b) in an atomic absorption spectroscope (Analyst 200, Perkin Helmer, USA).

Water vapor transmission was determined according to ASTM E96-15 using the desiccant method (ASTM, 2015). Specimens were sealed to the open mouth of a test dish with a 2.5 cm diameter containing 10 g of silica 4-8 mm and the assembly was placed in a controlled atmosphere. In the controlled atmosphere, the relative humidity was maintained at 75% by using a sodium chloride saturated solution. The assembly was weighted every 1.5 h for 11.5 h. The ratio between the assembly weight variation (g) and the test dish open mouth area (m^2) was ploted against elapsed time. The slope of the line ploted is the rate of water vapor transmission ($g/(h.m^2)$). All weight measurements were performed using an analytical balance (AUY 220, Shimadzu, Japan).

Thickness of the films was determined with a layer thickness meter (345, Elcometer, USA).

3 Results and Discussion

The films produced in this work are suggested to be used as agricultural mulches. Figure 1 presents an image of this material applied to the soil. After used, the films can be mixed to the soil in which they will degrade. When degrading, the components present in the film will be released to the soil. Therefore, the film may be a nitrogen and carbon source to the soil. Nitrogen is present in the films due to the protein used for its production; carbon is mainly present due to starch utilization.

Figure 1 – Protein/starch films applied on the soil as a mulch.

Water vapor transmission and thickness of the films produced with protein extracted from CLW and starch are presented in Table 2. The films in which glycerol was employed as plasticizer presented higher water vapor transmission than films produced without any plasticizer. Adding glycerol to the films leads to an interaction between the plasticizer and the protein and the starch chains. It breaks the network of starch and of protein inter-chain hydrogen-bonding. Considering that glycerol is more hygroscopic than starch and than gelatin, the affinity for water molecules is higher in films plasticized with glycerol (AL-HASSAN & NORZIAH, 2012). It results in higher water diffusion through the samples and, therefore, higher water vapor transmission values.

Table 2: Water vapor transmission and thinkness of the protein/starch films.

Film[a]	**Thickness µm**	**Water vapor transmission ($g/(h.m^2)$)**
6.4S0G	107 ± 7	11.7 ± 1.4
6.4S20G	116 ± 6	15.2 ± 3.5
8.0S0G	128 ± 7	11.9 ± 1.5
8.0S20G	129 ± 10	14.8 ± 4.3
No film	--	54.3 ± 3.5

[a] All films were produced with 200 ml of protein extracted from CLW. 6.4S0G: produced with 6.4 g of starch and no glycerol; 6.4S20G: produced with 6.4 g of glycerol and 20% (of the starch mass) of glycerol; 8.0S0G: produced with 8.0 g of starch and no glycerol; 8.0S20G: produced with 8.0 g of glycerol and 20% (of the starch mass) of glycerol.

When the water vapor transmission test was conducted with no film on the open mouth of the test dish, the water transmission to the silica was from 3.6 to 4.6 times higher than when films were sealed on the test dish open mouth. It indicates that a considerable reduction in water transfer may be achieved when these films are employed as agricultural mulches. It results in less water needed for irrigation since less evaporation occurs.

Thickness of the films varied from 107 to 129 µm. Higher amounts of starch led to higher dry mass of the final film and, therefore, higher thickness. Both commercial biodegradable films and low density polyethylene films usually present lower thickness, from 20 to 40 µm (ABRUSCI *et al.*, 2013; ANDRADE, 2011; TOUCHALEAUME *et al.*, 2015).

Protein extracted from CLW used for film production in this work presented TKN content of 2.2 g/L^{-1}. Given that 200 ml of protein in aqueous media is used to produce a film of approximately 12 g and 0.036m², TKN concentration in the film could be calculated and is shown in Table 3. Table 3 also presents chromium concentration in the films, determined according to the method presented in item 2.2.3.

Table 3: TKN and chromium content of the protein starch films.

Material	**TKN[a]**		**Chromium[a]**	
	g/kg	g/m²	mg/kg	mg/m²
Protein/starch films	36.6	12.2	2.6	0.9

[a] Results presented are an average for all film formulations presented in Table 1.

Chromium content in the protein/starch films presented in Table 3 was evaluated in terms of limits for chromium in fertilizers. Worldwide, average chromium content in the soil is of 60 mg/kg. However, this value may be as high as 3000 mg/kg (BINI & BECH, 2014). Total chromium concentration in fertilizers is, in some countries, limited to a certain amount, as it is shown in Table 4. If compared chromium content in the protein/starch films and the limits from Table 3, it can be concluded that the films have from 38 to 192 times less chromium than the amounts allowed in fertilizers. It indicates that chromium amounts in the material studied in this work is low enough to allow it to be used.

Table 4: Limits for chromium content in fertilizers.

Country	Total chromium limit in fertilizers
Hungary	100 mg Cr/kg fertilizers[a]
Brazil	200 mg Cr/kg fertilizers[b]
China	500 mg Cr/kg fertilizers[c]
USA	0.6 per unit (1%) of Zn content[d]

Notes: [a] (BINI & BECH, 2014); [b] (MAPA, 2006); [c] (MCLAUGHLIN, 2004); [d] Federal rule applied for by-products recycled materials used as Zn fertilizers (MCLAUGHLIN, 2004)

In Brazil, according to the World Bank Group (WBG) (WBG, 2014) consumption of fertilizer per hectare per year is of 175.7 kg, which is the same as applying 0.017 kg/m² of fertilizer. Taking into consideration the limit of 200 mg of Cr per kg of fertilizer, it means that, at most, 3.4 mg/m² of chromium are applied to the soil per year. If the polymeric films produced in this work were applied in the soil and considering that these films degraded in the same soil, 0.9 mg/m² of chromium would be added to it, value calculated from Table 3 data. This amount of chromium released to the soil by protein/starch film may be reduced by reducing thickness of the film. It would not reduce the concentration of chromium in mg/kg of film, but it would reduce the mass of film applied in a certain area. Thickness reduction from 120 µm (thickness average of the protein/starch films studied in this work) to 30 µm (typical thickness of commercial films) would reduce from 0.9 to approximately 0.2 mg/m² the amount of chromium released to the soil by the use of protein/starch agricultural film mulches.

4 Conclusion

From the data presented in this work, it is possible to conclude that films produced from protein extracted from chromed leather waste, cornstarch and glycerol are feasible for use as agricultural mulch films. Water vapor transmission tests indicated that they reduce the amount of water evaporation, reducing the quantity of water used for irrigation. If degraded in the soil, the films would be a carbon and nitrogen source. Chromium concentration in the material is in accordance to international standards.

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