

Biodegradable and Edible Starch Composites with Fiber-Rich Lentil Flour to Use as Food Packaging

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Following the new eco-friendly technologies for food packaging, biodegradable composites with edible components as starch, glycerol, and lentil flour rich in fiber (0, 0.5 wt.% and 1.0 wt.%) are developed. The lentil flour, obtained from the residue of a commercial lentil protein extraction process, have micrometer size and, unlike typical lentil flour, have three times higher concentration of fiber. Its use leads to increments in the storage modulus, strength at break, and toughness of the composites, and to decreases in water vapor permeability, with respect to the matrix, showing that the additive can act as reinforcement for starch films. Composites with 0.5 wt.% of flour result in more flexibility due to their homogeneous dispersion in the matrix. All films are thermally stable up to 240 °C and biodegradable in vegetal compost after 4 weeks. These new composites are high promising for use as biodegradable and edible food coatings. They could enrich food nutritional value by the fiber-rich flour addition.

biodegradability and ability for replacing synthetic plastics, and have two fundamental conditions to satisfy the market necessities, low cost and high biodegradability. The effect of the component amount in a thermoplastic material and amylose/amylopectin in starches has been subject of study for years. According to the literature, flexibility increase and rigidity decrease when plasticizer or amylopectin concentration increase.^[8–10] Some disadvantage of starch films such as high water solubility and water permeability, and poor mechanical properties,^[11–15] making them not suitable for several food packaging applications.^[16] A solution using natural fillers as reinforcement of starch films in concentrations that ensure non-agglomeration could be found.^[17–28]

On other hand, in last decades, different kinds of additives such as antioxidants, antimicrobials, nutrients, or flavors were

incorporated in starch films to give them greater benefices.^[29–34] This, either to transfer their properties to the food they cover or to enrich the consumer if they want to eat the film. This for transfer their properties to the food they wrap and/or to enrich the consumer if they want to eat the film.

Lentils are natural legumes rich in fiber and their production and market sales are massive.^[28] Lentil flour is a good source of carbohydrates ($\approx 50\%$), fiber ($\approx 6.3\%$), and proteins ($\approx 26\%$), and contains essentials and no essential amino acids.^[36] In particular, fiber consumption in the daily diet provides many health benefits, such as reductions on the incidence of cardiovascular diseases, diabetes, colon cancer, obesity, and it could improve immune system functioning.^[37] According to Food and Drug Administration (FDA, 2017)^[30] and European Food Safety Authority (EFSA, 2017),^[31] the intake of dietary fiber recommended for adults is 25 g/day and 25–28 g/day, respectively. Rich fiber lentil flour are great promising to be implemented as additive in biodegradable materials for food packaging.^[35] Particularly, in the production, many lentils are discarded because they do not meet to some requirements such as shape or size, even when their properties keep. These discarded lentils could be used for others purposes such as additive of biopolymer based films, and take advantage of lentil wastes. Some researches in the literature studied lentil flour properties^[40] or lentil protein isolates^[41] and their use as raw material for edible films,^[35] however, the use of lentil flour as additive of thermoplastic starch films has not been investigated to date.

1. Introduction

Preservation of food products as long as possible and improvements in their added value to benefice people has been subject of great global interest in recent decades. In order to contribute to these yearnings, researchers, and packaging industries have been approached in developing materials with great mechanical resistant and low barrier properties, as well with antioxidant activity.^[1–3] Most of actual packaging materials derive from petroleum, which is a non-renewable resource, damaging the environment.^[4,5] According to Nova (2017),^[6] in 1960, the world produced 7 million tons of plastics and the prediction for 2020 is an increase of 540 million tons. A vast proportion of these are used to protect products from the food industry.^[7] Starch comes from many renewable sources and it is an excellent film forming material. Starch based films successfully demonstrated their fast

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The aim of this work was to investigate the effect of the incorporation of rich fiber lentil flour in thermoplastic starch films on the structure, physicochemical properties, and biodegradability. Thus, to achieve develop new edible film for use as food packaging, able to protect products from external damage, biodegrade within weeks, and high in fiber, contributing to consumers nutrition if they want to ingest it.

2. Experimental Section

2.1. Materials

All the raw materials used in the manufacture of the films were of food grade (FDA). Cassava starch (18 wt.% amylose and 82 wt.% amylopectin) was provided by Industria Del Maíz S.A. (Buenos Aires, Argentina) and NaOH and glycerol from commercial supplier (Sigma–Aldrich). Lentils (*Lens Culinaris*) were from the commercial market (*Ciudad del Lago*, Buenos Aires, Argentina).

2.2. Lentil Flour

Lentil flour was obtained following Swanson (1990) procedure,^[42] from the exploitation of the residue of commercial lentils (*Lens Culinaris*) after a process to extract a great protein fraction for other uses. Commercial lentils were hydrated with tap water and crushed to produce a suspension (paste). Then, the paste was dried at 70 °C for 24 h and grout to obtain a homogeneous flour. The flour was diluted in distilled water in proportion of 1:10 with magnetic stirring for 40 min. Then, 1N NaOH solution was incorporated to the system to increase its pH to 9 and kept for 4 h under refrigeration at 4 °C. This system was centrifuged at 3500 rpm for 30 min and the supernatant was removed for further processing. Precipitate was washed four times with distilled water to remove the remaining alkali and dried for 24 h at 70 °C. The final product, a fine powder, was the lentil flour used in this work.

2.3. Preparation of Films

Starch-lentil flour films were obtained by casting technique, following the methodology reported by Fama et al. (2010)^[10] with some modifications. This methodology involves a physical process (mechanical and thermal energy) keeping the edibility properties of the resultant materials. Matrix (TPS) consisted in a mix of starch (5 wt.%), glycerol (1.5 wt.%), and distilled water (93.5 wt.%). For composites, lentil flour in the desired concentration (0.5 and 1.0 wt.%, namely TPS-LP05 and TPS-LP1, respectively) was mixed with the components of the starch matrix in the same concentrations. All components were initially mixed in a magnetic stirrer with stainless heating plate at 25 °C for 40 min to form an homogeneous system. The mixture was subjected to heating at 3 °C min⁻¹ until 80 °C, ensuring starch gelatinization. Then, the gel was degassed using a vacuum pump for 7 min, deposited in polypropylene

boxes and dried in a forced convection oven at 50 °C for 24 h. The thickness of the obtained films was 0.30 ± 0.02 mm. All the developed films resulted edible because the nature of their components and the methodology used for their production (casting), which implies a physical process (mechanical and thermal energy), and not a chemical process. Film were conditioned for 2 weeks in desiccators at 25 °C and 56.7% relative humidity (equilibrium with a saturated NaBr solution) before being analyzed.

2.4. Characterizations

2.4.1. Bromatological Characterization of Lentil Flour

Lentil flour was analyzed using AOAC methods to determine protein fraction (AOAC, 1990a), dietary fiber (AOAC, 1995a), and ash (AOAC, 1990b),^[43] while carbohydrates were determined by subtracting. Protein fraction was obtained by acid digestion with sulphuric acid (H₂SO₄) using Micro-Kjedahl technique. In the case of soluble dietary fiber, dried lentil flour (m_t) was first gelatinized with thermally stable α -amylase and enzymatically digested with protease and amyloglucosidase, in order to remove protein and carbohydrates. Then, the system without protein and carbohydrates was precipitated by the addition of ethanol, filtered, washed, dried, and weighed (m_r).

Total dietary fiber was calculated using the equation (1):

$$\%FDT = \frac{m_r - P - C - B}{m_t} * 100 \quad (1)$$

Where

m_t = total mass of the lentil four sample in grams (g)

m_r = residue mass from m_t in grams (g)

P = protein mass in grams (g)

C = ash mass in grams (g)

B = blank = $m_rB - PB - CB$ (m_rB = blank residue, PB = blank protein from m_rB and CB = blank ash from m_rB) in grams (g).

In all cases, performances were done by duplicate.

2.4.2. Thickness Measurement

The thickness of films was determined using a manual micrometer Micromaster IP54 (TESA-Capasystem), taking 10 random positions of sample. The report results are the mean and statistic error.

2.4.3. Scanning Electron Microscopy (SEM)

The morphology of both lentil flour and films were studied using a scanning electron microscope with a Field Emission Gun (FEG) Zeiss DSM982 GEMINI. In the case of the films, samples were frozen under liquid nitrogen, fractured, glued on a support and coated with a thin sputtered platinum layer of ≈ 10 nm before the analysis.

2.4.4. Moisture Content (MC)

The moisture content (MC) of films was determined according to the gravimetric method proposed by the AOAC (1995a).^[43] Samples (≈ 0.5 g) of each system were subjected at 100°C for 24 h. The tests were performed in triplicate.

2.4.5. Thermogravimetric Analysis (TGA)

Thermogravimetric tests (TGA) of lentil flour and films were performed using a TGA/DTA (DTG-60 Shimadzu, Kyoto, Japan) instrument, under a nitrogen flow of 30 ml min^{-1} , at a heating rate of $10^\circ\text{C min}^{-1}$ and from 40 to 400°C . Aluminum capsules containing ≈ 10 mg of sample (flour dispersed in water in the ratio 1:10, or films) were tested. The weight loss curves in function of the temperature were reported. Three replicates of each sample were performed.

2.4.6. Fourier Transform Infrared Spectroscopy (ATR/FTIR)

The most important functional groups of the matrix and composites were analyzed by infrared spectra using a Nicolet spectrometer Series 6700 FTIR with attenuated total reflectance as accessory (ATR). Spectra were obtained with a resolution of 4 cm^{-1} as the average of 40 scans in the range of $4000\text{--}800\text{ cm}^{-1}$.

2.4.7. Water Vapor Permeability (WVP)

Water vapor permeability (WVP) of the films was performed using a modified ASTM E96-00 procedure^[17,44] at room temperature (25°C). Film samples of each system were sealed over circular acrylic cells containing CaCl_2 as desiccant (exposed circular area of $3.7 \times 10^{-4}\text{ m}^2$). Cells were stored in desiccators containing saturated NaCl solution (70% of RH). The weight of each cell was measured at the initial time and every 24 h for ten days, until constant mass. Changes in the weight difference were plotted as a function of time. WVP (g/msPa), was calculated using equation (2):

$$\text{WVP} = \frac{G \times e}{\Delta P \times A} \quad (2)$$

Where G (g s^{-1}) is the slope of plotted curve, e (m) the film thickness, ΔP (Pa) the saturation vapour pressure of water at ambient temperature and A (m^2) the exposed area.

2.4.8. Tensile Uniaxial Properties

Uniaxial tensile parameters were determined using an Instron dynamometer (Instron model TM1144, USA), at a rate of 1.2 mm min^{-1} and following ASTM D882-02 (2002)^[45] standard recommendations. Pieces of $25 \times 5\text{ mm}^2$ of each system were cut according to Famá et al (2005)^[1] to minimize the uneven stress distribution and to avoid the break in the area of contact with the grips. From nominal stress-strain curves, Young's modulus (E'),

strength at break (σ_b), strain at break (ϵ_b), and tensile toughness (T) values of all developed films were obtained. Ten tests per system were performed. Average and standard error of each parameter was reported.

2.4.9. Biodegradability

The biodegradability of the films was tested qualitatively. Procedures for soil burial were performed as described by González et al. (2016)^[46] and Medina Jaramillo et al. (2016).^[2] Pieces of samples of $2 \times 2\text{ cm}^2$ were weighed and buried in vegetal compost contained in plastics boxes of $22 \times 15 \times 8\text{ cm}^3$, at a depth of 5 cm from the surface in order to ensure the aerobic degradation. The soil was sieved to remove large clumps and plant debris. At different times, samples of each system were dried in oven at 50°C for 24 h and photographed to register their degradation.

2.4.10. Data Processing and Statistical Analysis

Data were analyzed through two-way ANOVA with 95% confidence level ($p < 0.05$) and Tukey test as post hoc test. The exposed results are the mean and the standard error of the mean. A "t" test for the difference of medias was applied to compared results.

3. Results and Discussions

3.1. Scanning Electron Microscopy (SEM) of Lentil Flour

In order to evaluate the morphology of lentil flour FE-SEM of lentil flour was made (Figure 1). As can be seen, the flour consisted on particles with oval form of ≈ 16 and $\approx 25\text{ }\mu\text{m}$ diameters. These characteristics are similar to that reported by Joshi et al. (2013),^[47] who showed particles of lentil flour between 10 and $45\text{ }\mu\text{m}$. On other hand, the particles presented smooth surfaces with only few adhering impurities fragments and did

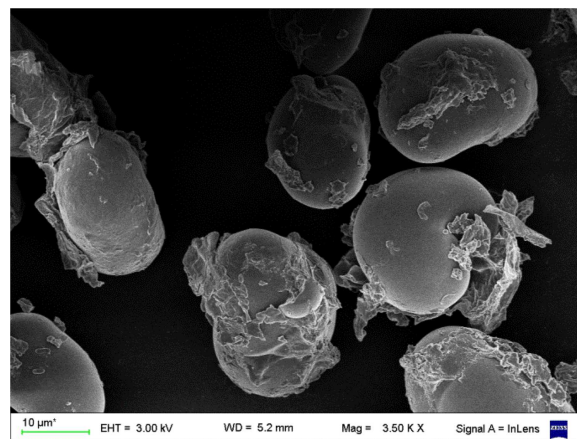


Figure 1. FE-SEM micrograph of lentil flour.

not show fissures on their surface, as reported by Sotomayor et al. (1999).^[48]

The composition of lentil flour (Table 1) revealed a high content in dietary fiber (≈ 19.8 wt.%), becoming three times higher than typical lentil flour reported in the literature.^[36,49] Then, if evaluate the fiber concentration on a film of $20\text{ cm} \times 30\text{ cm} \times 0.30\text{ mm}$ (weight of $19.2 \pm 0.8\text{ g}$), it can reach $\approx 1.9\text{ g}$ and $\approx 3.8\text{ g}$ in TPS-LP05 and TPS-LP1, respectively. Consequently, the intake of these films could contribute to the diet of the consumer, according to FDA (2017)^[38] and EFSA (2017),^[39] in 10–20% of the dietary fiber recommended per day. Relevant investigations about the effect of dietary fiber revealed its importance in human.^[50] Taking this into account the implementation of these films as food coating, even in small amounts, could contribute adding dietary fiber to the food product that cover. In the same way, if consumers ingest the food with the coating, it could collaborate even in slight percentages in their daily fiber.

3.2. Scanning Electron Microscopy (SEM) of Films

The images of the cryogenic fracture surface micrographs (FE-SEM) of the matrix and both composites are exposed in Figure 2. Matrix showed a soft surface without pores, typical of homogeneous thermoplastics films (Figure 2a).^[51,52]

In the composite containing the lowest concentration of lentil flour (TPS-LP05), a well-developed vein pattern could be observed (Figure 2b). This typically occurs in composites when the fillers that act as reinforcement are compatible with the matrix and are homogeneously dispersed.^[20] This effect could indicate that part of the flour did not dissolved in the water used for the film preparation, leaving particles that were homogeneously dispersed in the matrix. When the concentration of the rich-fiber lentil flour increased (TPS-LP1), the vein pattern was less marked and the structure tended to resemble the matrix but with some irregular areas (Figure 2c). This behavior was probably due to the possible agglomeration of the lentil flour microparticles when the concentration was high. It is known that when the amount of particles exceeds the percolation point, they tend to agglomerate^[13,20,26] and decreases in veins concentration are observed.

3.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the fiber-rich lentil flour, matrix and composites are exposed in Figure 3. In the lentil flour

Table 1. Lentil flour chemical composition.

| Parameter | Value |
|-------------------|------------------|
| Protein (%) | 12.04 ± 0.02 |
| Ash (%) | 0.90 ± 0.04 |
| Fat (%) | 2.16 ± 0.02 |
| Dietary fiber (%) | 19.8 ± 0.1 |
| Moisture (%) | 10.0 ± 0.1 |
| Carbohydrates (%) | 55.1 ± 0.2 |

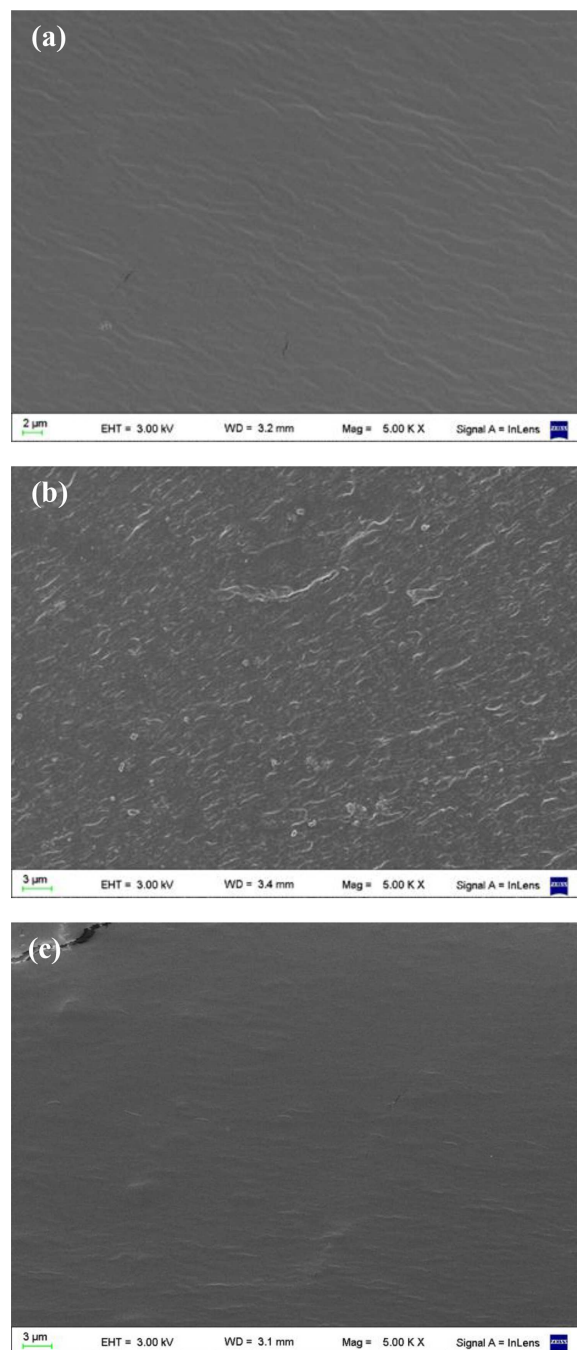


Figure 2. FE-SEM micrograph of the cryogenic fracture surface of: a) TPS, b) TPS-LP05, and c) TPS-LP1.

curve, two important thermal degradation processes (marked by mass loss steps) are observed (Figure 3d). One, until $\approx 100^\circ\text{C}$, which is due to water evaporation used in the suspension prepared to be tested (note that the system was 1:10, flour:water), and the other, between 27 and 350°C , which corresponds to the degradation of the components of the flour.

Three thermal degradation processes can show in the curves of the films (Figure 3a–c). The first, which corresponds to the evaporation of water and/or volatiles compounds,^[53] occurred

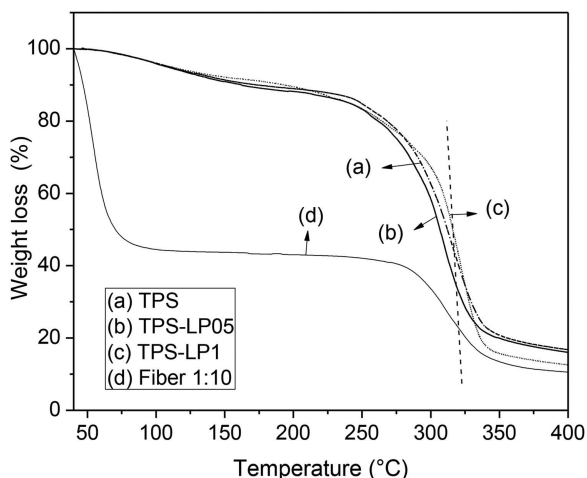


Figure 3. Thermogravimetric Analysis (TGA) of: (a) TPS, (b) TPS-LP05, (c) TPS-LP1, and (d) lentil flour.

between 40 and 150°C. The second, associated to the decomposition of the plasticizer (Glycerol), was between 150 and 220°C.^[2] The last process, with the highest weight loss, is related to the decomposition of starch when thermoplastic starch films are evaluated^[54,55] and can be observed between 250 and 350°C. The mass loss observed in all films around 100°C has not been affected by the use of the additive. In the step between 150 and 220°C, associated to the glycerol degradation, the composites presented a slightly higher mass loss with respect to the matrix. In those films, some hydroxyl groups of the starch interacted with the OH of the lentil flour, probably decreasing the hydrogen bond interactions between the glycerol and starch; therefore, more available glycerol to degrade is expectable.

In addition, composites showed a slight shift towards lower temperatures of the step between ≈ 250 and ≈ 350 °C with respect to the matrix, being ≈ 320 °C (TPS), ≈ 310 °C (TPS-LP05), and ≈ 315 °C (TPS-LP1). These results are reasonable considering the degradation temperature of the flour (Figure 3d), which occurred around 310°C. The fact that only one mass loss was detected could indicate compatibility between the lentil flour and the starch to form thermoplastic films.^[16] The great interaction of the lentil flour particles with the starch generated a catalytic effect, accelerating the degradation of the composites.^[12] It should be noted that this effect is slightly more notorious in the case of the composite with 0.5 wt.% of flour, indicating greater interactions between the flour and the starch when the concentration of the additive was the lowest. The fact that TPS-LP1 did not thermally degrade before TPS-LP05 can be also attributed to the possible lentil particles agglomerations, as suggested in the literature,^[53] which is consistent with SEM micrograph observations (Figure 2d).

3.4. ATR/FTIR Analysis

ATR/FTIR spectra of the matrix and the composites (Figure 4) presented typical characteristic bands of starch plasticized films. A peak around 3300 cm^{-1} , which corresponds to the stretching of OH group, belonging to starch, glycerol and water,^[46] two

between 2950 and 2850 cm^{-1} , associated with symmetric and asymmetric vibration CH stretch methylene group CH_2 , and other bands at ≈ 1640 , ≈ 1430 , and ≈ 1350 cm^{-1} assigned to the water adsorbed by starch molecules, were observed. No shifts of these bands after the lentil flour addition have been observed. This could be due, on one hand, because great amount of flour components are carbohydrates, similar to starch, and on the other hand, probably due to the compatibility between the flour and the starch in the composites. In addition, it could be also due to the very low concentration of the additive used in the films. According to the literature, lentil flour has an important peak between 3500 and 3300 cm^{-1} that corresponds to amines N–H stretching.^[56] This band is probably hidden in the band of OH groups in our materials. Furthermore, the main spectral features of lentils flour consist of other four intense bands located around 1163, 1408, 1550, and 1658 cm^{-1} .^[40] In particular, Carbonaro et al. (2008)^[40] reported two bands at around 1520 cm^{-1} , which corresponds to amide II (N–H bending) and at 1660 cm^{-1} , associated to amide I (C=O stretching).

3.5. Moisture Content

Moisture content decreased about 23% with the addition of the rich-fiber lentil flour in both concentrations, 0.5 and 1 wt.% (Table 2). This behavior is consistent with the investigations of starch-based composites with different micrometer size particles reinforcements.^[31] In our case, the decrease in moisture content in composites can be explained taking into account that the hydroxyl groups of the lentil flour could interact with the OH groups of starch but also with water molecules, decreasing the available OH groups.^[11,31]

3.6. Water Vapor Permeability (WVP)

An evident decrease in water vapor permeability of the films due to the addition of the lentil flour was observed (Table 2). The composites revealed decreases of 33% (TPS-LP05) and 43% (TPS-LP1) in WVP value compared to TPS. This can be

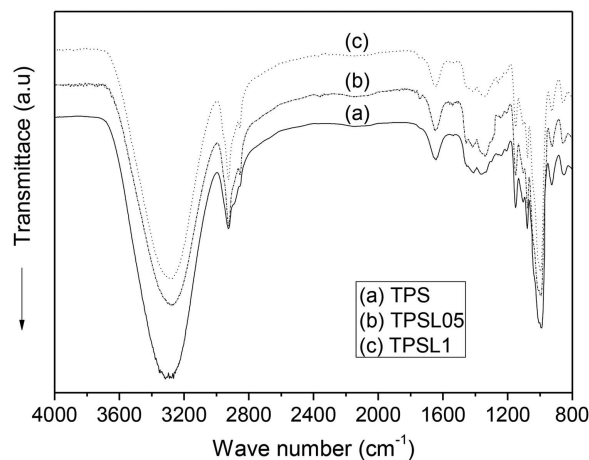


Figure 4. FTIR spectrum of matrix and composite materials.

Table 2. Moisture content (MC) and water vapor permeability (WVP) of matrix and composites.

| Film | MC (wt. %) | WVP (g msPa^{-1}) $\times 10^{-10}$ |
|----------|------------------------------|--|
| TPS | 30.1 \pm 0.1 | 2.81 \pm 0.05 |
| TPS-LP05 | 23.1 \pm 0.3 ^{a)} | 1.87 \pm 0.05 |
| TPS-LP1 | 23.0 \pm 0.2 ^{a)} | 1.61 \pm 0.05 |

^{a)} Similar letters in the same column indicate non-significant differences ($p < 0.05$).

attributed, on a one hand to the less water content, and on the other hand, to the tortuous path for the water molecules to pass through the film due the presence of the lentil flour microparticles, typical for composites.^[13,57,58] This behavior lead to the idea that the rich-fiber lentil flour acts as reinforcement of starch plasticized films. The decrease of WVP has great significance in terms of the use of these films as food coatings and packaging, because high barrier may decrease water vapor transference between the product and the environment.

3.7. Tensile Uniaxial Properties

Stresses (σ)–strain (ϵ) curves of the films, obtained under quasi-static uniaxial tensile conditions, are shown in **Figure 5**. As can be seen, all curves present two characteristic regions. One zone, at low strains, where the stress increased linearly with the strain (linear viscoelastic range), with values up to $\approx 4\%$ in the case of the matrix and TPS-LP05, and around 8% in the composite with 1 wt.% of lentil flour, occurs. Then, at higher strain, a nonlinear behavior happened without arriving to plastic deformation region until failure. In matrix and when only 0.5 wt.% of lentil flour was used, the deformation under an applied load was typical of ductile plastics in terms of the stress-strain curves.^[1] Both composites presented higher values of Young's modulus (E') and strength at break (σ_b) than matrix (**Table 3**). The increment in E' was around 14 and 640% for TPS-LP05 and TPS-LP1, respectively, while σ_b increased $\approx 32\%$ in TPS-LP05 and almost three times more in the

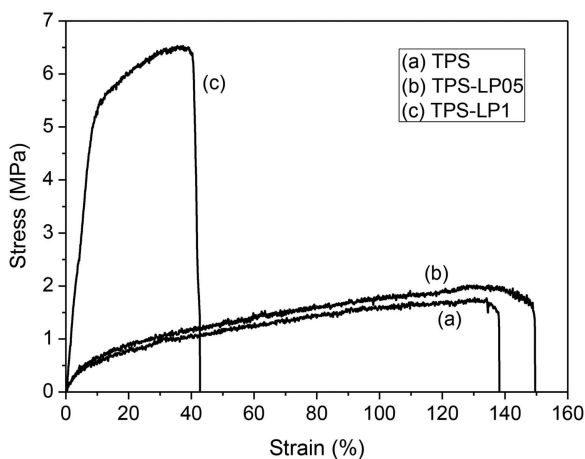


Figure 5. Stress (σ)–strain (ϵ) curves of: (a) TPS, (b) TPS-LP05, and (c) TPS-LP1.

case of TPS-LP1 than matrix. This behavior is in agreement with the results reported in the literature about starch films reinforced with different kinds of natural particles.^[12,13,58] In particular, Famá et al. (2010) reported increases of $\approx 70\%$ in E' and the stress at break with the addition of 1.5 wt.% of wheat bran in TPS films.^[13] The strain at break (ϵ_b) of TPS was at around 138% and, for the composite with 0.5 wt.% of lentil flour, it increased $\approx 8\%$. In the case of TPS-LP1, ϵ_b decrease respect to the matrix, reaching break in $\approx 42\%$ of deformation. It is known that the agglomeration of fillers in a composite tends to generate crack initiation, decreasing the tensile strength propagation through the material, and leading to decreases in the strain at break.^[59] According to SEM micrographs explanation, microparticle agglomerations could have occurred in the composite with high concentration of lentil flour, being expectable the decrease in ϵ_b of this composite with respect to the others films. Avérous et al. (2007),^[57] obtained similar behavior in starch composites with cellulose particles: increments in both strength and strain at break when the amount of particles was 0.5%, while decreases in ϵ_b with higher concentration of particles. Tensile toughness, calculated as the area under the stress-strain curves, also increased with the addition of the lentil flour, without significant differences between TPS-LP05 and TPS-LP1. It is important to note that when the concentration of the rich-fiber lentil flour was lower (0.5 wt.%), the film presented the best uniaxial tensile results since all parameters (E' , σ_b , ϵ_b , and T) increased respect to the matrix. This behavior is not frequently observed in the literature; some works reported increments in E' and strength at break but decreases in the strain break when a reinforcement is added.^[58,60] The increments of E' , σ_b , and toughness in uniaxial tensile properties of the composites demonstrated the possibility to use the lentil flour as reinforcement of starch plasticized films; and it is consistent with the decrease in WVP of composites (Table 2). The fact that TPS-LP05 had the best strain at break is coherent to the homogeneous dispersion of the flour within the starch, which it was concluded by FE-SEM micrographs (Figure 2b). The modulus and tensile strength of the films resulted lower than those of conventional plastics used as food coating or packaging such as polyethylene or polystyrene (σ_b around 20–30 MPa and 30–50 MPa, respectively),^[61,62] and polymers such as polylactic acid (PLA) or polyvinyl alcohol (PVA)^[63,64]. However, the first cases are synthetic, so they biodegrade in long times and can be harmful to humans, while PLA and PVA take more time to biodegrade than starch and are not edible.^[65,66] The mechanical parameters of the films are of the order of those reported in the literature.^[11,12,67] In particular, Slavutsky et al. (2014) reported results of strength at break of around 2.8 MPa for thermoplastic starch films and Müller et al.

Table 3. Uniaxial tensile parameters of matrix and composites films.

| Film | E' (MPa) | σ_b (MPa) | ϵ_b (%) [$\pm 3\%$] | T (J m^{-3}) $\times 10^6$ |
|----------|-----------------|------------------|--------------------------------|---------------------------------------|
| TPS | 0.75 \pm 0.05 | 1.6 \pm 0.2 | 138 | 1.7 \pm 0.1 |
| TPS-LP05 | 0.86 \pm 0.05 | 2.1 \pm 0.2 | 149 | 2.1 \pm 0.2 ^{a)} |
| TPS-LP1 | 4.8 \pm 0.3 | 6.3 \pm 1.1 | 42 | 2.3 \pm 0.2 ^{a)} |

^{a)} Similar letters in the same column indicate non-significant differences ($p < 0.05$).

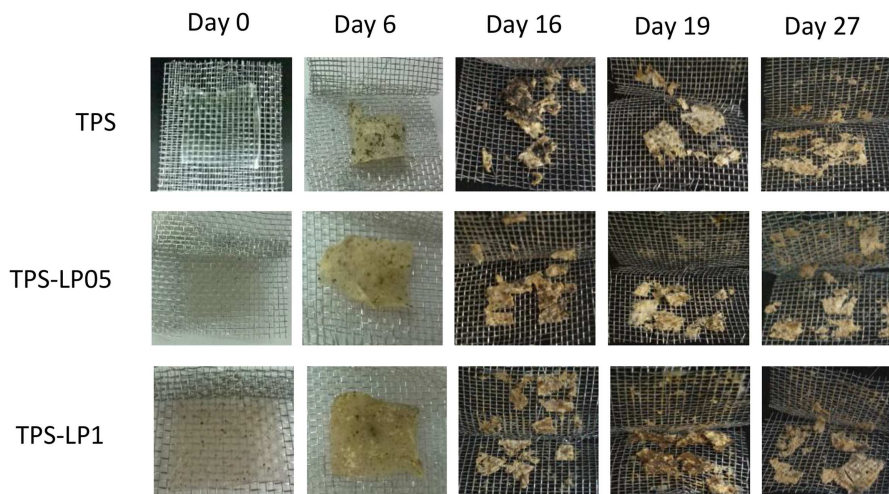


Figure 6. Macroscopic appearances of the biodegradation in vegetal compost of matrix and composites in function of the time.

(2009) of ≈ 1.59 and ≈ 1.39 MPa for starch matrices stabilized in 58 and 75% of relative humidity, respectively.

3.8. Biodegradability

The biodegradability of all films was evaluated qualitatively. **Figure 6** shows the images of samples of each system after buried in vegetal compost at different times. On day 6 all films noticeably changed their tonality losing their outline shape but composites were preserved a little more whole, resisting slightly more their degradation. Significant degradation in all cases began after day 19, showing marked disintegration of the films. All systems exhibited almost entirely degradation after buried in vegetal compost for 27 days. No significant differences with the addition of lentil flour were observed at that moment.

Taking into account that lentil flour is from vegetable origin (it can be readily attacked by microorganism), and that most of its components are the same of those of starch (e.g., carbohydrates), the similar time of biodegradability of all films was expectable. Biodegradability in soil occurs due to the action of biological agents, such as plants, animals, microorganisms and fungi, under natural environmental conditions. The fast biodegradability of the films probably was due to their organic nature and edibility characteristic that contribute as a food substrate for the reproduction of microorganisms.^[68]

As it was previously discussed, the studied films are edible due to their components and the not toxics involved processes.^[69] If they are also readily biodegradable, they have significant possibilities to be used as packaging and/or coating of food products, contributing to both environment and consumers nutrition if they decided to ingest them.

4. Conclusions

Starch films with different concentrations of lentil flour rich in fiber derived from commercial lentils (0, 0.5 wt.%, and 1.0 wt.%) were prepared by casting. The lentil presented two significant characteristics: it has three times higher content of dietary fiber

than typical lentil flour and consists on micrometer size particles. The incorporation of the flour led to increments in Young's modulus, strength at break and toughness of the composites, demonstrating to be an excellent additive to use as reinforcement of starch-glycerol films, making it more resistant and with capacity to protect food products from blows and damages. The composite with 0.5 wt.% of the additive also revealed higher strain at break than starch matrix, leading to a more resilient and flexible coating. Water vapor permeability was also improved with the addition of lentil flour, showing decreases up to $\approx 43\%$ with 1 wt.% of the additive. All films resulted thermally stable until 240°C and completely biodegraded in vegetal compost in 3 weeks.

Based on the results, those new edible and biodegradable composites based on thermoplastic starch and rich-fiber lentil flour are very promising to be used as coatings to protect food products and contribute to consumer's nutrition when ingesting them.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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- [1] L. Famá, A. M. Rojas, S. Goyanes, L. Gerschenson, *LWT Food Sci. Technol.* **2005**, *38*, 631.
- [2] C. Medina-Jaramillo, T. J. Gutiérrez, S. Goyanes, C. Bernal, L. Famá, *Carbohydr. Polym.* **2016**, *151*, 150.
- [3] T. A. Nascimento, V. Calado, C. W. P. Carvalho, *Food Res. Int.* **2012**, *49*, 588.
- [4] C. R. Álvarez-Chávez, S. Edwards, R. Moure-Eraso, K. Geiser, *J. Clean. Prod.* **2012**, *23*, 47.
- [5] T. Garrido, A. Etxabide, I. Leceta, S. Cabezudo, K. de la Caba, P. Guerrero, *J. Clean Prod.* **2014**, *64*, 228.
- [6] Nova. **2016**, <http://www.nova.org.au/earth-environment/future-plastics>. (Accessed January 2017).
- [7] Looking Ahead: Food and Beverage Packaging Trends in 2015 and 2016. <https://www.comar.com/news-room/looking-ahead-food-and-beverage-packaging-trends-in-2015-and-2016> (Accessed 2016).
- [8] F. Xie, P. J. Halley, L. Avérous, *Prog. Polym. Sci.* **2012**, *37*, 595.
- [9] N. L. García, L. Famá, A. Dufresne, M. Aranguren, S. Goyanes, *Food Res. Int.* **2009**, *42*, 976.
- [10] B. Montero, M. Rico, S. Rodríguez-Llamazares, L. Barral, R. Bouza, *Carbohydr. Polym.* **2017**, *157*, 1094.
- [11] L. Avérous, C. Fringant, L. Moro, *Polymer* **2001**, *42*, 6565.
- [12] A. A. S. Curvelo, A. J. F. de Carvalho, J. A. M. Agnelli, *Carbohydr. Polym.* **2001**, *45*, 183.
- [13] L. Fama, A. M. B. Q. Bittante, P. J. A. Sobral, S. Goyanes, L. N. Gerschenson, *Mater. Sci. Eng. C* **2010**, *30*, 853.
- [14] A. Gennadios, A. H. Brandenburg, J. W. Park, C. L. Weller, R. F. Testin, *Ind. Crops Prod.* **1994**, *2*, 189.
- [15] T. J. Gutiérrez, N. J. Morales, E. Pérez, M. S. Tapia, L. Famá, *Food Packaging and Shelf Life* **2015**, *3*, 1.
- [16] X. Ma, J. Yu, J. F. Kennedy, *Carbohydr. Polym.* **2005**, *62*, 19.
- [17] L. Famá, P. G. Rojo, C. Bernal, S. Goyanes, *Carbohydr. Polym.* **2012**, *87*, 1989.
- [18] M. Lamanna, N. J. Morales, N. L. García, S. Goyanes, *Carbohydr. Polym.* **2013**, *97*, 90.
- [19] S. Mali, M. V. E. Grossmann, M. A. García, M. N. Martino, N. E. Zaritzky, *Carbohydr. Polym.* **2004**, *56*, 129.
- [20] N. J. Morales, R. Candal, L. Famá, S. Goyanes, G. H. Rubiolo, *Carbohydr. Polym.* **2015**, *127*, 291.
- [21] F. Zia, K. M. Zia, M. Zuber, S. Kamal, N. Aslam, *Carbohydr. Polym.* **2015**, *134*, 784.
- [22] S. Mali, M. V. E. Grossmann, F. Yamashita, *Semin Cienc. Agrar.* **2010**, *31*, 137.
- [23] C. Silvestre, D. Duraccio, S. Cimmino, *Prog. Polym. Sci.* **2011**, *36*, 1766.
- [24] X. Tang, S. Alavi, *Carbohydr. Polym.* **2011**, *85*, 7.
- [25] R. Kumar, T. Singh, H. Singh, *Int. J. Adv. Eng. Res. Appl.* **2015**, *1*, 21.
- [26] P. Oymaci, S. A. Altinkaya, *Food Hydrocolloids* **2016**, *54*, 1.
- [27] Z. Qazanfarzadeh, M. Kadivar, *Int. J. Biol. Macromol.* **2016**, *91*, 1134.
- [28] M. o. World, **2016**, Lentil producing countries. <http://www.mapsofworld.com/world-top-ten/lentil-producing-countries.html>
- [29] P. Alzate, S. Miramont, S. Flores, L. Gerschenson, *Starch/Stärke* **2017**, *69*, 1600261.
- [30] Na. Ji, Y. Qin, T. Xi, L. Xiong, Q. Sun, *Starch/Stärke* **2017**, *69*, 1.
- [31] C. M. O. Müller, J. B. Laurindo, F. Yamashita, *Food Hydrocolloids* **2009**, *23*, 1328.
- [32] L. Lendvai, J. Karge-Kocsis, A. Kmetty, S. X. Drakopoulos, *J. Appl. Polym. Sci.* **2016**, *133*, 42397 (1-8).
- [33] C. A. Teacă, R. Bodîrlău, I. Spiridon, *Carbohydr. Polym.* **2011**, *93*, 307.
- [34] S. L. M. E. Halal, G. P. Bruni, J. A. Evangelho, B. Biduski, F. T. Silva, A. R. G. Dias, M. Mello Luvielmo, *Starch/Stärke*. **70**, 1700115 (1-10). <https://doi.org/10.1002/star.201700115>
- [35] F. Bamdad, A. H. Goli, M. Kadivar, *Food Res. Int.* **2006**, *39*, 106.
- [36] D. Shuang-kui, J. Hongxin, Y. Xiuzhu, J. Jay-lin, *LWT Food Sci. Technol.* **2014**, *55*, 308.
- [37] D. King, A. Mainous, C. Lambourne, *J. Acad. Nutr. Diet.* **2012**, *112*, 642.
- [38] Food and Drug Administration-FDA. <https://www.fda.gov/downloads/Food/NewsEvents/WorkshopsMeetingsConferences/UCM403514.pdf>. (Accessed March 2017).
- [39] European Food Safety Authority-EFSA. <https://www.efsa.europa.eu/en/topics/topic/dietary-reference-values-and-dietary-guidelines>. (Accessed March 2017).
- [40] M. Carbonaro, P. Maselli, P. Dore, A. Nucara, *Food Chem.* **2008**, *108*, 361.
- [41] M. Jarpa-Parra, F. Bamdad, Y. Wang, Z. Tian, F. Temelli, J. Han, L. Chen, *LWT Food Sci. Technol.* **2014**, *57*, 461.
- [42] B. G. Swanson, *J. Am. Oil Chem. Soc.* **1990**, *67*, 276.
- [43] AOAC. *Official Methods of Analysis*. Official Methods of Analysis. Association of Official Analytical Chemists, Washington, DC **1995**, pp. 934.05–17ed.
- [44] ASTM-E96–00. Standard test methods for water vapor transmission of materials. *Am. Soc. Testing Mater.* West Conshohocken, USA **1996**.
- [45] ASTM-D882-02. Standard test method for tensile properties of thin plastic sheeting official methods of analysis, West Conshohocken, USA **2002**.
- [46] P. Gonzalez Seligra, C. Medina Jaramillo, L. Famá, S. Goyanes, *Carbohydr. Polym.* **2016**, *138*, 66.
- [47] M. Joshi, P. Aldred, S. McKnight, J. F. Panozzo, S. Kasapis, R. Adhikari, B. Adhikari, *Carbohydr. Polym.* **2013**, *92*, 1484.
- [48] C. Sotomayor, J. Frias, J. Fornal, J. Sadowska, G. Urbano, C. Vidal-Valverde, *Starch/Stärke* **1999**, *51*, 152.
- [49] Z. Kohajdová, J. Karovičová, M. Magala, *Chem. Pap.* **2013**, *67*, 398.
- [50] M. Chandalia, A. Garg, D. Lutjohann, K. von Bergmann, S. M. Grundy, L. J. Brinkley, *N. Engl. J. Med.* **2000**, *342*, 1392.
- [51] L. Castillo, O. López, C. López, N. Zaritzky, M. A. García, S. Barbosa, M. Villar, *Carbohydr. Polym.* **2013**, *95*, 664.
- [52] K. M. Dang, R. Yoksan, *Carbohydr. Polym.* **2016**, *150*, 40.
- [53] J. Raabe, A. D. S. Fonseca, L. Bufalino, C. Ribeiro, M. A. Martins, J. M. Marconcini, G. H. D. Tonoli, *J. Nanomater.* **2015**, *2015*, 6.
- [54] F. K. V. Moreira, D. C. A. Pedro, G. M. Glenn, J. M. Marconcini, L. H. C. Mattoso, *Carbohydr. Polym.* **2013**, *92*, 1743.
- [55] V. A. Álvarez, R. A. Ruseackaite, A. Vázquez, *Polym. Degrad.* **2006**, *91*, 3156.
- [56] M. Basu, A. K. Guha, L. Ray, *J. Env. Chem. Eng.* **2015**, *3*, 1088.
- [57] L. Avérous, *Compos. Interfaces* **2007**, *14*, 787.
- [58] A. M. Slavutsky, M. A. Bertuzzi, *Carbohydr. Polym.* **2014**, *110*, 53.
- [59] R. Jumaidin, S. Sapuan, M. Jawaid, M. Ishak, J. Sahari, *Int. J. Biol. Macromol.* **2017**, *99*, 265.
- [60] M. Pereda, G. Amica, I. Rácz, N. E. Marcovich, *J. Food Eng.* **2011**, *103*, 76.
- [61] S. Lin, M. A. Anwer, Y. Zhou, A. Sinha, L. Carson, H. E. Naguib, *Compos. Part B-Eng.* **2018**, *132*, 61.
- [62] K. Suresh, M. Kumar, G. Pugazhenthir, R. Uppaluri, *J. Sci.: Adv. Mater. Devices* **2017**, *2*, 245.
- [63] S. Mallakpour, F. Motirasoul, *Prog. Org. Coat.* **2017**, *103*, 135.
- [64] Z. Zhu, H. Wu, C. Ye, W. Fu, *J. Nat. Fibers* **2017**, *14*, 875.
- [65] S. Maiti, D. Ray, D. Mitra, *J. Polym. Environ.* **2012**, *20*, 749.
- [66] G. Ozkoc, S. Kemaloglu, *J. Appl. Polym. Sci.* **2009**, *114*, 2481.
- [67] C. A. Teacă, R. Bodîrlău, I. Spiridon, *Carbohydr. Polym.* **2013**, *93*, 307.
- [68] P. Shah, R. Prajapati, P. Singh, *Eur. J. Adv. Eng. Technol.* **2017**, *4*, 282.
- [69] O. Paredes-López, C. Ordorica-Falomir, M. R. Olivares-Vázquez, *J. Food Sci.* **1991**, *56*, 726.