# Casting and extrusion processes to produce bio-based plastics using cassava starch modified by the dry heat treatment (DHT)

Carla I.A. La Fuente[a*], Larissa do Val Siqueira[b,d], Pedro Esteves Duarte Augusto[a,d,**], and Carmen C. Tadini[b,c,d]

[a] Universidade de São Paulo, School of Agriculture Luiz de Queiroz (ESALQ), Department of Agri-food Industry, Food and Nutrition (LAN), Piracicaba, SP, 13418-900, Brazil

[b] Universidade de São Paulo, Escola Politécnica, Department of Chemical Engineering, Main *Campus*, São Paulo, SP, 05508-010, Brazil

[c] Universidade de São Paulo, Food Research Center (FoRC/NAPAN),SP, Brazil

[d] University of São Paulo (USP), Food and Nutrition Research Center (NAPAN), São Paulo, SP, Brazil

***Corresponding author:** C.I.A. La Fuente; Universidade de São Paulo, School of Agriculture Luiz de Queiroz (ESALQ), Department of Agri-food Industry, Avenida Pádua Dias, 11, Piracicaba, SP, 13418-900, Brazil. (carlalfa@usp.br)

** Present affiliation of PED Augusto: Université Paris-Saclay, CentraleSupélec, Laboratoire de Génie des Procédés et Matériaux, SFR Condorcet FR CNRS 3417, Centre Européen de Biotechnologie et de Bioéconomie (CEBB), 3 rue des Rouges Terres 51110 Pomacle, France.

**Abstract**

Although the number of studies focused on bio-based plastics is constantly rising, an important challenge to overcome is migrating from casting to extrusion, an industrially scalable method of production. In this work, we studied starch modification by dry heating treatment (DHT) and the production of cassava starch films or sheets, by casting or extrusion processes, respectively. The molecular changes promoted by the DHT process resulted in a new matrix. Furthermore, the slower drying in casting, and the faster drying in extrusion, promoted different molecular arrangements, which affected the material performance. The main results showed that DHT for 4 h in cassava starch produced bio-based plastics with increased mechanical properties and opacity while decreasing water permeability, moisture content and light transmittance. In conclusion, DHT showed to be an interesting alternative to produce biodegradable plastics with potential use in different industries.

**Keywords:** films, sheets, biodegradable composites, biodegradable plastics, biobased plastics

## Nomenclature

| | |
|---|---|
| *A* | area ($m^2$) |
| *DHT*_2h | dry-heating treatment for 2 h |
| *DHT*_4h | dry-heating treatment for 4 h |
| *E* | Young's Modulus (MPa) |
| *p* | pressure (kPa) |
| *RC* | Relative Crystallinity |
| *t* | time (h) |
| *TS* | Tensile Strength (MPa) |
| *WVP* | Water Vapor Permeability ($g \cdot mm/m^2 \cdot day \cdot kPa$) |
| *x* | thickness (mm) |
| *Y* | opacity (%) |

**Subscripts**

| | |
|---|---|
| *b* | black standard |
| *w* | white standard |

**Greek**

| | |
|---|---|
| ε | elongation at break (%) |

## 1. Introduction

Packaging developed from renewable sources is gaining increasing attention, but to substitute conventional plastics deriving from petroleum is currently a challenge. In fact, biopolymer films rarely have a competitive edge against synthetic plastics (Bora and Mishra, 2016). In this sense, some alternatives are being proposed to overcome their limitations, such as polymer modification, reinforcement with nanoparticles, blend of polymer matrices and multilayer strategies (Siqueira et al., 2020).

Starch is one of the most used biopolymers to obtain biodegradable plastics, due to aspects such as availability, costs, and efficiency. However, the native starches are limited by nature and the properties of the plastics obtained fall short. Among the different types of starch modifications, dry heating treatment (DHT) is a simple physical technique with the potential to increase starch performance: it does not generate effluents to be treated and the products obtained do not present traces of chemical components, therefore making it a "green technology" (Maniglia et al., 2020; Maniglia et al., 2021). According to these studies, starch molecules are oxidized during dry heating treatment to produce carbonyl groups; nevertheless, this oxidation was not drastic enough to produce carboxyl groups. Moreover, molecular depolymerization occurred mainly for the intermediate size molecules, forming two well-defined groups with larger and smaller molecules. All these modifications change the tendency of the molecule's re-association and their interactions. To our knowledge, few studies in the literature focused on the production and characterization of films from dry heated starches (Freitas et al., 2021; Gao et al., 2017; Li et al., 2008) – while there are many related to the heat moisture treatment (HMT).

Moreover, most of the studies are conducted with the lab-scale casting technique as the production method. Although it is a well-known method characterized by its simplicity, there are challenges to overcome when planning to scale up this technology, such as the long processing time and the need to evaporate large amounts of solvents (Siqueira et al., 2020). In turn, extrusion is the technology most used to produce plastics at the industrial level, with a wide variety of thicknesses and thus a promising approach to produce bio-based plastics. Several studies are reported in the literature using different starch matrixes, e.g. corn (Dean et al., 2007), potato (Thuwall et al., 2006), cassava (Huntrakul et al., 2020), cassava modified by acetylation, hydroxypropylation, or oxidation (Zanela et al., 2020) and mixtures of native (Zanela et al., 2018) and cationic (Wang et al., 2017) cassava starches with other polymers e.g. Polyvinyl alcohol. However, there is no study in the literature on the production of plastics by extrusion based on starches modified by dry-heating technology.

Moreover, few studies compare both casting and extrusion technologies considering different matrices e.g., gelatin (Andreuccetti et al., 2012; Park and Whiteside, 2008); and a mixture of gelatin and commercial maize starch (Fakhouri et al., 2013) or commercial cassava with lentil protein (Ochoa-Yepes et al., 2019).

Therefore, this study is the first to report the production and characterization of cassava starches films and sheets, priorly modified by the dry heating treatment (DHT), focusing on comparing both technologies and correlating the material characteristics with the starch modification processes.

## 2. Material and Methods

### *2.1.Materials*

Native cassava starch (Amilogill 1500, moisture content of 12.0 g/100 g) was provided by Cargill Agrícola - Brazil. Samples of 50 g of cassava starch were distributed into aluminum foil envelops (30 x 30) $cm^2$ and then set in a hot-air convective oven

(FABBE-PRIMER, model MOD.219, Brazil), in which dry heating treatment (DHT) was performed at 130 °C for 2 h or 4 h according to Maniglia et al. (2020), then cooled, grounded and, sieved (250 mm). The starch dry-heated for 2h (*DHT*_2h, moisture content of 6.8 g/100 g) or 4h (*DHT*_4h moisture content of 6.7 g/100 g) were packaged and stored, at room temperature, until further use. Glycerol P.A. grade (Sigma-Aldrich, Brazil) and distilled water were also used for plastic production.

### *2.2. Starch characterization*

The complete characterization of modified starches was performed by Maniglia et al. (2020). Even so, gels were produced from the starches obtained to evaluate and compare them with previous literature. A suspension containing 10.7 g/100 g of cassava starch (native and DHT modified) was homogenized for 10 min with a magnetic stirrer (GEHAKA, HU-30/2, Brazil), followed by heating at ~95 °C in a jacked glass reactor with water recirculation for 20 min, then rested in cups (40 mm diameter × 20 mm height) and kept at 5 °C. After 24 h, the gel firmness was evaluated through a puncture assay to a distance of 10 mm using a cylindrical probe P/6 (d = 6 mm) at 1 $mm \cdot s^{-1}$ in a texture analyzer TA TX Plus (Stable Micro Systems Ltd., Surrey, UK) with a load cell of 5 kgf (49 N). The firmness was expressed by the energy required to penetrate the gel (obtained by integrating the curve of force *versus* penetration depth).

### *2.3. Bio-based plastic production*

#### *2.3.1. Casting process*

The casting process was based on our previous study (La Fuente et al., 2019). A suspension of 5 g/100 g of starch (native, *DHT*_2h or *DHT*_4h) was homogenized for 10 min with a magnetic stirrer (GEHAKA, HU-30/2, Brazil). Then, it was heated for 45 min until starch gelatinization, which occurred at ~70 °C. Glycerol was added as the plasticizer (43.1 g/100 g of starch) and then heated for 15 min more under agitation. Next, the filmogenic solution was ultrasonicated for 30 min at 70 ºC (154 W, 25 kHz; UNIQUE, model USC-1850, Brazil). Finally, it was poured into acrylic Petri dishes (0.15 g/cm$^2$) and dried at 35 °C for ~ 12 h in a hot-air convective oven (NOVA ÉTICA, model 410/4, Brazil).

### *2.3.2. Extrusion process*

The formulation for extrusion was set to maintain the same starch/glycerol proportion of the casting, although a different proportion of water was needed, which was based on Vedove et al. (2021).

Pre-mixes of starch (native, *DHT*_2h and *DHT*_4h), glycerol (43.1 g/100 g of starch) and water (25.9 g/100 g of starch) were homogenized in a mixer (Brastemp, Kitchen Aid 525 Brazil) and then extruded in a co-rotating twin-screw extruder (Process 11, Thermo Fisher Scientific - Germany) L/D 40, and 11-mm screw diameter to produce pellets. The premixes were fed through a double screw feeder (Volumetric Minitwin Process 11, Brabender, Germany), at a feed rate of 0.05 kg/h and a thread speed of 80 rpm. The temperature profile to obtain the pellets from the feed zone (1) to the extrudate outlet (zone 8) was (60, 75, 90,100,110, 110, 105, 100) °C based on the study reported by Vedove et al. (2021), with some modifications. Then, the cylindrical material obtained was cut into pieces of 2 mm to obtain the pellets.

To fabricate the sheets, the pellets were fed from a conical feeder (Kulturstrasse 55-73, Brabender, Germany), at a flow rate of 0.2 kg/h to the same co-rotating twin-screw extruder (Process 11, Thermo Fisher Scientific - Germany). The sheets were obtained by the extrusion process using the same temperature profile (60, 75, 90,100, 110, 110, 105, 100 °C), the die (3 cm x 1 mm) with the mold for forming the sheet at 105 °C and the thread speed at 80 rpm.

*2.4.Bio-based plastics characterization*

The materials from the casting and extrusion processes were conditioned for 7 days in desiccators (75 % RH) at room temperature (~ 25 °C) and then evaluated through their morphology, structure, mechanical, physical and thermal characteristics.

*2.4.1. Morphology*

Bio-based plastics were visualized by both scanning electron microscopy (SEM) and atomic force microscopy (AFM).

For SEM, the materials were coated with 10-nm platinum and observed using the microscope (FEI, model Quanta 600FEG, Netherlands) at 15 kV. The magnification for surface images was 350x with insets at 1000x, for cross-section images at 130x with insets at 600x (sheets) and 2500x with insets at 5000x (films).

The materials were also analyzed by AFM (Multimode 8, Bruker, UK) at a scan speed of 1.0 Hz. The treatment of the images was performed through the Nanoscope Analysis 1.50 software (Bruker, UK). The arithmetic average of the surface height deviations ($R_a$) and the root mean square average of height deviations ($R_q$) were calculated according to Eq. (1) and (2).

$$R_q = \sqrt{\frac{\sum z_i^{2}}{N}} \quad (1)$$

$$R_a = \frac{1}{N}\sum_{j=1}^{N} |z_j| \quad (2)$$

wherein: $z$ is the peak to valley difference in height values within the analyzed region, and $N$ is the number of points within the box cursor (during the image capture).

#### *2.4.2. Crystallinity*

The crystallinity of the materials was analyzed through an X-ray diffractometer (PANalytical, model X'Pert PRO, Netherlands) operating at 45 mA, and a voltage of 40 kV. The scanning rate was 0.02°/s with 2Θ angles varying between 2° to 40°. The software Origin 2020 was employed for data analyses (OriginLab Corporation, Massachusetts, USA).

#### *2.4.3. Fourier-transform infrared (FTIR) analysis*

The films and sheet spectra were investigated by Fourier-Transform Infrared Spectroscopy (Pekin Elmer Frontier IR-4700, USA) in attenuated total reflectance (ATR) mode using a diamond ATR crystal at a wavenumber range from 540 to 4000 $cm^{-1}$; 32 scans were recorded per sample.

#### *2.4.4. Mechanical Properties*

The thickness was determined at five random positions using a digital micrometer (precision of 0.001 mm) (MITUTOYO, Japan).

The mechanical properties for the bio-based plastics were evaluated for ten strips (100 mm x 25 mm) of each formulation through a uniaxial tensile assay, according to ASTM D882-12 - Standard Method (ASTM, 2012). Tensile strength (*TS*) and percent elongation at break (ε) were evaluated using the A/TGT self-tightening roller grips fixture on a texture analyzer (TAXT2i Stable Micro Systems, UK) with a load cell of 5 kgf (49 N) at a crosshead speed of 1 $mm \cdot s^{-1}$. Young's modulus ($E$) was calculated as the slope of the initial linear portion of the stress versus strain curve.

#### *2.4.5. Water vapor permeability*

The water vapor permeability (WVP) of films was determined through the gravimetrical method according to the ASTM E96/E96M-16 Standard Method (ASTM, 2013b), in triplicate. The bio-based plastics were placed in circular permeation cells containing silica gel and then placed in a desiccator (75 % RH) and at a temperature of 25 °C. The weight gain was recorded hourly for 8 h and the WVP was calculated according to Eq. (3).

$$WVP = \frac{\Delta m \cdot x \cdot 24}{\Delta t \cdot A \cdot \Delta p} \qquad (3)$$

wherein: $\Delta m/\Delta t$ is the moisture gain per unit of time ($g \cdot h^{-1}$); $A$ is the film area exposed to permeation ($4.9 \cdot 10^{-4}$ $m^2$); $x$ is the film thickness (mm); $\Delta p$ is the vapor pressure difference (kPa) of the atmosphere over silica gel and pure water.

### *2.4.6. Wettability*

The bio-based plastic wettability was determined by the measurement of the contact angle with water, according to ASTM D7334 − 08 Standard Methods (ASTM, 2013) thought an OCA15- Dataphysiscs (OCA 15, Dataphysiscs, Germany). The contact angle was defined as the average of six angle measurements quickly carried out due to water vaporization.

### *2.4.7. Moisture content*

The bio-based plastic moisture was determined according to Gontard et al. (1993) in an oven at 105 °C until a constant mass was reached (~24 h).

### *2.4.8. Opacity*

The bio-based plastic opacity was determined, in triplicate, with the CIELab scale ($L^*$, $a^*$, $b^*$), using a colorimeter (HUNTERLAB, model ColorQuest XE, USA). The opacity ($Y$) was determined using Eq. (4).

$$Y = \frac{Y_b}{Y_w} \qquad (4)$$

wherein: $Y_b$ is the opacity on the black standard and, $Y_w$ is the opacity on the white standard.

#### *2.4.9. Light Transmittance*

UV to a visible light transmission of the materials was measured with a spectrophotometer from 200 nm to 800 nm (FEMTO, model 700 Plus, Brazil).

#### *2.4.10. Thermogravimetric analysis (TGA)*

The thermogravimetric analysis was performed using a thermal analyzer (TA Instrument model TGA-Q500 V20.13, EUA), using ~ 10 mg of samples, which were heated from 25 °C to 700 °C, at a rate of 10 °C/min under nitrogen flow.

### *2.5. Statistical analyses*

Experimental data was evaluated through a Multifactor Analysis of Variance (ANOVA), applying Tukey`s test ($p < 0.05$) through Statgraphics Centurion XV software (StatPoint, Inc., USA).

## 3. Results and Discussion

Figure 1 presents the firmness and visual aspect of the native cassava starch gels and those produced with the modified starches (DHT for 2 h and 4 h). The dry heating treatment produced several changes in the structure of cassava starch, affecting the molecular interaction and the properties obtained: for instance, the DHT process increased the firmness of the gel, which is easily visualized (Fig. 1) as described previously in Maniglia et al. (2020). However, the behavior of the starches obtained for bio-plastic production was still unknown – being evaluated in the present work.

Figure 2 presents the visual aspect of the materials produced by casting and extrusion. For the extruded materials, the cylinders obtained before pelletizing are also presented. The different aspects of both plastics can be easily visualized: while the casting materials are transparent and thinner (with ~ 0.10 mm), extruded materials look opaquer and thicker (~ 1.00 mm) (Table 2). In this sense, according to the standard terminology of ASTM D882-18 (ASTM, 2018), the plastics obtained from casting techniques are considered "films", while those obtained from extrusion are "sheets" (the value of 0.250 mm is considered the limit). These differences in thickness due to the different processing techniques (casting *vs.* extrusion) were already reported in the literature (Andreuccetti et al., 2012; Park and Whiteside, 2008), while in a few studies the thickness of the materials was similar (Ochoa-Yepes et al., 2019).

### *3.1.Morphology*

Figure 3 presents the morphology of the materials obtained by MEV. In general, native and DHT films (2h and 4h) present compact and smoother structures on the surfaces and cross-sections. Homogeneity in cassava films (modified or not) produced by casting was described in the literature (La Fuente et al., 2019, 2020).

However, heterogeneity and roughness were observed in the extruded sheets. Moreover, the surface images also show that the starch granules did not completely gelatinize in those treatments, with marked presence in *DHT*_2h, followed by *DHT*_4h and then the native extruded material. Additionally, in the inset images, some granules partially damaged (*DHT*_4h, extrusion) can be seen. In the cross-section images, porous can also be observed in *DHT*_2h and *DHT*_4h materials, in comparison to the native one.

The rapid evaporation occurred in extrusion in comparison to casting, results in micropores and cracks due to the expansion of water vapor (Fakhouri et al.,2013; Park and Whiteside, 2008), which favored by the high temperature and mechanical shearing, leading to the destructurization of starch granules, as reported in previous studies (Fitch-

Vargas et al., 2016; M. Li et al., 2015). Horvat et al. (2014) reported bubbles/droplets formation in the exit section of the extruder favoring the formation of porous morphology, which in this study was intensified by the DHT modification process.

Previous studies reported that the treatment of DHT in cassava starch provokes partial damages in the semi-crystalline and crystalline regions of the granules (Chandanasree et al., 2016). Regarding films, Freitas et al. (2021) observed that DHT (130 ºC -4 h) in corn films resulted in ungelatinized starch granules into the polymeric matrix, which is in accordance with the results reported herein. However, the authors observed enhanced mechanical and barrier properties of DHT corn starch films, in comparison to non-modified corn starch (Freitas et al., 2021). Fitch-Vargas et al., (2016) proposed that the physical damage caused by the extrusion process in corn starch granules favored the interactions with the plasticizers, improving mechanical and barrier properties.

Figure 4 presents the morphology, by AFM, of the films and sheets obtained, whose roughness (average and the root square) are presented in Table 1. In the figure, note that due to the difference in roughness, the color scales (in *z* dimension) are different for casting and extruded materials. Indeed, all values of roughness were higher for the extruded sheets in comparison to the casting films. The average roughness ($R_a$) and the root mean square roughness ($R_q$) were higher for DHT sheets (2 h and 4 h), as shown in Table 1, and. These results are in accordance with those reported by Park and Whiteside (2008) and Fakhouri et al. (2013), which are caused by rapid evaporation, resulting in micropores and cracks due to the expansion of water vapor within the material.

Therefore, the casting films resulted in homogenous morphology and lower roughness values, regardless of the DHT modification process, which was probably favored by the lower gelatinization temperature (70 ºC). For extruded sheets, the combination of both high temperature and mechanical shearing and DHT resulted in the presence of partially ungelatinized and damaged starch granules of the polymeric matrix, and higher values of roughness.

### *3.2. Crystallinity*

The X-ray diffraction patterns of the films and sheets obtained show the semi-crystalline characteristics (presence of amorphous and crystalline zones) as can be observed in Figure 5. Amorphous zones are caused by the disruption of the double helix conformations of the starch due to the starch gelatinization, while the crystalline regions were formed by the recrystallization favored by the formation of microcrystalline connections due to the presence of glycerol (Bergo et al., 2008).

Casting films showed peaks at 5.5 °, 17.0 °, 19.5 ° and 22.0 °, in the same region as those reported for cassava films produced by casting (Gutiérrez et al., 2015; La Fuente et al., 2019; Valencia et al., 2018). The extruded sheets showed three peaks at 13.4 °, 20.0 ° and 22.3°, similar to those observed in native cassava starch sheets produced in similar conditions (Vedove et al., 2021). According to Gonzáles-Seligra et al. (2017), a decrease in the number of peaks from casting to extrusion is probably caused by the destruction of the crystalline structure of starch granules during extrusion.

For the casting films, a significant increase was observed in the relative crystallinity for the *DHT*_4h in comparison to those others ($p$<0.05), while for the extruded sheets, no significant differences were observed among native and the DHT (2h and 4h) ($p$>0.05). Comparing both processes, no statistical difference was observed between native film and sheet, while, for the DHT materials (2 h and 4 h) a statistical difference was observed due to the process production ($p$<0.05). In the latter case, this could be explained by the new structured matrix formed due to the dry-heating process. Indeed, the drying conditions were quite different: the sheets were quickly dried at high temperatures and high shear stress during extrusion, while the films were slowly dried (~12 h) at rest by casting at low temperatures. Therefore, the casting conditions might promote better recrystallization in the matrix, which might be enhanced by the DHT treatment - while the quick drying at high temperatures and shears during extrusion results in the destruction of this crystalline structure.

Those differences in process conditions can also change the molecular interaction, potentially affecting the plastic properties – as evaluated as follows.

### *3.3.Fourier-transform infrared (FTIR) spectra*

Figure 6 presents the FTIR spectra of the films and sheets obtained from native cassava starch and modified by DHT (2 h and 4 h). In general, both spectra showed a typical behavior for cassava starch films plasticized with glycerol (Bergo et al., 2008; Colivet and Carvalho, 2017). The band at 3200 $cm^{-1}$ is associated with the free hydroxyl groups (O—H), while near 2900 $cm^{-1}$ is related to C—H stretch present in the starch (Bergo et al., 2008; Colivet and Carvalho, 2017). Moreover, Colivet and Carvalho (2017) assigned the region close to 1650 $cm^{-1}$ to the bending vibration of H—O—H water molecules absorbed in the amorphous region, while in the region between 1200 and 900 $cm^{-1}$ the bands are associated to C—O, C—C and C—O—H vibrations (Bergo et al., 2008; Colivet and Carvalho, 2017), usual spectra for this kind of materials. No differences were observed between samples (native, *DHT*_2h and *DHT*_4h) or processes (casting and extrusion), probably because changes in starch molecules were not drastic enough to be identified by this technique.

### *3.4.Mechanical properties*

Table 2 shows the mechanical behavior during a tensile assay of the obtained materials by casting and extrusion. In general, an increase in the tensile strength and decrease in the elongation at break is observed due to the dry heat treatment for 4 h. Moreover, the Young's modulus was significantly higher for the *DHT*_4h film in comparison to the native ones. The results indicate that the DHT processing of cassava starch produced stronger plastics - it is worth mentioning the relevance of this result.

Similar values were reported in native starch extruded materials by Vedove et al. (2021) and casting by Gao et al. (2017) and Li et al. (2008) also using DHT. Indeed, Gao et al. (2017) produced films with waxy corn starch, zein and distarch phosphate mixtures, reporting an increase in tensile strength (*TS*) of >20 % due to the dry heating treatment. The same behavior was observed by Li et al. (2008) on casting films produced using rice starch modified by DHT.

As exposed previously, dry heating results in depolymerization and oxidation of the starch molecules, producing carbonyl groups. Zhang et al. (2013) described that carbonyl groups are accessible to form strong hydrogen bonds with the hydroxyl groups of starch, resulting in more rigid films with reduced elongation. Furthermore, depolymerization facilitates the tendency of molecules reassociation, with potential greater interaction (La Fuente et al., 2019, 2020). Therefore, the new polymeric matrix formed has different interactions among the molecules of starch, glycerol, and water, here resulting in stronger plastics.

Comparing both processes, casting films were proportionally stronger than the extruded sheets, a similar behavior observed in gelatin films (Andreuccetti et al., 2012; Park and Whiteside, 2008). According to Park and Whiteside (2008), even though the film made from the extruded/hot-pressed method was 3 times thicker than that of casting, the tensile strength and the Young Modulus values were higher for the casting films, due to the different film-forming mechanisms e.g., melting and dissolving, which resulted in a different polymer matrix. Andreuccetti et al. (2012) suggested that the extrusion favors a chain alignment in the direction of the flow, which results in a more flexible material. Therefore, extrusion is expected to produce plastics whose molecules are more aligned and organized, while they may be entangled in the casting technique. Consequently, different polymeric matrixes can be obtained. Those differences could explain the resulting behavior, as well as how organized the biopolymer network is and how water can later interact and permeate it.

### *3.5. Water vapor permeability, wettability, and moisture content*

Table 2 allows observing that the DHT decreased the water vapor permeability. This is in accordance with the study conducted by Li et al. (2008), in which both water vapor and oxygen permeabilities were reduced for the DHT modified starch-based films. This is a good achievement, attributed to the new highly structured matrix formed inhibiting the diffusion of gases and decreasing the water vapor permeability.

Regarding the plastic process production, higher values of water vapor permeability (WVP) for extruded sheets were found in comparison to casting films. The same behavior was observed for gelatin films (Park and Whiteside, 2008). This can be explained by the presence of micro-voids (Park and Whiteside, 2008) and cracks (Fakhouri et al., 2013) in extruded plastics, probably caused by the accelerated drying process. Allied to that, the more aligned matrix from extrusion, different from the entangled and denser matrix from casting, which causes less interstitial space between the molecules, might explain the lower WVP values in casting films (Park and Whiteside, 2008).

Furthermore, the DHT materials (2 h and 4 h) produced from casting resulted in a more hydrophobic surface, in comparison to the native ones, the same behavior observed by Gao et al. (2017) in waxy corn DHT casting film. However, the sheet behavior was the opposite: the native sheet resulted in more hydrophobicity than the DHT sheets. La Fuente et al. (2019) discussed that the hydrophilicity could be related to the new molecular allocation due to the newest conformation, which could cause a decrease of hydrophobicity, explaining the results observed in the casting films. Regarding the extruded sheets, the higher hydrophilicity in the DHT modified sheet can be explained by the different structure configurations due to the process production, which probably changed the accessibility of the polar groups and the surface characteristics (higher roughness -Table 1).

Comparing both processes, the native sheet presented a higher hydrophobic characteristic than the native casting film; the same was observed by Ochoa-Yepes et al. (2019) in native cassava films and sheets, which could be possibly explained again by the higher value of roughness for the native sheet in comparison to native film (Table 1).

Both cassava starch films and sheets produced from the DHT for 4 h presented the lowest moisture content ($p<0.05$) that, according to Gutiérrez et al. (2015), which can be explained by the increased crystal phase (increased *RC*), confirming the results observed in casting films ( Fig. 5A).

Therefore, water vapor permeability and wettability were affected by the new matrix conformation, as a result of the DHT, which explains the results from casting films. However, the micropores and cracks caused by the rapid evaporation of water increased the roughness, and the more aligned matrix during extrusion was the predominant phenomenon that shapes the characteristics of the sheet. Those characteristics also influence other properties described as follows.

### *3.6. Opacity and Light transmittance*

DHT films and sheets presented higher opacity than the native materials and the process production (casting or extrusion - Table 2) did not significantly influence that behavior. Furthermore, sheets (native and DHT modified) increased opacity in comparison with the films (native and DHT modified), which can easily be visualized in Figure 2, probably affected by the higher thickness of the extruded sheets (Table 2) and the roughness surface (Table 1).

In this sense, the transmittance of the materials for different wavelengths is presented in Figure 7. It can be observed that, in general, the extruded sheets had less transmittance than casting films. Moreover, the modified starches (*DHT*_2h and *DHT*_4h) are observed to produce bio-based plastic with less transmission, confirming the results of opacity (Table 2) and the hypothesis of the denser network due to the new interactions. Furthermore, Fakhouri et al. (2013) reported that higher crystallinities (as observed in Figure 5 for casting films) result in more compact polymer chains that make it difficult for light to pass through (Trifol et al., 2019). Indeed, in the UV – region (200 to 400 nm), significantly lower values could be observed, which means that dry-heating treatment in starch improves the ability of the films to protect against UV radiation (Nouri and Nafchi, 2014). This is an interesting application for the food industry, once it can help to prevent the oxidation of lipids or vitamins in foodstuffs, enhancing the quality and shelf-life (Cazón et al., 2019). In turn, in the red color region (625 to 740 nm) all casting films and native sheets showed good transmittance, which also could be an interesting application, e.g., for the package of red foodstuffs, in which those plastics could promote a better visual aspect.

### *3.7. Thermal properties*

The thermo gravimetrical analysis (TGA) curves are shown in Figure 8. In general, no remarkable changes in the thermal properties due to the DHT can be seen, and all plastics obtained can be considered stable at normal temperatures of storage. The first stage of degradation from 100 ºC to 150 ºC corresponds to water evaporation, a second stage from 180 ºC to 280 ºC is related to the decomposition of glycerol-rich phase and from 280 ºC to 350 ºC is attributed to starch degradation. (Gonzáles-Seligra et al., 2017; Ochoa-Yepes et al., 2019). Finally, up to 350 ºC, the breakdown of the glucose ring occurs (Liu et al., 2013). It can be observed that the casting films and sheets degrade at the same rate showing that DHT does not interfere with the thermal degradation of starch plastics.

## 4. Final Remarks

To summarize, the dry heating treatment promoted molecular changes resulting in a higher compact matrix. Different materials were obtained regarding the process production. Films obtained from casting and sheets from extrusion presented different crystallinities and morphologies, and possibly different polymeric matrix organization and entanglement, which affected their mechanical, barrier, thermal characteristics, and wettability.

For the casting films, the slow drying at low temperatures and steady conditions probably resulted in an entangled matrix, which was favored by the DHT. In turn, the extruded sheet production promoted different phenomena, such as crack and micro-void spaces formation probably by the faster drying and molecular alignment in the direction of the flow. Casting films resulted in homogenous morphology and lower roughness. In the extruded sheets, the combination of both DHT and extrusion resulted in partially ungelatinized and damaged starch granules inside the polymeric matrix, and higher values of roughness.

The results showed that the starch DHT processing produced bio-based plastics with increased tensile strength, decreased elongation at break, water vapor permeability and moisture content, independently of the process of production (casting or extrusion). Regarding wettability, the behavior of films and sheets was the opposite: DHT increased hydrophobicity of the films, while for the sheets, the highest hydrophobicity was observed for the native sheet.

## 5. Conclusions

This work evaluated the dry heating treatment (DHT) as a modification process to obtain starch focused on producing bio-based plastics by both casting and extrusion techniques. Casting produced films (smaller thickness), while extrusion produced sheets (higher thickness). In both cases, DHT produced plastics with enhanced performance. The materials obtained presented different visual aspects, morphology, crystallinity, mechanical, barrier, thermal characteristics and wettability.

Specifically, the DHT treatment of cassava starch for 4 h, produced films and sheets with increased tensile strength, Young's modulus, and roughness, while with decreased water vapor permeability, moisture content, elongation at break and light transmittance (especially in the UV- region, which is suitable to prevent undesirable oxidation reactions).

Consequently, DHT showed to be an interesting alternative to produce biodegradable plastics.

## Acknowledgments

The authors acknowledge the São Paulo Research Foundation (FAPESP) for the post-doctoral fellowship of CIA La Fuente (2017/05307-8), the Ph.D. fellowship of L Siqueira (2019/21700-7), and the funding project EMU (2016/12385-2); the National Council for Scientific and Technological Development (CNPq, Brazil) for funding the project of CIA La Fuente (429043/2018-0) and the productivity grants of PED Augusto (310839/2020-3) and CC Tadini (306414/2017-1).

## References

Andreuccetti, C., Carvalho, R. A., Galicia-García, T., Martinez-Bustos, F., González-Nuñez, R., & Grosso, C. R. F. (2012). Functional properties of gelatin-based films containing Yucca schidigera extract produced via casting, extrusion and blown extrusion processes: A preliminary study. In *Journal of Food Engineering* (Vol. 113, Issue 1, pp. 33–40). https://doi.org/10.1016/j.jfoodeng.2012.05.031

ASTM. (2012). ASTM Standard D 882-12 Standard test method for tensile properties of thin plastic sheeting. *ASTM Standards*, 1–11.

ASTM. (2013a). ASTM D7334-08: Standard practice for surface wettability of coatings, substrates and pigments by advancing contact angle measurement: active standard. *American Society for Testing and Materials*, *08*(Reapproved 2013), 1–3. https://doi.org/10.1520/D7334-08R13.2

ASTM. (2013b). Standard Test Methods for Water Vapor Transmission of Materials E96/E96M. *Annual Book of ASTM Standards*, *i*, 1–10. https://doi.org/10.1520/E0096

ASTM. (2018). *Standard Test Method for Tensile Properties of Thin Plastic Sheeting*.

https://doi.org/10.1520/D0882-18

Bergo, P., Sobral, PJA., Prison, J. (2008). Effect of glycerol on physical properties of cassava starch films. *Journal of Food Processing and Preservation*, *34*(2), 401–410.

Bergo, PVA., Carvlho, RA., Sobral, PJA., dos Santos, RMC., SIlva, FBR., Prison, JM., Solorza-Feria, J., Habitante, AMQB. (2008). Physical properties of edible films based on cassava starch as affected by the plasticizer concentration. *Packaging Technology and Science*, *21*, 85–89.

Bora, A., & Mishra, P. (2016). Characterization of casein and casein-silver conjugated nanoparticle containing multifunctional (pectin–sodium alginate/casein) bilayer film. *Journal of Food Science and Technology*, *53*(10), 3704–3714. https://doi.org/10.1007/s13197-016-2343-4

Cazón, P., Vázques, M., Velazquez, G. (2019). Composite films with UV_barrier properties based on bacterial cellulose combinated with chitosan and poly (viyl alcohol): study of puncture and water interaction properties. *Biomacromolecules*, *20*, 2084–2095.

Colivet, J., Carvalho, R. (2017). Hydrophilicity and physicochemical properties of chemically modified cassava starch films. *Industrial Crops and Products*, *95*, 599–607.

Dean, K., Yu, L., & Wu, D. Y. (2007). Preparation and characterization of melt-extruded thermoplastic starch/clay nanocomposites. *Composites Science and Technology*, *67*(3–4), 413–421. https://doi.org/10.1016/j.compscitech.2006.09.003

Fakhouri, F. M., Costa, D., Yamashita, F., Martelli, S. M., Jesus, R. C., Alganer, K., Collares-Queiroz, F. P., & Innocentini-Mei, L. H. (2013). Comparative study of processing methods for starch/gelatin films. *Carbohydrate Polymers*, *95*(2), 681–689. https://doi.org/10.1016/j.carbpol.2013.03.027

Fitch-Vargas, P. R., Aguilar-Palazuelos, E., de Jesús Zazueta-Morales, J., Vega-García, M. O., Valdez-Morales, J. E., Martínez-Bustos, F., & Jacobo-Valenzuela, N. (2016). Physicochemical and Microstructural Characterization of Corn Starch Edible Films Obtained by a Combination of Extrusion Technology and Casting Technique. *Journal of Food Science*, *81*(9), E2224–E2232. https://doi.org/10.1111/1750-3841.13416

Gao, P., Wang, F., Gu, F., Ning, J., Liang, J., Li, N., & Ludescher, R. D. (2017). Preparation and characterization of zein thermo-modified starch films. In *Carbohydrate Polymers* (Vol. 157, pp. 1254–1260). https://doi.org/10.1016/j.carbpol.2016.11.004

Gontard, N., Guilbert, S., & Cuq, J. -L. (1993). Water and Glycerol as Plasticizers Affect Mechanical and Water Vapor Barrier Properties of an Edible Wheat Gluten Film. *Journal of Food Science*, *58*(1), 206–211. https://doi.org/10.1111/j.1365-2621.1993.tb03246.x

Gonzáles-Seligra, P., Guz, L., Ochoa-Yepes, O., Goyanes, S., F. (2017). Influence of extrusion process conditions on starch film morphology. *LWT - Food Science and Technology*, *84*, 520–528.

Gutiérrez, ., Morales, NJ., Pérez, E., Tapia, MS., Famá, L. (2015). Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches. *Food Packaging and Shelf Life*, *3*, 1–8.

Huntrakul, K., Yoksan, R., Sane, A., & Harnkarnsujarit, N. (2020). Effects of pea protein on properties of cassava starch edible films produced by blown-film extrusion for oil packaging. In *Food Packaging and Shelf Life* (Vol. 24). https://doi.org/10.1016/j.fpsl.2020.100480

La Fuente, C. I. A., Castanha, N., Maniglia, B. C., Tadini, C. C., & Augusto, P. E. D. (2020). Biodegradable Films Produced from Ozone-Modified Potato Starch. *Journal of Packaging Technology and Research*, *0123456789*. https://doi.org/10.1007/s41783-020-00082-0

La Fuente, C. I. A., de Souza, A. T., Tadini, C. C., & Augusto, P. E. D. (2019). Ozonation of cassava starch to produce biodegradable films. *International Journal of Biological Macromolecules*, *141*, 713–720. https://doi.org/10.1016/j.ijbiomac.2019.09.028

Li, M., Xie, F., Hasjim, J., Witt, T., Halley, P. J., & Gilbert, R. G. (2015). Establishing whether the structural feature controlling the mechanical properties of starch films is molecular or crystalline. *Carbohydrate Polymers*, *117*, 262–270. https://doi.org/10.1016/j.carbpol.2014.09.036

Li, Y., Shoemaker, C. F., Ma, J., Shen, X., & Zhong, F. (2008). Paste viscosity of rice starches of different amylose content and carboxymethylcellulose formed by dry heating and the physical properties of their films. *Food Chemistry*, *109*(3), 616–623. https://doi.org/10.1016/j.foodchem.2008.01.023

Liu X., Wang Y., Yu L., Tong Z., Chen L., Liu H., L. X. (2013). Thermal degradation and stability of starch under different processing conditions. *Starch - Stärke*, 48–60.

Maniglia, BC., Polachini TC., Norwood EA., Le-Bail P., L. A. (2021). Thermal technologies to enhance starch performance and starchy products. *Current Opinion* *in Food Science*.

Maniglia, B. C., Lima, D. C., Matta Junior, M. D., Le-Bail, P., Le-Bail, A., & Augusto, P. E. D. (2020). Preparation of cassava starch hydrogels for application in 3D printing using dry heating treatment (DHT): A prospective study on the effects of DHT and gelatinization conditions. *Food Research International*, *128*(November 2019). https://doi.org/10.1016/j.foodres.2019.108803

Nouri, L., Nafchi, A. (2014). Antibacterial, mechanical, and barrier properties of sago starch film incorporated with betel leaves extract. *International Journal of Biological Macromolecules*, *66*, 254–259.

Ochoa-Yepes, O., Di Giogio, L., Goyanes, S., Mauri, A., & Famá, L. (2019). Influence of process (extrusion/thermo-compression, casting) and lentil protein content on physicochemical properties of starch films. *Carbohydrate Polymers*, *208*, 221–231. https://doi.org/10.1016/j.carbpol.2018.12.030

Park, J. W., Scott Whiteside, W., & Cho, S. Y. (2008). Mechanical and water vapor barrier properties of extruded and heat-pressed gelatin films. *LWT - Food Science and Technology*, *41*(4), 692–700. https://doi.org/10.1016/j.lwt.2007.04.015

Siqueira, L., La Fuente, CI., Maniglia, BC., Tadini, C. (2020). *Starch-based biodegradable plastics: methods of production, challenges and future perspectives*.

Thuwall, M., Boldizar, A., & Rigdahl, M. (2006). Extrusion processing of high amylose potato starch materials. *Carbohydrate Polymers*, *65*(4), 441–446. https://doi.org/10.1016/j.carbpol.2006.01.033

Trifol, J., van Drongelen, M., Clegg, F., Plackett, D., Szabo, P., & Daugaard, A. E. (2019). Impact of thermal processing or solvent casting upon crystallization of

PLA nanocellulose and/or nanoclay composites. *Journal of Applied Polymer Science*, *136*(20), 0–23. https://doi.org/10.1002/app.47486

Valencia, G. A., Luciano, C. G., Lourenço, R. V., & do Amaral Sobral, P. J. (2018). Microstructure and physical properties of nano-biocomposite films based on cassava starch and laponite. *International Journal of Biological Macromolecules*, *107*, 1576–1583. https://doi.org/10.1016/j.ijbiomac.2017.10.031

Vedove, T. M. A. R. D., Maniglia, B. C., & Tadini, C. C. (2021). Production of sustainable smart packaging based on cassava starch and anthocyanin by an extrusion process. *Journal of Food Engineering*, *289*, 110274. https://doi.org/10.1016/j.jfoodeng.2020.110274

Wang, W., Zhang, H., Dai, Y., Hou, H., & Dong, H. (2017). Effects of low poly(vinyl alcohol) content on properties of biodegradable blowing films based on two modified starches. *Journal of Thermoplastic Composite Materials*, *30*(7), 1017–1030. https://doi.org/10.1177/0892705715614080

Zanela, J., Bilck, A. P., Casagrande, M., Grossmann, M. V. E., & Yamashita, F. (2018). Polyvinyl alcohol (PVA) molecular weight and extrusion temperature in starch/PVA biodegradable sheets. *Polímeros*, *28*(3), 256–265. https://doi.org/10.1590/0104-1428.03417

Zanela, J., Bilck, A. P., Reis, M. O., Grossmann, M. V. E., & Yamashita, F. (2020). Modified Starches on the Properties of Extruded Biodegradable Materials of Starch and Polyvinyl Alcohol. *Journal of Polymers and the Environment*, *28*(12), 3211–3220. https://doi.org/10.1007/s10924-020-01851-3

Zhang, Y. R., Wang, X. L., Zhao, G. M., & Wang, Y. Z. (2013). Influence of oxidized starch on the properties of thermoplastic starch. *Carbohydrate Polymers*, *96*(1), 358–364. https://doi.org/10.1016/j.carbpol.2013.03.093

## Figure Caption

**Figure 1.** Gel Firmness (measured by the energy needed in a punctual assay) and visual aspect of the gels produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Figure 2.** Films (casting) and sheets (extrusion) produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Figure 3.** Surface and Cross-section images of native, *DHT*_2h and *DHT*_4h cassava starch films (casting) and native, *DHT*_2h and *DHT*_4h sheets (extrusion) obtained by a Scanning Electron Microscopy (MEV). Surface images were taken at 350x with insets at 1000x. Cross-section images were taken at 130x with insets at 600x for sheets and at 2500x with insets at 5000x for films.

**Figure 4**. Morphology of native, *DHT*_2h and *DHT*_4h cassava starch films (casting) and native, *DHT*_2h and *DHT*_4h sheets (extrusion) observed through atomic force microscopy (AFM).

**Figure 5.** X-ray diffraction patterns of the films (casting) and sheets (extrusion) prepared with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Figure 6.** FTIR spectra of films (casting) and sheets (extrusion) produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Figure 7.** The light transmittance of films and sheets produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Figure 8**. Thermo gravimetrical analysis of films (casting) and sheets (extrusion) produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

**Table 1.**

Average roughness ($R_a$), root mean square roughness ($R_q$) and Relative Crystallinity (*RC*) of films produced by casting and sheets produced by extrusion, prepared from cassava starch (native, *DHT*_2h, and *DHT*_4h)

| **Process** | | **$R_a$ (nm)** | **$R_q$ (nm)** | ***Relative Crystallinity* (*RC*) (%)** |
|---|---|---|---|---|
| Casting | Native | 11.4 | 8.4 | $4.24 \pm 0.40^{bA}$ |
| | *DHT*_2h | 9.0 | 7.0 | $6.87 \pm 0.44^{bA}$ |
| | *DHT*_ 4h | 7.8 | 6.0 | $7.09 \pm 0.66^{aA}$ |
| Extrusion | Native | 13.0 | 9.2 | $4.14 \pm 0.88^{aA}$ |
| | *DHT*_2h | 75.3 | 53.7 | $4.47 \pm 0.53^{aB}$ |
| | *DHT*_ 4h | 127.0 | 99.2 | $4.92 \pm 0.61^{aB}$ |

Means with different lower letters in the same column are significantly different and means with different capital letters in the same row are significantly different ($p$<0.05).

**Table 2.**

Thickness, Tensile strength, elongation at break, Young modulus, Water Vapor Permeability (*WVP*), water contact angle, moisture content and opacity of films (casting) and sheets (extrusion) produced with cassava starch (native, *DHT*_2h, and *DHT*_4h).

| Process | | Thickness (mm) | Tensile strength (MPa) | Elongation at break (%) | Young modulus (MPa) | *WVP* (g·mm/m²·dia·kPa) | Contact Angle (°) | Moisture content (g/100 g) | Opacity (-) |
|---|---|---|---|---|---|---|---|---|---|
| Casting | Native | $0.10 \pm 0.02^{a}$ | $1.79 \pm 0.28^{b}$ | $35.40 \pm 5.88^{a}$ | $14.85 \pm 2.79^{c}$ | $30.53 \pm 1.65^{a}$ | $37.49 \pm 4.91^{b}$ | $22.06 \pm 1.14^{a}$ | $10.33 \pm 0.58^{b}$ |
| | *DHT*_2h | $0.09 \pm 0.01^{a}$ | $2.11 \pm 0.34^{b}$ | $21.94 \pm 3.52^{b}$ | $26.42 \pm 5.92^{b}$ | $22.64 \pm 3.31^{ab}$ | $56.99 \pm 8.35^{a}$ | $20.54 \pm 0.32^{ab}$ | $20.00 \pm 1.00^{a}$ |
| | *DHT*_4h | $0.09 \pm 0.02^{a}$ | $3.63 \pm 0.48^{a}$ | $29.16 \pm 9.31^{ab}$ | $47.66 \pm 8.41^{a}$ | $15.29 \pm 1.40^{b}$ | $49.56 \pm 10.23^{a}$ | $18.90 \pm 0.31^{b}$ | $17.33 \pm 2.08^{a}$ |
| Extrusion | Native | $1.19 \pm 0.00^{a}$ | $1.13 \pm 0.11^{ab}$ | $38.81 \pm 1.32^{a}$ | $5.23 \pm 0.70^{a}$ | $150.79 \pm 14.31^{a}$ | $56.52 \pm 8.15^{a}$ | $20.47 \pm 0.35^{a}$ | $49.33 \pm 1.15^{b}$ |
| | *DHT*_2h | $1.55 \pm 0.19^{a}$ | $0.95 \pm 0.20^{b}$ | $29.62 \pm 4.49^{b}$ | $5.44 \pm 1.49^{a}$ | $142.01 \pm 7.52^{ab}$ | $47.57 \pm 9.70^{b}$ | $19.70 \pm 1.08^{a}$ | $97.33 \pm 1.53^{a}$ |
| | *DHT*_4h | $1.43 \pm 0.27^{a}$ | $1.47 \pm 0.21^{a}$ | $24.60 \pm 1.81^{b}$ | $8.60 \pm 2.11^{a}$ | $121.94 \pm 8.49^{b}$ | $41.01 \pm 6.42^{b}$ | $16.60 \pm 0.29^{b}$ | $98.33 \pm 1.15^{a}$ |

Means with different superscripts in the column are significantly different ($p<0.05$); each process production (casting or extrusion) was analyzed separately.