



Horse chestnut (*Aesculus hippocastanum* L.) starch: Basic physico-chemical characteristics and use as thermoplastic material

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ABSTRACT

Starch isolated from non-edible *Aesculus hippocastanum* seeds was characterized and used for preparing starch-based materials. The apparent amylose content of the isolated starch was 33.1%. The size of starch granules ranged from 0.7 to 35 μm , and correlated with the shape of granules (spherical, oval and irregular). The chain length distribution profile of amylopectin showed two peaks, at polymerization degree (DP) of 12 and 41–43. Around 53% of branch unit chains had DP in the range of 11–20. *A. hippocastanum* starch displayed a typical C-type pattern and the maximum decomposition temperature was 317 °C.

Thermoplastic starch (TPS) prepared from *A. hippocastanum* with glycerol and processed by melt blending exhibited adequate mechanical and thermal properties. In contrast, plasticized TPS with glycerol:malic acid (1:1) showed lower thermal stability and a pasty and sticky behavior, indicating that malic acid accelerates degradation of starch during processing.

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1. Introduction

The growing accumulation of plastic residues in landfills and oceans and the strong dependency of plastic production on fossil petroleum resources have stimulated research on bio-based plastic alternatives. Starch is a renewable and inherently biodegradable raw material of low-cost that can be transformed into bio-plastics with technologies currently used for manufacturing synthetic plastics. The worldwide production of starch-based plastics is estimated to exceed 150,000 tons/year (European Bioplastic, 2014).¹

Thermoplastic starch (TPS) can be obtained by physical modification of starch, mixing starch with a plasticizer, with and without shear stress, at temperatures over 100 °C. Water, the main

plasticizer of TPS, is used together with other plasticizers, such as polyols (sorbitol, xylitol, pentaerythritol and glycerol), sugar alcohols and non-ionic and anionic surfactants (Vieira, da Silva, dos Santos, & Beppu, 2011). There are many reports of starch coming from different botanical sources to prepare TPS. In most studies starch comes from edible fruits, vegetables, seeds and so on (van Soest, Benes, de Wit, & Vliegenthart, 1996; Zullo & Iannace, 2009). The use of edible sources for fabrication of plastics is controversial, especially in developing countries with a deficit of arable land and food. Therefore, non-edible starch has gained much attraction for use in starch-based materials (Bharadwaj, 2010).

TPS has limited use in the plastic industry because its mechanical properties depends on the humidity condition, (Bertuzzi, Castro Vidaurre, Armada, & Gottifredi, 2007; Han, 2014, chap. 9). An alternative to reduce water absorption of TPS is the chemical modification of starch before or during melt blending. When the modification is made during the extrusion, the process is known as reactive extrusion. Poly(carboxylic acid)s such as citric, tartaric and malic acids have been used as cross-linking agents and coplasticizers to elaborate TPS. Poly(carboxylic acid)s delay water uptake, retrogradation and improve mechanical properties of TPS

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¹ Bioplastic facts and figures. European Bioplastic 2013 (<http://en.european-bioplastics.org/multimedia/>).

(Shi et al., 2007) and are also non-toxic and of low-cost. Zuraida, Yusliza, Anuar, and Mohd Khairul Muhaimin (2012) reported the preparation of TPS from Malaysian sago and different ratios of citric acid and glycerol. TPS prepared with glycerol: citric acid ratio of 1:1 showed higher tensile strength than those prepared only with glycerol. Jiugao, Ning, and Xiaofei (2005) showed by FTIR spectroscopy and X-ray diffractometry that citric acid reduced hydrogen bonding between starch and glycerol during storage, inhibiting the formation of amylose–glycerol inclusion complexes and therefore the formation of V-type structures associated with re-crystallized starch (i.e. retrogradation). Citric, malic and tartaric acids were also used as a cross-linking agent of starch/poly(butylene adipate co-terephthalate) blends to improve the compatibility of the polymeric phase. However, these organic acids promote the hydrolysis of starch, degrading them to dextrin and fragments of low molecular weight (Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2012). It would be interesting to explore the effect of malic acid on TPS plasticized by glycerol, because of its lower tendency to promote chemical modification of starch (Olivato, Grossmann, Bilck, & Yamashita, 2012; Olivato et al., 2012b; Ruxanda & Teacă, 2012).

An attractive source of non-edible starch is the seed of horse chestnut (*Aesculus hippocastanum* L.), which a starch content over 35 wt.% (Čukanović et al., 2011). The horse chestnut was introduced in Chile around XVIII century with arrival of European immigrants, and due to its exceptional adaptability has spread throughout the whole country. It is often found as ornamental trees in urban communities and in grassland of Chilean fields. Currently, seeds of *A. hippocastanum* are used for ornamental purposes, but most of them end up in landfills. Most reports related to seeds of *A. hippocastanum* are focused on their biochemical composition and morphoanatomical character; however, we have not found detailed studies about the chemical and physical characteristics of *A. hippocastanum* starch.

In this work, *A. hippocastanum* starch was characterized and used to prepare TPS by the melt blending method. We studied the rheological, mechanical and thermal properties of this TPS and the effect of incorporating malic acid as co-plasticizer. In addition, we compared the morphological and mechanical properties of TPS from *A. hippocastanum* starch with TPS from starch of *Araucaria araucana* seeds, an edible source with C-type semi-crystalline structure and excellent precursor for starch-based materials with adequate performance (Castaño, Bouza, Rodríguez-Llamazares, Carrasco, & Vinicius, 2012).

2. Experimental

2.1. Materials

Starch of ripe *A. hippocastanum* seeds, collected at the campus of the University of Concepción, Chile, was isolated by the wet milling method. The plasticizers used were glycerol (99.5% purity) and DL-malic acid (99% purity) supplied by Oceanquímica S.A. (Valparaíso, Chile) and Sigma Aldrich (Santiago, Chile), respectively.

2.2. Characterization of *A. hippocastanum* starch

Physical–chemical and morphological features of *A. hippocastanum* starch granules are summarized in Table 1. Ash and moisture content were determined gravimetrically in triplicate according to ASTM D1102–56 and Chilean Standard 176/1 of 84, respectively. Nitrogen content was assessed by using Kjendhal technique (AOAC, 1990). Swelling power (g/g of starch on dry weight) and solubility (g/g of starch on dry weight) were determined in triplicate using the method reported by Singh, McCarthy, Singh, Moughan, and Kaur (2007). In short, a suspension of *A. hippocastanum* starch was

Table 1

Physico-chemical and morphological features of *A. hippocastanum* starch.

% Small granule size (0.5–10 μm) ^a	30.7
% Medium granule size (11–30 μm) ^a	67.6
% Large granule size (>31 μm) ^a	1.7
Moisture content ^b	7.1 \pm 0.1
Ash content	0.20
Apparent amylose content (%)	33
Nitrogen content	0.5 \pm 0.1
Phosphorus content (%)	0.0118
Calcium content (%)	0.0179
Sulfur content (%)	0.0033
Potassium content (%)	0.0465
Swelling power (g/g of starch on dry weight)	6.5 \pm 0.2
Solubility (g/g of starch on dry weight)	3.1 \pm 0.1
Color	White

^a Determined by laser diffraction particle size analyzer.

^b Determined by thermogravimetric analyzer.

heated at 60 °C for 30 min followed by centrifugation at 4000 rpm for 30 min. The supernatant was decanted and dried over night at 70 °C (soluble solid). The solid residue of centrifugation was weighed for swelling power measurement.

The apparent amylose content was assessed by using a colorimetric method according to EN ISO 6647 parts I and II, which is based on amylose–iodine complex formation. The absorbance was measured at 620 nm by using an UV spectrophotometer (UV mini – 1240 Shimadzu, Japan). The particle size distribution was determined with a laser diffraction particle size analyzer (Beckman Coulter LSTM 200, Brea CA, USA). At least three measurements were done to obtain the average particle size distribution curves. The phosphorus, sulfur, calcium and potassium content were quantified by X-ray fluorescence spectrometry (S4 Pioneer, Bruker-AXS, Germany). 5 g of powdered starch were mounted on prolene films, and analyzed under helium atmosphere. The results were evaluated by SpectraPlus v.1.6 spectrometer software (Socabim). Thermal stability of *A. hippocastanum* starch was evaluated by thermogravimetric analyses (TGA). Morphological of starch granules was examined with scanning electron microscopy. X-ray diffraction (XRD) was used to analyze crystalline structure of starch granules.

A. hippocastanum starch was debranched using isoamylase 3U (Megazyme International, Ireland) enzyme according to Wong and Jane (1995). The branch chain length distribution of amylopectin was analyzed according to Moraes, Alves, and Franco (2013) using high-performance anion-exchange chromatography with pulsed amperometric detector (HPAEC-PAD) system (ICS 3000, Dionex Corporation, Sunnyvale, USA) equipped with an AS40 automatic sampler. Samples were filtered (0.22 μm membrane) and injected into the HPAEC-PAD system (20 μL sample loop). The flow rate was 0.8 mL/min at 40 °C. The standard quadrupole potential (E) waveform was employed with the following periods and pulse potentials: $E_1 = 0.10 \text{ V}$ ($t_1 = 0.40 \text{ s}$); $E_2 = -2.00 \text{ V}$ ($t_2 = 0.02 \text{ s}$); $E_3 = 0.60 \text{ V}$ ($t_3 = 0.01 \text{ s}$); $E_4 = -0.10 \text{ V}$ ($t_4 = 0.06 \text{ s}$). All eluents were prepared with ultrapure water (18 $\text{m}\Omega\text{cm}$) with N_2 sparging. Eluent A was 150 mM NaOH and eluent B was 500 mM sodium acetate and 150 mM NaOH. The branched chains of amylopectin were separated using a Dionex CarboPacTM PA-100 guard column (4 \times 50 mm) and a Dionex CarboPacTM PA-100 column (4 \times 250 mm). The gradient of eluent B was 28% at 0 min, 40% at 15 min, and 72% at 105 min. The data were analyzed using the Chromeleon software, version 6.8 (Dionex Corporation, USA). The analyses were performed in duplicate.

2.3. Preparation of thermoplastic starch

Before melt-blending, *A. hippocastanum* starch and plasticizers were premixed by hand at room temperature. A Brabender internal mixer (Plastograph[®] EC plus, Mixer 50EHT32, Germany) was used

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