



Plant-crafted starches for bioplastics production



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ARTICLE INFO

Article history:

Received 22 February 2016

Received in revised form 27 June 2016

Accepted 10 July 2016

Available online 12 July 2016

Keywords:

Amylose
Bioplastics
Crystallinity
Mechanics
Rheology
Thermoplastic starch

ABSTRACT

Transgenically-produced amylose-only (AO) starch was used to manufacture bioplastic prototypes. Extruded starch samples were tested for crystal residues, elasticity, glass transition temperature, mechanical properties, molecular mass and microstructure. The AO starch granule crystallinity was both of the B- and Vh-type, while the isogenic control starch was mainly A-type. The first of three endothermic transitions was attributed to gelatinization at about 60 °C. The second and third peaks were identified as melting of the starch and amylose-lipid complexes, respectively. After extrusion, the AO samples displayed Vh- and B-type crystalline structures, the B-type polymorph being the dominant one. The AO prototypes demonstrated a 6-fold higher mechanical stress at break and 2.5-fold higher strain at break compared to control starch. Dynamic mechanical analysis showed a significant increase in the storage modulus (E') for AO samples compared to the control. The data support the use of pure starch-based bioplastics devoid of non-polysaccharide fillers.

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1. Introduction

Starch consists of two major components, amylose and amylopectin, which differ in their degree of branching and molecular size. Amylose is mostly a linear polymer composed of mainly α -(1-4)-linked glucose residues, with a molecular weight (Mw) of approximately 10^5 – 10^6 g mol⁻¹. Amylopectin is a much larger molecule than amylose (Mw = 10^7 – 10^9 g mol⁻¹) and is a more branched polymer with an α -(1-4)-linked D-glucose backbone and approximately 5% α -(1-6)-linked branches (Blennow et al., 2013). At a higher level of organization starch is arranged in different crystalline polymorphs. These are dependent on the botanical origin and type of organ of the plant and are characterized by two main crystalline structures called A-type and B-type (Pérez, Baldwin, & Gallant, 2009). These complexes, if hydrated, can crystallize into different so-called Vh-type polymorphs, which are classified as type I and type II depending on their melting point and structural stability (Goderis, Putseys, Gommès, Bosmans, & Delcour, 2014).

Being one of the most abundant and versatile polysaccharides on earth, starch is a suitable raw material for the production of new environmentally-friendly bioplastics (e.g. Materbi®, Novamont). Starch is readily transformable using existing technologies and is an abundant and low-cost commodity that can be easily refined. Starch-based plastics can be transformed into edible and compostable products (Ali Shah, Hasan, Hameed, & Ahmed, 2008). Conventional plastic (e.g. polyolefin based plastics), on the other hand, can be a cause of environmental problems related to their low degradability rates. In fact, the degradation of conventional plastic takes place by producing macro- and micro-plastic fragments that persist in both soil and water (Cole, Lindeque, Halsband, & Galloway, 2011). Alternatively, conventional plastic can be mixed with additives that catalyze the degradation of the polymers through light, heat or mechanical stress, leaving pro-degrading additives in the environment but allowing full degradation of the polymer (Ammala et al., 2011). Thermoplastic starch (TPS) is an alternative that can be produced using different existing techniques including casting, thermo-molding, extrusion and injection molding, traditionally used for the processing of synthetic polymers. An interesting advantage of TPS is the modularity of its different properties. For example, the molecular structure (e.g. the molecular size) and amylose/amylopectin ratio influence

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List of symbols and abbreviations

λ	Wavelength of the incident laser beam
ν_G	Hydrodynamic coefficient
\bar{R}_G	Z-average radius of gyration
\bar{M}_n	Number average molar mass
\bar{M}_w/\bar{M}_n	Dispersity
\bar{M}_w	Weight-average molar mass
AO	Amylose-only
DMTA	Dynamic mechanical thermal analysis
dn/dc	Refractive index increment
DSC	Differential scanning calorimetry
F_c	Cross flow rate
F_{in}	Channel flow in
F_{out}	Channel flow rate
M_i	Molar mass of the i^{st} slice
R_{Gi}	Radius of gyration of the i^{st} slice
R_H	Hydrodynamic radius
RH	Relative humidity
T_g	Glass transition temperature
WAXS	Wide-angle X-ray scattering

the final properties of starch-based bioplastic (Gillgren, Blennow, Pettersson, & Stading, 2011). Also minor differences in the amylose and phosphate contents and chain length distribution of the amylopectin, as well as granular organization, can result in major differences in physical properties. The modification of such structures may also result in the extensive alteration of film functionality as has been demonstrated for transgenic starches (Gillgren et al., 2011). The amylose/amylopectin ratio is an important factor influencing the mechanical properties of such materials, especially since amylose affects the degree of crystallinity and entanglement. Increased amylose content is typically related to an increase in tensile strength and a decrease in strain (Alves, Mali, Beléia, & Grossmann, 2007). Low elasticity can be avoided by including a plasticizer, usually glycerol. This enables the material to endure increased strain but leads to an unavoidable decline in the original strength of the material (Lourdin, Della Valle, & Colonna, 1995; Myllärinen et al., 2002). In addition, high amylopectin content is correlated with higher strain as a result of its structural characteristics e.g. high molecular size (Hulleman, Jannesen, & Feil, 1998).

Commercial starch-based plastics are chemically modified or blended with synthetic polymers, such as polycaprolactone (PCL), to enhance the plastic behavior of these materials (Bastioli, Bellotti, Del Giudice, & Grilli, 1993).

Alternatively, TPS may be improved by other methods, such as the use of genetically modified (GM) organism. Starch-modifying enzymes produced by GM microorganisms can modulate starch structure and functionality, or GM crops can be engineered to produce tailor-made starches directly in their starch-producing organs by coordinated expression of starch-modifying enzymes (Hebelstrup, Sagnelli, & Blennow, 2015).

In the present study, a new plant-crafted starch (engineered and crafted *in planta*) synthesized by an engineered barley-line called amylose-only (AO, Carciofi et al., 2012), composed of 99% of a rather homogeneous amylose-like α -glucan, was used to produce thermoplastic starch-based prototypes. The samples were manufactured by molding and extrusion and finally tested for crystallinity, dynamic mechanical analysis (DMA) and stress and strain at break. The study demonstrates the potential of using GMO plants for the production of new environmentally-friendly polymers as part of a sustainable production of plastics.

2. Materials and methods**2.1. Materials**

The barley starches used in this study were extracted and purified from two barley lines; a control Golden Promise and amylose only a genetically modified (GM) line, which was generated by RNA interference suppressing all three starch branching enzymes in the Golden Promise background. Briefly, the silencing of all three identified genes of the starch branching enzyme family (SBE1, SBE2a and SBE2b) was achieved by using RNAi suppression. Embryos were isolated from juvenile seeds and used for genetic transformation, mediated by *Agrobacterium tumefaciens*. SBE activities were suppressed to below 20% of the control. The full protocol and details on the transgenic lines is given in Carciofi et al. (2012). All chemicals used were provided by Sigma-Aldrich.

2.2. Methods**2.2.1. Water content determination**

The water content of starch granules were determined for each sample using a thermo-balance (TA instruments, New Castle, DE, USA). The instrument was programmed with a ramp of $10^\circ\text{C min}^{-1}$ to 130°C and then an isotherm for 10 min. Water content was calculated based on the weight variation. For the extruded samples the isotherm was increased up to 3 h to achieve a constant weight at the end of the experiment.

2.2.2. Differential scanning calorimetry (DSC)

The melting temperatures of the native starches were determined by differential scanning calorimetry (DSC) using an automated TA Q100 instrument (TA Instruments, New Castle, DE, USA). Experiments were carried out on aliquots of approximately 15 mg starch placed in stainless steel airtight cells. A single scan was run at 3°C min^{-1} from 0 to 150°C . The melting temperature was defined from the endotherm peak value (Garcia et al., 1996).

2.2.3. Sample preparation and melt processing

The formulations used were prepared by mixing the starch with water and/or glycerol using a pestle and mortar. The mixtures were then stored at 4°C for 24 h to achieve equilibrium between the phases. All the blends were prepared taking into account the native water content of the starch, which was measured as described above. The formulations consisted of starch mixed with water alone (30, 40 and 50% water/dry weight, d.w.) and water plus glycerol (30, 40 and 50% water/d.w. and 23% glycerol/d.w.). The formulations were considered as ratios of all three components. For example, the AO5023 had a 50:50 ratio of starch:water. This is an optimal ratio to achieve melting. The starch:glycerol ratio for this sample was 77:23. Two kinds of thermomechanical processes were employed: compression molding and extrusion. Compression molding was performed using a mold with a circular shape (6 cm diameter 0.01 cm height), heated at 130°C and with a pressure of 10 MPa applied for 10 min. All samples were prepared with a density of 1.5 g cm^{-3} (taking into account the volume of the mold). The pressure was released as the mold was cooled to room temperature. The dimensions of the thermo-molded specimens were measured with a micrometer screw gauge (Mitutoyo) and the samples were stored in a desiccator at $57 \pm 2\%$ relative humidity (RH), which was obtained with saturated NaBr salt solution at $20 \pm 3^\circ\text{C}$ (Lourdin et al., 1995), before analysis.

Extrusion was performed with a twin-micro-compounder (HAAKE Minilab II), which allows the simulation of the extrusion process on batches of less than 10 g (Coativy et al., 2015). This device consisted of a conical twin-screw extrusion chamber and a recirculation channel, which allowed the residence time of the

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