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Understanding the role of plasticisers in spray-dried starch

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ABSTRACT

Amorphous thermoplastic starch (TPS) films were produced by compression moulding of solution spray-dried TPS powder and by direct solution casting. Oxidised potato starch was used as a feedstock for production of plasticised formulations containing glycerol or urea, or their combinations with maltodextrin (DE = 19.1) as processing aid.

The crystallinity index of freshly moulded films made from solution spray-dried powder was significantly lower than that for casted films. FTIR analysis showed that starch interacted in hydrogen bond formation with glycerol and urea plasticisers, reducing the glass transition temperature to 136 °C and 106 °C, respectively. Formulations containing maltodextrin did not show a T_g. Glycerol-plasticised and co-plasticised films immediately started to retrogradate in the presence of moisture, while urea based systems only showed slow recrystallization at the highest moisture exposure. In line with retrogradation behaviour, urea plasticised and co-plasticised films exhibited a more ductile behaviour, whereas glycerol based ones showed more brittle behaviour.

1. Introduction

Starch is a natural polymer of D-glucose found in the majority of plants. It is low cost, abundant, and biodegradable, and, after plasticising, exhibits appealing material properties (Chaudhary, Torley, Halley, McCaffery, & Chaudhary, 2009; Koch, Gillgren, Stading, & Andersson, 2010; Zhou, Zhang, Ma, & Tong, 2008), as amorphous thermoplastic starch (TPS). TPS films are currently attracting significant attention as potential packaging material from both scientific and commercial entities. In 2002, 25% of all plastics throughout the world were used for packaging purposes (Adeodato Vieira, da Silva, dos Santos, & Beppu, 2011; Weber, Haugaard, Festersen, & Bertelsen, 2002).

However, challenges in creating thermoplastic starch films with suitable and consistent mechanical properties still exist as starch, being semi-crystalline by nature, suffers from retrogradation (Adeodato Vieira et al., 2011; Liu, Xie, Yu, Chen, & Li, 2009; Ma & Yu, 2004b). A higher crystallinity index leads to film brittleness and reduced flexibility, thus limiting practical use (Adeodato Vieira et al., 2011; Chaudhary et al., 2009; Hu, Chen, & Gao, 2009; Liu et al., 2009; Ma & Yu, 2004a, 2004b).

Casting and thermoplastic extrusion are the predominant techniques used for creating TPS films. Though these methods are simple and cost efficient, the starch is processed using water as plasticiser which contributes to the retrogradation of the formulations (Mathew & Dufresne, 2002). Especially long drying times required in film casting counteract the formation of amorphous TPS films (Galdeano et al., 2009; Hu et al., 2009).

In addition to water, plasticisers are used to disrupt the hydrogen bonds between the starch polymeric chains, hereby influencing the mechanical properties of starch films. Plasticisers results in a greater mobility of the starch chains in TPS films, leading to better process ability and more appealing film properties (Adeodato Vieira et al., 2011; Galdeano et al., 2009; Garcia, Martino, & Zaritzky, 2000; Laohakunjit & Noomhorm, 2004; Ma & Yu, 2004b).

From a product design point of view, it seems desirable to formulate and manufacture amorphous TPS films with better retrogradation and mechanical properties. Indeed, our previous studies showed that solution spray-drying (SSD) of starch/maltodextrin formulations could be a potential technology for the manufacture of amorphous thermoplastic starch based films. This technique produced amorphous TPS powder with low moisture contents and thus can play an important role to produce thin TPS films with better mechanical properties. This, as long as it can be processed into film structures (Bhandari, Datta, & Howes, 1997; Niazi & Broekhuis, 2012; Niazi, Zijlstra, & Broekhuis, 2013).

In order to create amorphous TPS films, this research will therefore focus on the processing of starch via compression moulding of spray-dried starch-plasticiser formulations. Glycerol and urea will be used as plasticiser, separately and in combination with

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Table 1
Code names and corresponding description.

Code	Description
Powder	
U.S	Untreated starch; Feedstock material
S.D	Spray dried starch
G.PS	Spray dried 30% Glycerol plasticised starch
U.PS	Spray dried 30% Urea plasticised starch
G.MD.PS	Spray dried 15% Glycerol and 15% maltodextrin (DE 19.1) plasticised starch
U.MD.PS	Spray dried 15% Urea and 15% maltodextrin (DE 19.1) plasticised starch
Films	
S.SC	Solution casted starch film
G.PS.SC	30% glycerol plasticised solution casted film
U.PS.SC	30% urea plasticised solution casted film
G.MD.PS.SC	15% glycerol and 15% maltodextrin (DE 19.1) plasticised solution casted film
U.MD.PS.SC	15% urea and 15% maltodextrin (DE 19.1) plasticised solution casted film

maltodextrins (DE = 19.1). For reference purposes, films will also be prepared by solution casting; this to study the role of moisture during the film-formation process. The high drying rate, attained in SSD, is expected to give rise to amorphous TPS powder containing little water and slow retrogradation of films, whereas moisture can play a role during the drying of solution casted films (Bhandari et al., 1997; Jayasundera, Adhikari, Adhikari, & Aldred, 2011).

Oxidised amylopectin is preferred as a feedstock for spray drying as it gives low viscosity solutions (Hu et al., 2009). Different end-product properties of powders and films were investigated. Crystallinity and thermal properties of spray dried powder were studied and analysed by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermal gravimetric analysis, respectively. Water uptake at different humidity levels, retrogradation, and mechanical properties of thermoplastic starch films were studied.

2. Materials and methods

2.1. Materials

Oxidised potato starch amylopectin (Perfecta-film X85; moisture content 15%) was a gift from AVEBE (the Netherlands). Analytical grade glycerol and urea were purchased from Sigma–Aldrich. Maltodextrin (DE = 19.1) was kindly supplied by Cargill (France). The coding of the samples used throughout this paper is given in Table 1.

2.2. Preparation of TPS-powder

Aqueous solutions of starch were prepared using 15% (w/w) of oxidised starch and 30% (w/w based on dry starch) plasticiser, which was heated at 95 °C for 25 min and stirred at a rate of 600 rpm. The obtained solution was fed to a Büchi mini-spray drier B-191 equipped with a 0.7 mm nozzle. SSD was carried out as described in previous work (Niazi & Broekhuis, 2012). All the spray-dried formulations were then converted into films by compression moulding while the solvent-casted films were made directly from water based solutions.

2.3. Preparation of TPS-films

TPS films (Ø10 mm × 0.5 mm) were obtained by compression moulding the TPS powder, using a Fontijne Holland Table Press TH400. The samples were compressed at 25 bars for 5 min. The applied moulding temperature for S.D, G.PS, and G.MD.PS was 140 °C, and respectively 120 °C and 130 °C for U.PS and U.MD.PS.

Solution casted films were made from the original water based solutions prepared in the same manner as described in Section 2.2. Subsequently 10 mL of the solution was poured into a Petri dish (7 cm diameter) and dried for 48 h at 45 °C. The solution-casted products are coded with the suffix SC.

2.4. X-ray diffraction (XRD)

The crystalline structures of the spray dried powders and the films were studied using X-ray diffraction. A Bruker D8 equipped with Cu radiation exhibiting a wavelength of 1.5418 Å was used to record diffractograms from 5° 2θ to 40° 2θ. A step size of 0.02° 2θ using a scan speed of 2 s/step was employed. The system was operated at 40 kV and 40 mA. The crystallinity index was determined using the method described by Shujun (2005). The software program Origin 8.1 was used for integrating the peaks. The total area was the area under the curve from 12° to 40° in the XRD spectrum (Shujun, 2005).

2.5. Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis of freshly prepared formulations was done using an open pan Perkin Elmer TGA 7 from 25 °C to 900 °C with 5–10 mg of sample applying a heating rate of 25 °C/min. The TGA and the derivative of the TGA were determined as described in literature (Soliman, ElShinnawy, & Mobarak, 1997).

2.6. Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of the freshly prepared samples was determined by DSC measurements, using a DSC-60 Shimadzu Co. Prior to the analysis a reference was constructed using an empty aluminium pan. Samples were scanned at a rate of 10 °C/min from 10 to 200 °C. Open pan measurement was performed in order to remove any remaining water from the sample in the first run.

2.7. Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) analyses were performed on freshly prepared samples. The spectra were recorded using a Perkin Elmer FT-IR spectrometer spectrum 2000 equipped with an attenuated total reflection (ATR) unit. For each spectrum 32 consecutive scans at 4 cm^{-1} resolution were averaged. All analyses were performed at ambient temperature.

2.8. Retrogradation of TPS films

Retrogradation was studied by storing the starch films (Ø10 mm × 0.5 mm) at three different relative humidity levels: 0% (dried silica), 50% (35.64% $CaCl_2$ solution) and 100% (distilled water). Rate of retrogradation measurements were carried out as described in the previous work. The crystallinity index was determined using the method described in Section 2.4.

2.9. Moisture uptake

To study moisture uptake, films were stored at 0%, 50% and 100% RH and gravimetrically analysed at regular time intervals. Measurements were taken every day during the first seven days. Hereafter, measurements were performed at day 14, 21, 28 and 56. Moisture uptake of the films was determined using Eq. (1) (Zhang, Zhang, Wang, & Wang, 2009).

$$\text{Moisture uptake} = \frac{\text{weight}_{\text{day},n} - \text{weight}_{\text{day},0}}{\text{weight}_{\text{day},0}} \times 100\% \quad (1)$$