



Studies on the effect of storage time and plasticizers on the structural variations in thermoplastic starch



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ABSTRACT

Starch was combined with plasticizers such as glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blends by means of high shear extrusion process to prepare thermoplastic starch (TPS). Effect of storage time and plasticizers on the structural stability of melt processed TPS was investigated. Morphological observation, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy reveal that melt extrusion process is efficient in transforming granular starch into a plasticized starch for all plasticizer compositions. XRD analysis highlights major changes in the microstructure of plasticized starch, and dependence of crystalline type and degree of crystallinity mainly on the plasticizer composition and storage time. Dynamical mechanical analysis (DMA) yields a decrease of the peak intensity of loss factor with aging time. The effect of ageing on tensile strength also appears to be highly dependent on the plasticizer composition. Thus, through different plasticizer combinations and ageing, starch-based materials with significant differences in tensile properties can be obtained, which may be tuned to meet the requirements of a wide range of applications.

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1. Introduction

In recent years, ecological awareness enormously increased within society due to the adverse effects from petroleum derived plastics as well as shrinking crude oil resources and rising prices. Much effort has recently been made to develop eco-friendly and biodegradable materials. In this context, the starch appears to be an alternative to synthetic materials because of its easy availability, low price and biodegradability.

The native starch is a semi-crystalline material mainly composed of amylose and amylopectine (98% of dried mass). Depending on the botanical origin of starch, different structure can be distinguished by X-ray diffraction namely A–C-type crystalline structures (Van Soest & Vliegthart, 1997). The differences between the crystallinity A-type and B-type lies in the density of the envelope of the double helix and the water content related to the network. The A-type structure is described as a compact monoclinic envelope ($a = 2.124$ nm, $b = 1.172$ nm, $c = 1.069$ nm, and $\gamma = 123.5^\circ$) containing 8 water molecules (Sarko & Wu, 197) (Imberty, Chanzy, Pérez, Buléon, & Tran, 1988) while the B-type structure is described as a hexagonal unit cell ($a = b = 1.85$ nm and $c = 1.04$ nm) with 6 double

helices and a column containing 36 molecules of water present in the centre of the hexagonal arrangement. The C-type, observed in legumes, is an intermediate structure between type A and B-type, in which the A-type surrounds B-type (Jiping et al., 2007).

Starch has poor processing ability and should be plasticized before processing and moulding (Van Soest, De Wit, & Vliegthart, 1996). Plasticization process transforms the semi-crystalline granules into a homogeneous, rather amorphous material by the destruction of hydrogen bonds between the starch molecules, and synchronously the formation of hydrogen bonds between plasticizer and starch molecules (Pang et al., 2007). Granular disruption could be achieved in the presence of appropriate plasticizer by applying thermomechanical energy in a continuous process (Schmitt, Prashantha, Soulestin, Lacrampe, & Krawczak, 2012a; Schmitt et al., 2012b). This combination of thermal and mechanical inputs can be obtained by an extrusion process, which is a cost effective and common plastic processing technique (Yu & Christie, 2001).

The development of a plasticized starch requires the addition of high (25–30 wt.%) plasticizer content. Water remains the best natural plasticizer, but starch being very hydrophilic, its moisture content strongly depends on the storage conditions. This dependence can be partially limited by replacing part of water by a less volatile plasticizer, such as polyols (glycerol, sorbitol, xylitol, glycol ...) or sugars. The nature and the composition of the plasticizer

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system (including water) greatly affect the transformation of granular starch into a homogenous thermoplastic phase (Hulleman, Janssen, & Feil, 1998) but also the glass transition temperature (T_g) of the final material (Shi et al., 2007) and, consequently its mechanical properties and kinetics of crystallization at the temperature of service.

The amylose crystallizes in single helices called V-amylose (Buleon, Delage, Brisson, & Chanzy, 1990). Depending on the hydration or dehydration, crystalline structures are denoted as V_H ($V_{Hydrate}$) amylose for hydration and V_A ($V_{Anhydrous}$) amylose for dehydration (Winter & Sarko, 1974). The most frequently observed crystalline structure is found to be V_H -type, which is packed in an orthorhombic unit cell (Zobel, French, & Hinkle, 1967) or in a hexagonal unit cell (Brisson, Chanzy, & Winter, 1991). A second most observed crystalline structure is V_A -type which is indexed as an orthorhombic unit cell (Zobel et al., 1967). The third observed crystalline form is the B-type, which is due mainly to the crystallization of amylopectine.

During storage, water/polyols plasticized starch can undergo recrystallization phenomena, named retrogradation. The retrogradation is a practical issue because it effects the quality and self life of final products (Delville, Joly, Dole, & Bliard, 2003; Tako, Tamaki, & Konishi, 2008). For instance, it can lead to opacity and hardening of the material and eventually decreases the elongation, at break (Smits, Ruhnau, & Vliegenthart, 1998; Yu, Prashantha, Soulestin, Lacrampe, & Krawczak, 2013). The retrogradation is mainly due to internal stresses in the material caused by the difference in the rearrangement rate of starch molecules.

The rate of retrogradation depends on the plasticizer content and the glass-transition temperature. The recrystallization process involves two phenomena which do not take place at the same speed. Firstly, the rapid recrystallization of single helical structures of amylose occurs after processing. Secondly, a slower development of the crystallization of amylopectine occurs (Van Soest et al., 1997).

Urea can be used as plasticizer to limit the retrogradation (Zullo & Iannace, 2009; Ma, Yu, & Ma, 2005). In this case, amide groups of plasticizer have the ability to create hydrogen bonds with starch which are more stable than those between starch and polyols, thereby promoting the ageing resistance ability. However the use of the urea yields to poor mechanical properties (materials are rigid and brittle) (Stein & Greene, 1997). To overcome this problem, the urea is generally mixed with ethanolamine, which can increase the flexibility of the plasticized starch (Ma, Yu, & Ma, 2006).

Although many studies have been reported on the processing of starch using different plasticizers, most of them are devoted to the processing and properties of the plasticized starch but reports on the ageing-induced structural changes in the plasticized starch are very limited. Therefore, the present study aims at investigating the structural stability of melt processed thermoplastic starch based on wheat starch combined with polyols such as glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blends. As a control system, water plasticized starch will also be reported. The effect of ageing on the physical and mechanical properties of these materials will be investigated, and some new viewpoints on ageing-properties will be pointed out.

2. Experimental

2.1. Materials

Wheat starch (Roquette, France) was used in this study. It was stored at 23 °C with 50% relative humidity (RH) to limit the fluctuation of its humidity content. In these conditions, the native starch contains 12 wt.% of moisture. Glycerol (99% purity, Sigma Aldrich, France), sorbitol (ACROS organics, Belgium), and urea and ethanolamine (Fisher Scientific, Belgium) were used as plasticizers.

A lubricant glycerol monostearate (Mosselman, Belgium) was also used to facilitate compounding.

2.2. Processing of thermoplastic starch

Thermoplastic starch was melt processed by mixing of starch, plasticizers composition and lubricants as follows. At first, 75 wt.% native starch, 24 wt.% plasticizer (glycerol, sorbitol, glycerol/sorbitol blend (ratio 1:1) or urea/ethanolamine blend (ratio 1:2)) with 1 wt.% glycerol monostearate (GMS) were physically blended in a mechanical mixer. As a control system, 75 wt.% native starch, 24 wt.% water with 1 wt.% GMS was also prepared. These mixtures were kept for 3 h at room temperature, then processed in a twin-screw extruder (screw diameter 16 mm, screw ratio L/D 40) (Haake Rheomex PTW 16 OS, Thermo Scientific, Germany) at a screw speed of 60 rpm. The temperature setting from the hopper to the die was 110–115–115 °C, 90–90–110 °C, 105–110–110 °C and 105–110–110 °C for the materials containing water, glycerol, sorbitol, glycerol/sorbitol and urea/ethanolamine blend, respectively. In the following, the corresponding plasticized materials will be named, WS (reference) GS, SS, GSS and UES, respectively.

After pelletizing and conditioning at 23 °C and 50% RH during one week, each material was injection-moulded (Babyplast 6/10P, Cronoplast, Italy) into standard test specimen for tensile test, dynamic mechanical analysis (bars) and into discs (diameter = 50 mm) for X-ray analysis. The injection-moulding process was carried out at a flow rate of 1.3 cm³ s⁻¹ with a holding pressure of 50 bars and a holding time of 10 s, at 145 °C for SS and UES materials and at 150 °C for SS and GSS materials; the cooling time was set at 10 s for all the materials. The discs of SS material for X-ray analysis could not be manufactured because the material injection-moulding was impossible, mainly due to high viscosity of the material which lead incomplete filling of the mould. In case of water plasticized starch (WS), moulding of samples for X-ray analysis and tensile properties of WS samples was not possible due to very high brittleness of the samples. All samples were stored in controlled humidity chamber at 23 °C with a relative humidity (RH) of 53% using saturated solution of magnesium nitrate during the entire testing period.

2.3. Characterization

The moisture content of all the samples was determined using a Karl Fischer titrator (V30, Mettler-Toledo, France) coupled with an oven (Mettler Stromboli, France). The sample was placed in falcon tube inside the oven operating at 150 °C. For 30 min., the evaporated water was transported by nitrogen from the sample vessel to the reaction medium. Afterwards, the water was titrated with reactive Hydranal (Sigma Aldrich, France) and solvent Hydranal (Sigma Aldrich, France) with a theoretical titer of 1 mg H₂O/ml. The analysis was performed five times per sample.

The scanning electron microscopy (SEM) observations were performed under high vacuum with a SEM instrument (S-4300SE/N, Hitachi, Japan) operating at 5 kV, on injection-moulded cryofractured samples previously coated with a thin gold layer.

The structural change in the materials was monitored by Fourier transform infrared (FTIR) spectroscopy (Nicolet 380 FT-IR, Thermo Scientific, France). The FTIR spectra were recorded in transmission mode. The native starch was previously mixed with KBr pellets. The FTIR spectra of plasticized starches were recorded using FTIR coupled with a microscope on a 5 μm thick sample slices cut with a microtome (Leica RM2165, Switzerland). The spectra of all materials were recorded after at least 32 scans with 4 cm⁻¹ resolution, in the spectral range of 4000–600 cm⁻¹. The native starch showed

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