



Influence of fatty chain length and starch composition on structure and properties of fully substituted fatty acid starch esters



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ABSTRACT

A series of almost fully substituted Fatty Acid Starch Esters (FASEs) has been obtained in a homogeneous LiCl/DMAc medium by grafting octanoyl (C8), lauroyl (C12) and palmitoyl (C16) chlorides onto 3 starch species: Amylo-Maize, Potato and Waxy Maize. Structure-property relationships of FASEs are investigated as a function of both fatty acid chain length and amylose/amylopectin ratio of the starch. The structural study has revealed a layered type organization in which starch chain planes are separated by fatty chains. The latter are interpenetrated and/or tilted for FASE-C16 whatever the origin of the starch is, and fatty chains partially crystallizes into a structure with hexagonal symmetry. FASEs with C8 and C12 side chains are totally amorphous. The mechanical behavior of FASEs is shown to depend on both side chain length and amylose/amylopectin ratio, and an increase in material ductility is observed at increasing amylose content for C8 and C12 side chains.

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1. Introduction

Considering the exhaustion of petroleum resources and consumer request for sustainable products, starch is one of the most inexpensive and readily available bio-based polymer that has attracted a great deal of interest as potential alternative to conventional plastics for packaging applications. Native starch is a semi-crystalline material composed of a mixture of two different macromolecules, amylose and amylopectin. Amylose is a linear α -D-glucopyranose polysaccharide with a molecular weight of 10^2 – 10^3 kDa. Amylopectin is a highly-branched polymer with a larger molecular weight, in the range 10^4 – 10^5 kDa. The ratio amylose/amylopectin in starch mainly depends on the botanic source (Buleon, Colonna, Planchot, & Ball, 1998; Pérez, Baldwin, & Gallant, 2009; Zobel, 1988). Native starch cannot be thermally processed without the addition of a plasticizer, since its decomposition tem-

perature is lower than its melting point. This phenomenon is related to its strong network of molecular hydrogen bonding (Liu, Xie, Yu, Chen, & Li, 2009). The most commonly used external plasticizers are water, various polyols (glycerol, sorbitol, maltitol ...), carbohydrates, urea... Their role is to increase the mobility of polysaccharide chains by forming hydrogen bonds between plasticizer molecules and starch hydroxyl groups. Physical and mechanical properties of these thermoplastic starches are strongly influenced by the nature and the amount of the plasticizer used (Da Róz, Carvalho, Gandini, & Curvelo, 2006). Upon addition of plasticizer, both flexibility and ductility are improved at the expenses of tensile strength. A concentration around 25–30 wt% of plasticizer is usually required to obtain a good compromise between flexibility and mechanical resistance, whatever the plasticizer is (Follain, Joly, Dole, & Bliard, 2005). Overall, applications of such externally plasticized starches remain greatly limited due to their high moisture sensitivity, low mechanical properties and poor long-term stability. In particular, numerous studies have reported plasticizer migration from the starch-based film, leading to structural changes inducing brittleness of the material (Lourdin, Coignard, Bizot, & Colonna, 1997; Schmitt et al., 2015; Zhang et al., 2016).

One strategy to overcome these drawbacks is to chemically modify starch. Modifications are generally achieved through cross-linking, grafting, esterification ... (Chen et al., 2015). Esterification

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of starch with organic acids is one route which allows to substitute hydroxyl groups, leading to less hydrophilic products. With the aim to achieve hydrophobic materials, literature reports numerous studies dedicated to the esterification of starch with fatty acid chlorides (Barrios, Giammanco, Contreras, Laredo, & López-Carrasquero, 2013; Liebert et al., 2011; Winkler, Vorweg, & Wetzel, 2013). Depending on the degree of substitution (DS) and the chain length of the fatty acid ester group, starch derivative properties may vary over a broad range, thus providing numerous opportunities for valuable applications for these materials. When the DS is high enough, esters of starch may result into a thermoplastic and hydrophobic material. Several studies have shown that fatty ester groups act as an internal plasticizer, leading to a decrease of the glass transition as the number and the length of fatty chains grafted onto starch are increased. Starch esters are mostly in amorphous state although some studies have revealed the presence of a crystalline phase, especially in the case of high amylose starch (Sagar & Merrill, 1995) and long ester-group chain length (Aburto, Hamaili, et al., 1999; Barrios et al., 2013; Thiebaud et al., 1997). Regarding the mechanical behavior, some studies report that starch triacetates are rather brittle (Whistler & Hilbert, 1944), especially when the amylopectin ratio is important (Fringant, Desbrières, & Rinaudo, 1996). Ductility seems to be improved as soon as the size of the substituent and the DS are high enough (Thiebaud et al., 1997). An extensive study on the physical properties of a series of fatty acid starch esters (FASEs) was recently reported (Winkler, Vorweg, & Rihm, 2014). In particular, mechanical properties of cast films of FASEs from C6 to C18 with medium and high DS were compared. Authors concluded that starch esters with medium DS behaved more in a “starch like” manner with relatively high stress levels and low drawability while the behavior of FASEs with high DS seems more dominated by the fatty acid phase.

A few years ago, our group has studied the effect of side chain length on the structure and thermomechanical behavior of fully substituted cellulose fatty esters (Crépy, Miri, Joly, Martin, & Lefebvre, 2011). Experimental results from X-ray and thermal analyzes have shown that these cellulose ester derivatives organize in a layered structure for which a model has been proposed. Regarding the mechanical behavior, the evolution of the yield stress has shown no clear trend while a decrease in the drawability has been highlighted when the length of the lateral chain is increased.

Based on a similar approach, the present study deals with the structure–physical property relationships of fully substituted starch esters using starches with various amylose/amylopectin ratios, and fatty acyl groups of different lengths (C8, C12, C16). The structural, mechanical and thermal characterizations were systematically performed using wide angle X-ray scattering (WAXS), uniaxial tensile tests, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) respectively. In order to better-understand the influence of the starch backbone chains and the fatty acid group on structural and physical properties of FASEs, a comparison of the starch esters with their cellulosic counterpart products will be performed.

2. Experimental part

2.1. Materials

Native amylo-maize and potato starches were provided by Roquette Frères (Lestrem, France) and waxy maize starch was purchased from Aldrich. Table 1 summarizes their amylose and amylopectin contents provided by suppliers and estimated using ISO 6647-2:2007 standard method. Prior to chemical modification, starch granules were oven dried at 105 °C for 24 h and stored in a dessicator.

All reagents were stored at room temperature and used without further purification: *N,N*-dimethyl-4-aminopyridine (DMAP, 99%, Acros); *N,N*-dimethylacetamide (DMAc, 99%, Acros); anhydrous lithium chloride (99%, Acros); octanoyl chloride (OCl, 99%, Aldrich); lauroyl chloride (LCl, 98%, Aldrich); palmitoyl chloride (PCL, 98%, Acros); chloroform ($\geq 99\%$, Carlo Erba); methanol ($\geq 99\%$, Carlo Erba). Deuterated chloroform used for NMR analyses was purchased from Aldrich and stored at 4 °C.

2.2. Acylation of starch by acyl chlorides

Acylation of starch samples with long chain fatty acids was performed using the same procedure as the one retained for cellulose acylation (Crépy, Chaveriat, Banoub, Martin, & Joly, 2009). In a typical experiment, 5 g of dried starch (31 mmol of anhydroglucose unit, 1 equiv.) were dissolved in 250 mL of 6.7% LiCl/DMAc (w/v) at 80 °C overnight. DMAP (11.3 g, 93 mmol, 3 equiv.) were added and stirred at 80 °C until complete solubilization. Fatty acyl chloride (10 equiv. per anhydroglucose unit according to fatty acid chloride, 310 mmol, corresponding to 53 mL of OCl, 72 mL of LCl and 90 mL of PCL) was then added and the mixture was stirred and classically heated at 80 °C during 3 h. The product was then poured into methanol (3 vol) to precipitate FASE and the solid was recovered by suction and purified by a repeated solubilization/precipitation process using chloroform and methanol, respectively. After drying in air at room temperature, products were obtained as light yellow powders whatever the fatty chain length and starch sample were. These products were converted into 300 μm thick films by casting in chloroform (15 g of FASE in 100 mL of chloroform). All cast films were translucent and they were stored under ambient conditions (23 ± 1 °C, $\sim 50\%$ R.H.).

2.3. Chemical characterization

Each FASE film has been characterized after casting by Fourier Transformed InfraRed (FTIR) spectroscopy using an Agilent Cary630 apparatus equipped with an ATR accessory, to probe the efficiency of reactions.

¹H NMR spectra were performed in CDCl₃ using a Bruker DRX-300 Spectrometer (operating at 300 MHz) to assess purity and determine the degree of substitution (DS) of FASEs by an integration method described elsewhere (Joly, Granet, Branland, Verneuil, & Krausz, 2005).

2.4. Structural characterizations

WAXS experiments were performed using a Genix microsource (XENOCs) equipment operating at 50 kV and 1 mA. The Cu-K α radiation used was selected with a curved mirror monochromator. The 2D patterns were recorded on a CCD camera from Photonic Science and the working distance was calibrated using a PLA sample. Before using FIT2D software, standard corrections were applied to the patterns such as dark current subtraction and background correction. Then, the WAXS intensity profiles were treated using Peakfit software. Pearson VII functions were used to fit the scattering profiles. Experiments were performed in transmission mode at room temperature. In order to investigate the thermally and mechanically induced structural evolution, some *in situ* X-ray experiments have been performed using a hot-stage thermal control unit and a homemade stretching device adaptable onto the X-ray equipment.

2.5. Thermal analysis

Thermogravimetric analysis (TGA) was used to accurately determine the water content and the degradation temperature of the films made and stored at ambient conditions. The measurements

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