Chapter 5

Synthesis of Fatty Acid Starch Esters in Supercritical Carbon Dioxide

Abstract
This paper describes an exploratory study on the synthesis of fatty acid/potato starch esters using supercritical carbon dioxide (scCO$_2$) as the solvent. The effects of process variables such as pressure (6 – 25 MPa), temperature (120 – 150 °C) and various basic catalysts and fatty acid derivatives (methyl and vinyl esters and anhydrides) on the degree of substitution (DS) were explored in a batch reactor set-up. Products with a broad range of DS values (0.01 - 0.31) were obtained, the actual values depending on process conditions, type of catalyst and the fatty acid reagent. The combination of K$_2$CO$_3$ and vinyl laurate gave the highest DS values (DS = 0.31 at 150 °C, 8 MPa). The introduction of the fatty acid chains has a profound effect on product properties like hydrophobicity and thermal behavior.

Keywords: potato starch, fatty acid starch esters, starch laurate, supercritical CO$_2$
5.1 Introduction

In the last decade, the synthesis of fatty acid starch esters has gained considerable interest from many research groups. The products have potential applications not only in the food but also in the non-food industry [1]. Examples of non-food applications are the use as reactive compounds for polyurethane resins [1] and as a substitute for oil-based polymers especially in the packaging industry [2-5].

Fatty acid starch esters may be synthesized by reacting starch with carboxylic acids (C₄-C₁₆) [5, 6], fatty acid vinyl esters (e.g. vinyl laurate, vinyl stearate) [2, 3, 7], fatty acid chlorides [8, 9], or fatty acid methyl esters (e.g. methyl palmitate, methyl laurate) [1, 4] as reactants, and basic salts such as potassium carbonate, sodium acetate, sodium dihydrogen phosphate, and potassium methoxide as catalysts in organic solvents such as pyridine and DMSO. A schematic representation of the esterification reaction of starch with various fatty acid derivatives is given in Scheme 5.1.

A major drawback of the existing synthetic methodology for fatty acid starch esters is the use of organic solvents such as pyridine and DMSO that have a negative environmental impact and may limit further commercialization of the process, particularly for food applications. Therefore, there is a strong incentive to develop green and environmentally friendly solvents for the process. A possible alternative is densified carbon dioxide, particularly supercritical carbon dioxide (scCO₂) [10]. Supercritical CO₂ is considered ‘green’, it is non-flammable, relatively non toxic and inert. Another advantage is the ease
of separation of product and solvent by simple depressurization [11-13]. The supercritical state (T_c = 31°C, P_c = 7.38 MPa) of CO_2 is also relatively easy to achieve experimentally.

The application of scCO_2 in polymerization reactions and polymer processing steps is currently receiving a great deal of attention [14]. ScCO_2 has shown to be a good solvent and processing aid for the chemical and physical modification of polysaccharides such as chitin, cellulose and starch [10, 15, 16]. In recent work from our group, the performance of scCO_2 was evaluated for starch acetylation reactions. It was found that scCO_2 is a good solvent and allows the synthesis of products with a range of degrees of substitution (DS) [17].

This paper deals with an experimental study to explore the potential of scCO_2 as solvent for the synthesis of fatty acid starch esters. In this study, various fatty acid vinyl/methyl esters and fatty acid anhydrides were tested to examine their reactivity in scCO_2. Furthermore, the effect of pressure (6 – 25 MPa), temperature (120 – 150 °C) and different basic catalysts on the (DS) was investigated. Important product properties were determined using contact angle measurements, Thermal Gravimetry Analysis (TGA), and Differential Scanning Calorimetry (DSC).

5.2 Materials and Methods
5.2.1 Materials

Potato starch was kindly supplied by AVEBE (The Netherlands). The water content was determined by drying the potato starch in a vacuum oven at 50 °C until constant weight and was found to be 16.2 % wt/wt. Pure potato amylose and amylopectin were obtained from Sigma. Analytical grade vinyl laurate and vinyl stearate were purchased from Fluka (Germany) and Aldrich (Japan), respectively. Analytical grade methyl laurate, methyl caprylate, butyric anhydride, and technical grade methyl oleate were purchased from Aldrich (Germany). Analytical grade stearic anhydride was obtained from Fisher Scientific (England). Analytical grade salt catalysts (potassium carbonate, sodium acetate, disodium hydrogen phosphate) and triethylamine (TEA) were purchased from Merck (Germany). Dimethyl sulfoxide-d_6 (DMSO-d_6) and trifluoroacetic acid-d_1 (TFA-d_1) were obtained from Aldrich. Technical grade methanol was purchased from Chemproha (The Netherlands). All chemicals were used as received without further purification. High purity CO_2 (≥ 99.7% volume) and N_2 (≥ 99.9% volume) were purchased from Hoekloos (The Netherlands).
5.2.2 Experimental set-up

The high pressure reactor setup consists of a stirred reactor (Parr Instrument), an electrical heating element with temperature controller, a high pressure pump unit, and CO$_2$ and N$_2$ storage bottles (Fig. 5.1). The reactor has a capacity of 100 ml and may be operated with a temperature range from -10 °C to 350 °C and a maximum pressure of 35 MPa.

The CO$_2$ is introduced to the reactor using a membrane pump (Lewa) with a capacity of 60 kg/hr at maximum pressure of 35 MPa. To prevent cavitation in the pump, CO$_2$ is first cooled down to 0 °C in a heat exchanger (Huber, The Netherlands). After pressurizing, a heat exchanger using hot-oil is used to heat the CO$_2$ to the desired temperature.

![Figure 5.1. Schematic representation of the high pressure reactor set up.](image)

5.2.3 Experimental Procedure

The fatty acid starch esters were prepared by reacting native potato starch with a fatty acid vinyl or methyl esters or a fatty acid anhydride, using an alkaline base salt as the catalyst. Native potato starch (3.53 g), the fatty acid derivative (3 mol/mol anhydroglucose unit (AGU)), and the basic salt (0.1 mol/mol AGU) were charged to the batch reactor. The reactor was flushed with N$_2$ to remove traces of air. Next, the autoclave was pressurized with CO$_2$ and heated till the desired temperature. CO$_2$ was added to increase the pressure to the desired level. After reaction, the reactor was cooled down to room temperature, depressurized. The solid product was separated from the liquid phase, washed several times with methanol (approximately 0.5 liter) according to a published procedure [2], filtered, and dried in a vacuum oven (5 mbar) at 70 °C until constant weight.
5.2.4 Analytical equipment

The DS of the product was determined using $^1$H-NMR on an Oxford NMR AS 400 spectrometer operating at 400 MHz. NMR spectra were recorded (64 scans) in DMSO-d$_6$ or when necessary in DMSO-d$_6$ with a small drop of TFA-d$_1$ to improve solubility [8, 18]. TGA measurements were performed on a Perkin Elmer TGA 7 Thermogravimetric Analyzer. The samples were heated to 900 °C in an inert atmosphere at a heating rate of 10 °C min$^{-1}$. DSC analyses were performed using a TA Instrument DSC 2920. The samples (about 10 mg) were placed in sealed aluminum cups. After a first heating run from room temperature to 200 °C to erase the thermal history of the material, each sample was cooled to 0 °C and then heated again to 200 °C (heating rate 10 °C/min).

Water contact-angle measurements were carried out by the sessile drop method (at 20 °C) using a custom-built microscope-goniometer system. The starch ester films were prepared according to a literature procedure [19]. A drop (1.5 µl) of milli-Q pore water was placed on a freshly prepared film using a precision micro-syringe (Hamilton) and after 30 s, the contact angle was measured at least at six different places on the film. The reported values are the average of the independent measurements.

5.2.5 Determination of the DS of the products

The DS was calculated from $^1$H-NMR spectra of the products (Eq 5.1) by comparing the area of the peaks corresponding with protons attached to the fatty acid carbon atoms (at δ 0.8 – 1.8 ppm) (Table 5.1) to the unit area of the starch protons (at δ 3.6 – 5.6 ppm) [2]. For some products, a correction was made for the unit area of the starch protons due to peak overlap with the olefinic H-atoms of the fatty acid chains (δ 5.1 – 5.6 ppm) (Eq 5.3).

\[
DS = \frac{A_{H-fatty}}{A_{H-starch}} \quad (5.1)
\]

\[
A_{H-fatty} = \frac{A_{0.8-1.8}}{n} \quad (5.2)
\]

\[
A_{H-starch} = \frac{A_{3.6-5.6} - y(A_{H-fatty})}{7} \quad (5.3)
\]

In these equations $A_{H-fatty}$ is the area of the fatty acid proton signals calculated from the peak intensity in the range δ 0.8 – 1.8 ppm, $A_{H-agu}$ is the area of the proton signals of the...
anhydroglucose unit, n is the amount of protons in the fatty acid side chain in the range $\delta$ 0.8 – 1.8 ppm, and y is the amount of fatty acid protons that overlap with peaks of the starch protons ($\delta$ 5.1 – 5.6 ppm). The values of n and y for the various fatty acid chains are given in Table 5.1.

### Table 5.1. Values of n and y used for the DS calculations

<table>
<thead>
<tr>
<th>Fatty acid chain</th>
<th>n</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butyrate (C4)</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Caprylate (C8)</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>Laurate (C12)</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>Stearate (C18:0)</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>Oleate (C18:1)</td>
<td>29</td>
<td>2</td>
</tr>
</tbody>
</table>

### 5.3 Results and Discussion

#### 5.3.1 Exploratory experiments

A number of preliminary experiments were carried out to investigate whether starch modification with fatty acid derivatives is indeed possible in scCO$_2$. The exploratory experiments were performed with vinyl laurate (3 mol/mol AGU) as the reactant and K$_2$CO$_3$ (0.1 mol/mol AGU) as the basic catalyst at various pressures and temperatures for 18 hours. After reaction, the product was washed thoroughly with methanol to remove unreacted reagents and catalyst and dried (70°C and 5 mbar) till constant weight. Reaction at a pressure of 15 MPa and a temperature of 140°C gave a yellowish granular product with DS of 0.02. At higher temperature (150°C) a yellowish/brown viscous paste was obtained with a higher DS value (0.26).

#### 5.3.2 Product characterization

##### 5.3.2.1 FT-IR analyses

The presence of fatty ester groups in the products was verified by FT-IR. Figure 5.2 shows the FT-IR spectra of native potato starch (Fig. 5.2a) and a starch laurate product with a DS of 0.02 (Fig 5.2b). In both spectra, the peaks between 3000 - 3600 cm$^{-1}$ and 2950 cm$^{-1}$ are assigned to OH and C-H stretching modes, the peaks at 1650 cm$^{-1}$ and 1420 cm$^{-1}$ to OH and C-H bending modes [20] and the absorption bands in the range of 900 – 1300 cm$^{-1}$ from highly coupled C-O and C-C vibrational modes [21, 22].

Clear differences between both spectra can be seen in the range of 2850 - 2920 cm$^{-1}$ and at 1750 cm$^{-1}$. These bands correspond to the C-H stretching vibrations of the alkyl
groups of the fatty ester chains and the C=O stretching vibrations of the carbonyl group, respectively [2, 20, 23-25]. These observations imply that the starch esterification reaction using scCO₂ as the solvent was successful.

![FTIR spectra](image)

**Figure 5.2.** FTIR spectra of native potato starch (a) and a starch laurate product with a DS of 0.02 (b).

### 5.3.2.2 $^1$H-NMR analyses

Almost all of the starch laurate products are soluble in DMSO-$_6$ except for the products with a DS higher than 0.26. These products were only partially soluble in DMSO-$_6$. To improve the solubility in DMSO-$_6$, one drop of TFA-d$_1$ was added to the mixtures [8, 18].

Figures 5.3a and 5.3b show the typical $^1$H-NMR spectra of native potato starch and the starch laurate product, respectively. The broad and overlapped peaks in the region $\delta$ 3.6 to 5.6 ppm are assigned to the starch protons [2, 26]. The peaks at $\delta$ 0.8 – 2.5 ppm correspond to the aliphatic hydrogen atoms of the fatty acid chain [2, 26]. The absence of resonances in the olefinic region ($\delta$ 7 – 7.2 ppm) indicates that the products are free from unreacted vinyl laurate and that the work-up procedure involving thorough washing of the product with methanol was successful.
Figure 5.3. $^1$H-NMR spectra of native potato starch (a) and starch laurate with DS of 0.08 (b).

### 5.3.3 Systematic studies

To study the effect of process conditions on the DS a number of experiments were performed at various pressures (8 – 25 MPa) and temperatures (120 – 150 °C) for 6 and 18 hours reaction time. Furthermore, the effect of the type of fatty acid derivative (vinyl/methyl esters and fatty acid anhydrides) and the type of basic catalyst were explored. An overview of the experimental conditions and results is given in Table 5.2.

#### Table 5.2. Overview of experiments $^a$

<table>
<thead>
<tr>
<th>No</th>
<th>Fatty acid reagent</th>
<th>$C_n$</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>t (h)</th>
<th>Catalyst</th>
<th>DS</th>
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<td>1</td>
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<td>12</td>
<td>15</td>
<td>120</td>
<td>6</td>
<td>$K_2CO_3$</td>
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<td>15</td>
<td>120</td>
<td>18</td>
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<td>15</td>
<td>150</td>
<td>6</td>
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<td>150</td>
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<td>$K_2CO_3$</td>
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</tr>
<tr>
<td>5</td>
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<td>15</td>
<td>150</td>
<td>18</td>
<td>TEA</td>
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</tr>
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<td>6</td>
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<td>150</td>
<td>18</td>
<td>$Na_3HPO_4$</td>
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Table 5.2. (continued)

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<th>Temperature (^\circ\text{C})</th>
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</tr>
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<td>140</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<td>10</td>
<td>140</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
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<td>140</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>0.01</td>
</tr>
<tr>
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<td>25</td>
<td>140</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
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</tr>
<tr>
<td>20</td>
<td>Methyl caprylate</td>
<td>8</td>
<td>15</td>
<td>150</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
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<tr>
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<td>15</td>
<td>150</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<tr>
<td>22</td>
<td>Methyl oleate</td>
<td>18:1</td>
<td>15</td>
<td>150</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
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</tr>
<tr>
<td>23</td>
<td>Vinyl butyrate</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
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<td>15</td>
<td>150</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>0.26</td>
</tr>
<tr>
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<td>Vinyl stearate</td>
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<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
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</tr>
<tr>
<td>26</td>
<td>Butyric anhydride</td>
<td>4</td>
<td>15</td>
<td>150</td>
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<td>( \text{K}_2\text{CO}_3 )</td>
<td>0.08</td>
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<tr>
<td>27</td>
<td>Stearic anhydride</td>
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<td>15</td>
<td>150</td>
<td>18</td>
<td>( \text{K}_2\text{CO}_3 )</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\(^a\) All experiments were performed with a catalyst to starch ratio of 0.1 mol/mol AGU and a vinyl or methyl ester to starch ratio of 3 mol/mol AGU

\(^b\) Number of carbon atoms in the fatty acid chain

\(^c\) not detectable

5.3.3.1 The effect of process conditions on the product DS for the esterification of starch with vinyl laurate

The influence of process conditions (temperature, pressure and reaction time) on the product DS for the reactions of starch with vinyl laurate was probed for a range of conditions (Table 5.2, entries 1-19). The effect of the temperature and reaction time at a fixed pressure of 15 MPa is shown in Fig 5.4a. It is evident that higher temperatures and prolonged reaction times have a positive effect on the DS. For instance, at 150°C, the DS increases from 0.05 to 0.26 when going from a reaction time of 6 h to 18 h. The positive effect of temperature is clearly illustrated when comparing the DS at 18 h at 120 °C (DS = 0.01) with that at 150°C (DS = 0.26). Such strong temperature effects were observed earlier in our group when performing starch acetylation reactions in sub-critical \( \text{CO}_2 \) [17] and related reactions in DMSO [3].

The effect of pressure on the DS is given in Figure 5.4b and shows a clear optimum. The application of pressures between 6 and 8 MPa leads to an increase in the DS. At higher
pressures, the DS is lowered considerably. The positive effect of pressure on the reaction at low pressures may be related to the plasticizing effect of scCO$_2$ in the starch matrix [27], which may enhance the diffusion rate of the reactants into the starch granules, leading to higher DS values [28].

A positive influence of pressure on the reaction rates may also be related to an increase in the kinetic constants for the chemical reactions due to an increase in the activation volume near the critical region of the mixtures, as reported in the literature [29]. However, the latter explanation likely does not hold in this case. Strong enhancements of the kinetic constants are expected only near the critical state of the mixture and above. It is very likely that at pressures below 10 MPa the reaction mixture is not yet in the supercritical state, as was estimated based on published data for the critical points of methyl laurate and CO$_2$ mixtures [30, 31].

The negative effect of pressure on the DS values at pressures higher than 8 MPa could be due to a change of the vinyl laurate distribution coefficient between the starch matrix and the solvent (supercritical CO$_2$). The solubility of vinyl laurate in scCO$_2$ is increased at elevated pressures [30, 31]. A higher solubility of vinyl laurate in scCO$_2$ leads to reduction of the concentration of vinyl laurate at the reaction locus, i.e. in the starch matrix [32].

Figure 5.4. The DS of starch laurate products at different temperatures (a) and pressures (b).

Another possible explanation to explain the negative effect of pressure on the DS at values above 8 MPa is a reduction of the free volume in the starch matrix due to compressive effects [27]. Contrary to the plasticizing effect at low pressure, this
compressive effect will reduce the rate of diffusion of the reactants into the starch granules, thus lowering the reaction rates and leading to lower DS values. The interplay between plasticizing and compressive effects is likely the cause for the observed maximum DS value as function of pressure.

5.3.3.2 Effects of the type of fatty acid derivative (esters/anhydrides) on the esterification reaction

The reactivity of the three different fatty acid derivatives (methyl- and vinyl ester and anhydride) with various fatty acid chain lengths was compared and evaluated. The results are shown in Figure 5.5 and Table 5.2 (entry 20-27).

Clearly, fatty acid vinyl esters (DS of 0.06 – 0.26) are more reactive than methyl esters (DS of 0.003 – 0.004) and anhydrides (DS of 0.01 – 0.08). Fatty acid methyl esters show the lowest reactivity among the tested fatty acid reagents.

![Figure 5.5. The effect of different types of esters reagents on the product DS](image)

The differences in the reactivity among the tested reagents are likely related to differences in properties of the leaving groups in the fatty acid reagents. The esterification of starch is expected to proceed via a nucleophilic substitution mechanism (Scheme 5.2) [20, 33, 34].
Scheme 5.2. Proposed reaction mechanism for the starch esterification reaction. R is the fatty acid chain in the starch backbone. OR’ is the leaving group.

The nucleophilic substitution reaction involves two steps. In the first, the carbonyl group is reacting with the starch nucleophile (starch alkoxide, ST-O’, formed by the reaction of starch with the base), forming a tetrahedral intermediate (3). In a subsequent step, the OR’ group is eliminated and the product is formed. According to this mechanism [20, 33, 34] a higher reactivity is expected for better leaving groups. In this context, a better leaving group is a weak base, or in other words, the conjugate base of a strong acid [35, 36]. Indeed, the experimental results agree with this reaction mechanism. The leaving group when using a fatty acid anhydride (butyrate) is the base of the strongest acid in the range and indeed gives a higher reactivity than the fatty acid methyl esters (Table 5.3).

<table>
<thead>
<tr>
<th>Fatty acid reagent</th>
<th>Leaving Group</th>
<th>Conjugate acid of the leaving group</th>
<th>pKₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂O₄R</td>
<td>O</td>
<td>Butyric Acid (C₄H₈O₂)</td>
<td>4.83&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Stearic Acid (C₁₈H₃₆O₂)</td>
<td>10.15&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>O</td>
<td>H₃C-OH</td>
<td>15.5&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
<td>O-CH₃</td>
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<td></td>
</tr>
<tr>
<td>R₂O₂</td>
<td>O-CH₂</td>
<td>HO=CH₂</td>
<td>n.a.&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Data taken from:  
<sup>a</sup> Lide (1998) [37]  
<sup>b</sup> Kanicky and Shah (2002) [38]  
<sup>c</sup> Bruice (2004) [35]  
<sup>d</sup> not available
Unfortunately, the $pK_a$ value of vinyl alcohol, being the leaving group of the fatty acid vinyl esters, is not available in the literature. This is not surprising as vinyl alcohol is not stable at ambient conditions and known to rearrange to acetaldehyde [39]. However, the vinyl alcohol acidity has been estimated with $ab\text{ initio}$ molecular orbital (MO) calculations [40] and shown to be higher than that of methanol. This suggests a higher reactivity of the fatty acid vinyl esters compared with fatty acid methyl esters, which is in agreement with the experimental results obtained in this study (see above).

Moreover, differences in the reactivity are observed not only for the different reagents but also for the different fatty acid chain lengths (Figure 5.5). It can be seen that the DS values of the products generally tend to decrease at higher carbon numbers. The only exception is vinyl laurate. The DS value of the starch laurate synthesized with vinyl laurate (DS of 0.26) is higher than that of the product made with vinyl butyrate (DS of 0.19).

The general trend of a reduction in the reactivity at longer carbon chain for fatty acid derivatives has also been reported in the literature. Junistia et al. (2008) published the synthesis of fatty esters of starch with vinyl esters (C12-C18:0) using DMSO as the solvent. A decrease in the DS value from 0.9 for vinyl laurate to 0.6 for vinyl stearate was observed [2]. The lower reactivity at longer chain length may be caused by a lower rate of diffusion of the longer fatty acid carbon chains into the starch matrix [2, 41].

However, this does not explain the relatively high DS for the reaction of vinyl laurate, which was actually higher than for vinyl butyrate. It may be anticipated that, especially at higher DS values, the starch matrix becomes more hydrophobic during reaction due to the presence of fatty acid chains. This is expected to have a positive effect on the accessibility of $CO_2$ in the matrix. Both effects will lead to higher diffusion rates of the fatty acid reagents in the starch matrix [27, 42] and thus lead to higher DS values [28]. This effect is likely more pronounced for longer fatty acid chains.

5.3.3.3 Catalyst screening

A number of catalysts were tested for the esterification reaction of starch with vinyl laurate. The results are shown in Fig 5.6 and Table 5.2 (entry no 4-7). It can be seen that $K_2CO_3$ is more active than the other basic salts. As reported in the literature, the reactivity of catalysts for the esterification of starch is assumed to a function of the basicity of the catalyst, with stronger bases (smaller $pK_b$ value) leading to higher activity [3]. Our data are in agreement with these findings, except for TEA. Despite its high $pK_b$ value, the catalytic activity of TEA is very low.
Figure 5.6. The influence of different catalyst on DS for the reaction of vinyl laurate with starch.

This may be the result of a different reaction mechanism for the TEA catalysed reaction [19, 35]. In this case, vinyl laurate is not the actual reagent but an amine-lauric acid complex, formed by a nucleophilic attack of TEA on the carbonyl group of vinyl laurate (1) (Scheme 5.3) [19, 35]. The amine-lauric acid complex reacts with the deprotonated starch alcohol group with the formation of a tetrahedral intermediate (Scheme 5.2). As TEA (pK$_b$ 3.25) is a strong base and thus a relatively poor leaving group, the elimination from the intermediate tetrahedral complex is more difficult than with weaker bases. This is expected to lead to a lower and thus a lower DS value, in agreement with the experimental results.

Scheme 5.3. Proposed mechanism for the first step of the nucleophilic substitution reaction of vinyl laurate with TEA.
5.3.4 Product properties

The thermal properties of the starch laurate products with various DS values (0.02 – 0.28) were determined and the results are discussed in this section. Examples of typical DSC thermograms are shown in Figure 5.7a, and the results for all measurements are given in Table 5.4.

Figure 5.7. The thermal properties of the products: DSC results (a) TGA results (b), and TGA derivatives (c).
Changes in the transition temperatures (melting temperature \( T_m \) and crystallization temperature \( T_c \)) of native potato starch after the esterification were clearly observed (Fig 5.7a). The decrease in the transition temperatures \( T_m \) and \( T_c \) compared with native potato starch suggests that the crystallinity of native potato starch is significantly reduced after the esterification reaction [3, 9]. This is confirmed by a lower melting enthalpy \( \Delta H_m \) and a lower crystallization enthalpy \( \Delta H_c \) at higher DS values (Table 5.4).

In contrast with the trend of the enthalpy values \( \Delta H_m, \Delta H_c \), the \( T_m \) (-13.7 – -13.9 °C) and \( T_c \) (1.2 – 1.8 °C) of the products are constant and are not influenced by the change in DS values [9]. The transition temperatures are not far off for those observed for pure vinyl laurate (Table 5.4, \( T_m \) of 5.76 °C and \( T_c \) of -10.72 °C). These findings suggest that the changes in the transition temperatures are mainly determined by the laurate side chains, as also reported in the literature [9, 43]. This assumption is further confirmed by the \( T_m \) (45.6 °C) and \( T_c \) (38.9 °C) values of starch stearate (Table 5.4) that are also close to the melting point of model compounds for the stearate side chain (methyl stearate, 40-42 °C; octadecane, 28-30 °C) [3].

The TGA results of the starch laurate and their derivatives are shown in Fig 5.7b and Fig 5.7c, respectively. The thermograms of the products (DS range of 0.02 – 0.26) show a decrease in the initial degradation temperature (230 – 240 °C) compared with native potato starch (270 °C). This effect, as also observed for similar products in the literature, is probably due to the disintegration of the intramolecular interactions such as hydrogen bonds in the starch chain during the reaction [41, 44].

Although the initial degradation temperature of the products is reduced, the overall thermal stability of the products are higher than native potato starch, as indicated by a broadening shoulder in the thermogram of our product at higher DS values (Fig 5.7b). The broadening shoulder is related to the appearance of two degradation steps (Fig. 5.7c) and it is clear that the second step (higher temperature peak in the first derivative curves) becomes more important at higher DS values.

As reported in the literature, the shoulder in the starch degradation peak is related to different degradation rates of amylose and amylopectin in the starch (Fig 5.7c) [45]. This suggests that the two peaks observed in starch laurate are from amylopectin laurate (low temperature peak) and amylose laurate (higher temperature peak). To check this hypothesis, we have independently synthesized amylopectin laurate and amylose laurate (Fig 5.7c). These two samples were prepared at a temperature of 150 °C and a pressure of 15 MPa using \( \text{K}_2\text{CO}_3 \) as the basic catalyst.
The area of the peaks of the amylose laurate in the starch laurate sample at higher DS values is much larger than that of the amyllopectine-laurate peaks (Figure 5.7c). This suggests that reaction in the amylose part of the starch is occurring at higher rates than in the amyllopectine parts. A higher fatty acid substitution in the amylose region can be caused by a higher accessibility of the reactants in the amorphous phase (consisting of amylose) compared with that of the crystalline phase (consisting of amyllopectin) [46, 47]. Moreover, in the presence of scCO$_2$, the extent of plasticization in the amorphous region will be higher than in the crystalline phase, and thus leading to higher accessibility of vinyl laurate in this region as well [27].

Table 5.4. Hydrophobicity and thermal properties of the products

<table>
<thead>
<tr>
<th>No</th>
<th>Products</th>
<th>DS</th>
<th>Contact angle</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g laurate)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g laurate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Starch laurate</td>
<td>0.28</td>
<td>90 ± 1.6</td>
<td>-13.8</td>
<td>36.6</td>
<td>1.8</td>
<td>41.6</td>
</tr>
<tr>
<td>2</td>
<td>Starch laurate</td>
<td>0.26</td>
<td>94 ± 2.1</td>
<td>-13.8</td>
<td>55.8</td>
<td>1.2</td>
<td>57.8</td>
</tr>
<tr>
<td>3</td>
<td>Starch laurate</td>
<td>0.15</td>
<td>104 ± 1.8</td>
<td>-13.9</td>
<td>53.9</td>
<td>1.3</td>
<td>56.1</td>
</tr>
<tr>
<td>4</td>
<td>Starch laurate</td>
<td>0.03</td>
<td>102 ± 1.9</td>
<td>-13.9</td>
<td>46.3</td>
<td>1.5</td>
<td>37.3</td>
</tr>
<tr>
<td>5</td>
<td>Starch laurate</td>
<td>0.02</td>
<td>96 ± 1.4</td>
<td>-14</td>
<td>99.8</td>
<td>1.5</td>
<td>97.8</td>
</tr>
<tr>
<td>6</td>
<td>Starch laurate (6 h)$^a$</td>
<td>0.05</td>
<td>n.m.$^c$</td>
<td>-13.7</td>
<td>217.2</td>
<td>1.4</td>
<td>230.9</td>
</tr>
<tr>
<td>7</td>
<td>Starch stearate</td>
<td>0.06</td>
<td>n.m.$^c$</td>
<td>38.9</td>
<td>66.1</td>
<td>45.1</td>
<td>64.8</td>
</tr>
<tr>
<td>8</td>
<td>Amylose laurate$^b$</td>
<td>0.1</td>
<td>n.m.$^c$</td>
<td>-11.5</td>
<td>73.9</td>
<td>1.1</td>
<td>73.5</td>
</tr>
<tr>
<td>9</td>
<td>Amylopectin laurate$^b$</td>
<td>0.15</td>
<td>n.m.$^c$</td>
<td>n.d.$^d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Native potato</td>
<td>45</td>
<td>45 ± 2.1</td>
<td>-10.72</td>
<td>164.4</td>
<td>5.76</td>
<td>166.1</td>
</tr>
</tbody>
</table>

$a$. The experiment was performed at 15 MPa and 150°C for 6 h

$b$. The experiments were performed at the same conditions as starch experiments

$c$. not measured

$d$. not detectable

Contact angle measurements were performed on native potato starch and the starch laurate samples with various DS (0.02 – 0.28). The results are shown in Figure 5.8 and also given in Table 5.4. Native potato starch had a contact angle of 45° which is in agreement with the reported values for native corn starch (43°) [48].

Clearly, all starch laurate products show higher contact angles (90 – 104°) compared to native potato starch (45°), which is indicative for a higher hydrophobicity of the products compared to native starch [9, 41]. The hydrophobicity increases with the DS values and reaches a maximum at a DS of 0.26. The small reduction of hydrophobicity at higher DS values (0.26 – 0.28) is probably related to an internal plasticizing effect of the lauric chain on the starch matrices. This is expected to cause a reduction in the starch chain interactions, leading to higher starch chain mobility and ultimately to a lower surface hydrophobicity [49].
5.4 Conclusions

This paper describes an exploratory study on the synthesis of fatty acid starch esters using different types of fatty acid reagents and catalysts in scCO\textsubscript{2} as the solvent. The occurrence of chemical reaction and the presence of a chemically bound fatty acid chains was verified with \textsuperscript{1}H-NMR and FT-IR. The DS of the products is a function of the temperature, pressure and reaction time. Clearly, higher temperatures and longer reaction times lead to product with a higher DS. The effect of pressure on the DS is more complex and a maximum DS is observed at an intermediate pressure. The type of catalyst also affects the DS. More basic catalysts lead to higher DS values. Furthermore, the DS of the product is a function of the different fatty acid reagents and the chain length of the fatty esters. Vinyl laurate showed the highest reactivity and in combination with K\textsubscript{2}CO\textsubscript{3} as the catalyst at a temperature of 150 °C and a pressure of 8 MPa, the highest DS value in this study (0.31) was obtained.
The thermal properties and the hydrophobicity of the products are different from that of native potato starch and depending on the product DS. This study not only demonstrates the potential of scCO$_2$ as a solvent for the synthesis of fatty acid starch esters, but also shows the possibility of tuning the product’s DS by changing the processing parameters.

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**References**
