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Synthesis of fatty acid starch esters in supercritical carbon dioxide

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ABSTRACT

This manuscript 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_2CO_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.

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 (Rooney, 1976). Examples of non-food applications are the use as reactive compounds for polyurethane resins (Rooney, 1976) and as a substitute for oil-based polymers especially in the packaging industry (Aburto, Alric, & Borredon, 2005; Junistia et al., 2008, 2009; Sagar & Merrill, 1995).

Fatty acid starch esters may be synthesized by reacting starch with carboxylic acids (C_4–C_{16}) (Sagar & Merrill, 1995; Yang & Montgomery, 2008), fatty acid vinyl esters (e.g. vinyl laurate, vinyl stearate) (Junistia et al., 2008, 2009; Mormann & Al-Higari, 2004), fatty acid chlorides (Aburto, Alric, & Borredon, 1999; Aburto, Alric, & Thiebaud, et al. 1999), or fatty acid methyl esters (e.g. methyl palmitate, methyl laurate) (Aburto et al., 2005; Rooney, 1976) 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 Fig. 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 supercritical carbon dioxide ($scCO_2$) (Harris et al., 1999). Supercritical CO_2 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 (Beckman, 2004; Eckert, Knutson, & Debenedetti, 1996; Savage, Gopalan, Mizan, Martino, & Brock, 1995). 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 (Kemmere, 2005). $ScCO_2$ has shown to be a good solvent and processing aid for the chemical and physical modification of polysaccharides such as chitin, cellulose and starch (Harris et al., 1999; Holser & Shogren, 2003; Yalpani, 1993; Yin et al., 2007). 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) (Muljana, Picchioni, Heeres, & Janssen, 2008).

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 gravimetric analysis (TGA), and differential scanning calorimetry (DSC).

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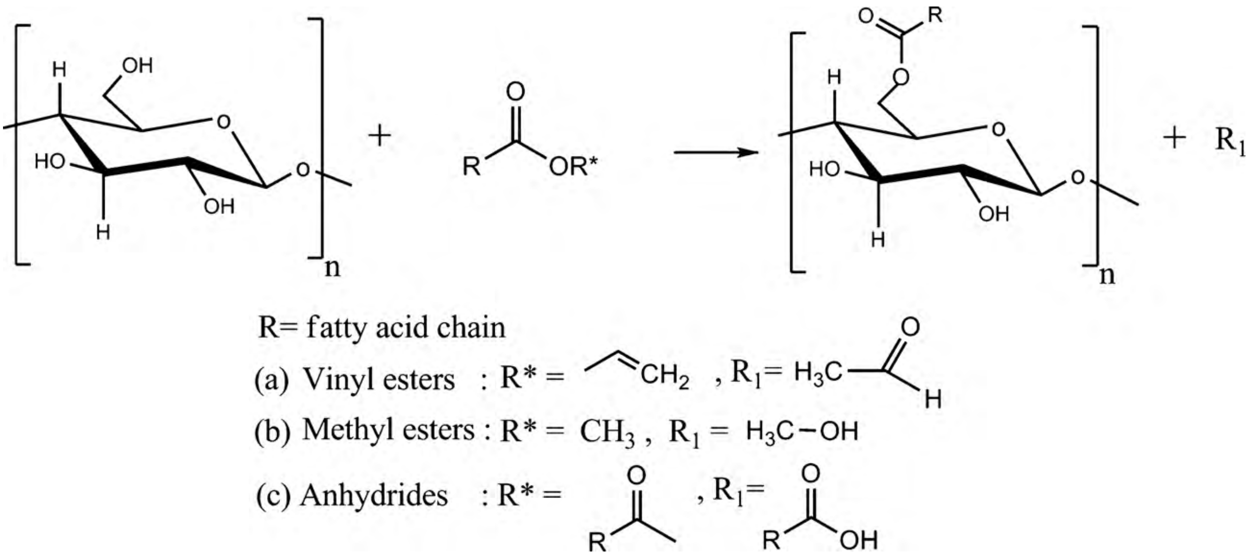


Fig. 1. Starch esterification using vinyl esters (a), methyl esters (b), and anhydrides (c).

2. Materials and methods

2.1. Materials

Potato starch (approximately 20.5% amylose and 79.5% amylopectin) was kindly supplied by AVEBE (Foxhol, 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% (w/w). Pure potato amylose (amylopectin free) and amylopectin (amylose free) were obtained from Sigma (Seelze, Germany). Analytical grade vinyl laurate (≥98%) and vinyl stearate (95.5%) were purchased from Fluka (Buchs, Switzerland) and Aldrich (Tokyo, Japan), respectively. Analytical grade methyl laurate (≥98%), methyl caprylate (≥99%), vinyl butyrate (≥99%), butyric anhydride (≥97.5%), and technical grade methyl oleate (70%) were purchased from Aldrich (Steinheim, Germany). Analytical grade stearic anhydride (≥98%) was obtained from Fisher Scientific (Loughborough, England). Analytical grade salt catalysts (potassium carbonate (≥99.5%), sodium acetate (≥99.5%), disodium hydrogen phosphate (≥99%)) and triethylamine (TEA, ≥99%) were purchased from Merck (Darmstadt, Germany). Dimethyl sulfoxide-d_6 (DMSO-d_6, 99.96 atom% D) and trifluoroacetic acid-d_1 (TFA-d_1, 99.5 atom% D) were obtained from Aldrich (Steinheim, Germany). Technical grade methanol (≥95%) was purchased from Chemproha (Dordrecht, The Netherlands). All chemicals were used as received without further purification. CO_2 (≥99.7 vol%) and N_2 (≥99.9 vol%) were purchased from Hoekloos (Amsterdam, The Netherlands).

2.2. Experimental set-up

The high pressure reactor set-up consists of a stirred reactor (Parr, type 35362B, Moline, IL, USA), an electrical heating element with temperature controller, a high pressure pump unit, and CO_2 and N_2 cylinders. The reactor has a capacity of 100 ml and may be operated with a temperature range from −10 to 350 °C to a maximum pressure of 35 MPa.

The CO_2 is introduced to the reactor using a membrane pump (Lewa, EH-1, Leonberg, Germany) with a capacity of 60 kg/h to a maximum pressure of 35 MPa. To prevent cavitation in the pump, the CO_2 admitted to the reactor is first cooled down to 0 °C using a heat exchanger (Huber, IC009, Offenburg, Germany). After pressurizing the CO_2 in the membrane pump, the CO_2 is heated up in a second heat exchanger (Huber, IC009, Offenburg, Germany) to the desired temperature.

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 l) according to a published procedure (Junistia et al., 2008), filtered, and dried in a vacuum oven (5 mbar) at 70 °C until constant weight.

2.4. Analytical equipment

The DS of the product was determined using ^1H 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 (Aburto, Alric, & Borredon, 1999; Kapusniak & Siemion, 2007). TGA measurements were performed on a PerkinElmer TGA 7 Thermogravimetric Analyzer. The samples were heated to 900 °C in an inert atmosphere at a heating rate of 10 °C/min. 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 (Bengtsson, Koch, & Gatenholm, 2003). 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.

2.5. Determination of the DS of the products

The DS was calculated from ^{1}H NMR spectra of the products (Eq. (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) to the unit area of the starch protons (at δ 3.3–5.6 ppm) (Junistia et al., 2008). 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. (3)).

$$\mathrm{DS} = \frac{A_{\text{H-fatty}}}{A_{\text{H-starch}}} \tag{1}$$

$$A_{\text{H-fatty}} = \frac{A_{0.8-1.8}}{n} \tag{2}$$

$$A_{\text{H-starch}} = \frac{A_{3.3-5.6} - y(A_{\text{H-fatty}})}{7} \tag{3}$$

In these equations $A_{\text{H-fatty}}$ is the area of the fatty acid proton signals calculated from the peak intensity in the range δ 0.8–1.8 ppm, $A_{\text{H-starch}}$ 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 δ 0.8–1.8 ppm, and y is the amount of fatty acid protons that overlap with peaks of the starch protons (δ 5.1–5.6 ppm). The values of y are 2 for oleate (C18:1) and 0 for all other fatty acid derivatives employed in this study.

3. Results and discussion

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_2CO_3 (0.1 mol/mol AGU) as the basic catalyst at various pressures and temperatures for 18 h reaction times. 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).

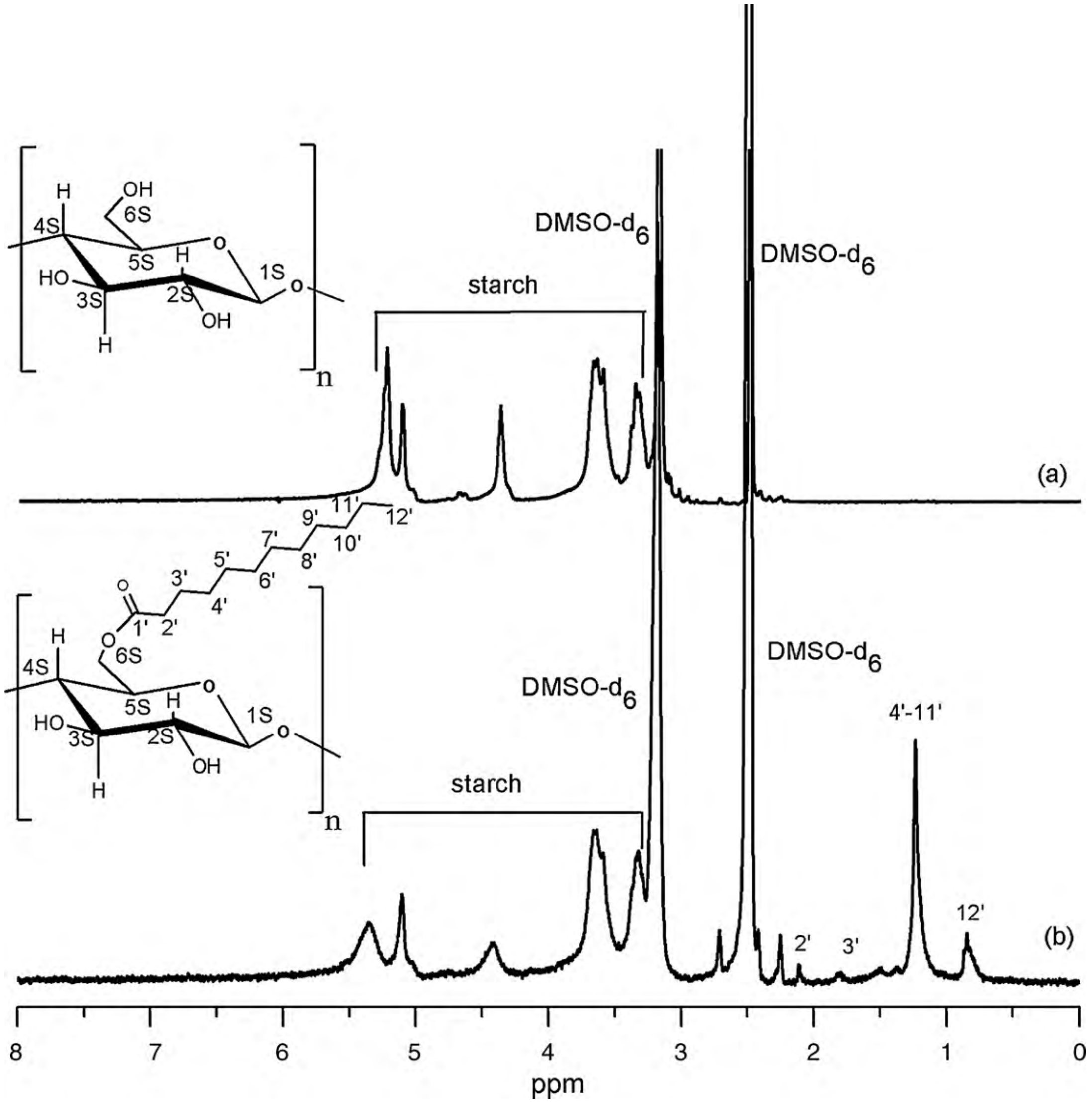


Fig. 2. ^{1}H NMR spectra of native potato starch (a) and starch laurate with DS of 0.08 (b).

Table 1
Overview of experiments[a].

No.	Fatty acid reagent	C_n[b]	Pressure (MPa)	Temperature (°C)	t (h)	Catalyst	DS
1	Vinyl laurate	12	15	120	6	K_2CO_3	n.d.[c]
2	Vinyl laurate	12	15	120	18	K_2CO_3	0.01
3	Vinyl laurate	12	15	150	6	K_2CO_3	0.05
4	Vinyl laurate	12	15	150	18	K_2CO_3 (pK_b 3.66)	0.26
5	Vinyl laurate	12	15	150	18	TEA (pK_b 3.25)	0.01
6	Vinyl laurate	12	15	150	18	Na_2HPO4 (pK_b 6.79)	0.09
7	Vinyl laurate	12	15	150	18	NaOAc (pK_b 9.24)	0.03
8	Vinyl laurate	12	6	140	18	K_2CO_3	0.08
9	Vinyl laurate	12	8	140	18	K_2CO_3	0.28
10	Vinyl laurate	12	10	140	18	K_2CO_3	0.03
11	Vinyl laurate	12	15	140	18	K_2CO_3	0.02
12	Vinyl laurate	12	20	140	18	K_2CO_3	0.01
13	Vinyl laurate	12	25	140	18	K_2CO_3	0.01
14	Vinyl laurate	12	6	150	18	K_2CO_3	0.18
15	Vinyl laurate	12	8	150	18	K_2CO_3	0.31
16	Vinyl laurate	12	10	150	18	K_2CO_3	0.28
17	Vinyl laurate	12	15	150	18	K_2CO_3	0.26
18	Vinyl laurate	12	20	150	18	K_2CO_3	0.15
19	Vinyl laurate	12	25	150	18	K_2CO_3	0.04
20	Methyl caprylate	8	15	150	18	K_2CO_3	n.d.
21	Methyl laurate	12	15	150	18	K_2CO_3	0.004
22	Methyl oleate	18:1	15	150	18	K_2CO_3	0.003
23	Vinyl butyrate	4	15	150	18	K_2CO_3	0.19
24	Vinyl laurate	12	15	150	18	K_2CO_3	0.26
25	Vinyl stearate	18:0	15	150	18	K_2CO_3	0.06
26	Butyric anhydride	4	15	150	18	K_2CO_3	0.08
27	Stearic anhydride	18:0	15	150	18	K_2CO_3	0.01

[a] All experiments were performed with a catalyst to starch ratio of 0.1 mol/mol AGU and a vinyl or methyl ester or anhydride to starch ratio of 3 mol/mol AGU.
[b] Number of carbon atoms in the fatty acid chain.
[c] Not detectable.

3.2. *Product characterization*

3.2.1. *FT-IR analyses*

The presence of fatty ester groups in the products was verified by FT-IR. A clear peak is visible at 1750 cm^{-1}, corresponding to the CO stretching vibration of the carbonyl group (Fang, Fowler, Sayers, & Williams, 2004; Junistia et al., 2008; Shogren, 2003; Singh, Chawla, & Singh, 2004; Xu, Miladinov, & Hanna, 2004). Peaks associated with the starch backbone are present at 3600–3000 cm^{-1} and 2950 cm^{-1} (OH and C=H stretching modes), at 1650 cm^{-1} and 1420 cm^{-1} (OH and C—H bending modes) (Xu et al., 2004) and absorption bands in the range of 900–1300 cm^{-1} from highly coupled C—O and C—C vibrational modes (Rubens & Heremans, 2000; vanSoest, Tournois, deWit, & Vliegenthart, 1995).

3.2.2. *^{1}H NMR analyses*

Almost all of the starch laurate products are soluble in DMSO-d_6 except for the products with a DS higher than 0.26. These products were only partially soluble in DMSO-d_6. To improve the solubility in DMSO-d_6, one drop of TFA-d_1 was added to the mixtures (Aburto, Alric, & Borredon, 1999; Kapusniak & Siemion, 2007).

Fig. 2(a) and (b) shows the typical ^{1}H NMR spectra of native potato starch and the starch laurate product, respectively. The broad and overlapped peaks in the region δ 3.3–5.6 ppm are assigned to the starch protons (Elomaa et al., 2004; Junistia et al., 2008). The peaks at δ 0.8–2.2 ppm correspond to the aliphatic hydrogen atoms of the fatty acid chain (Elomaa et al., 2004; Junistia et al., 2008). The absence of resonances in the olefinic region (δ 7–7.2 ppm) indicates that the products are free from unreacted

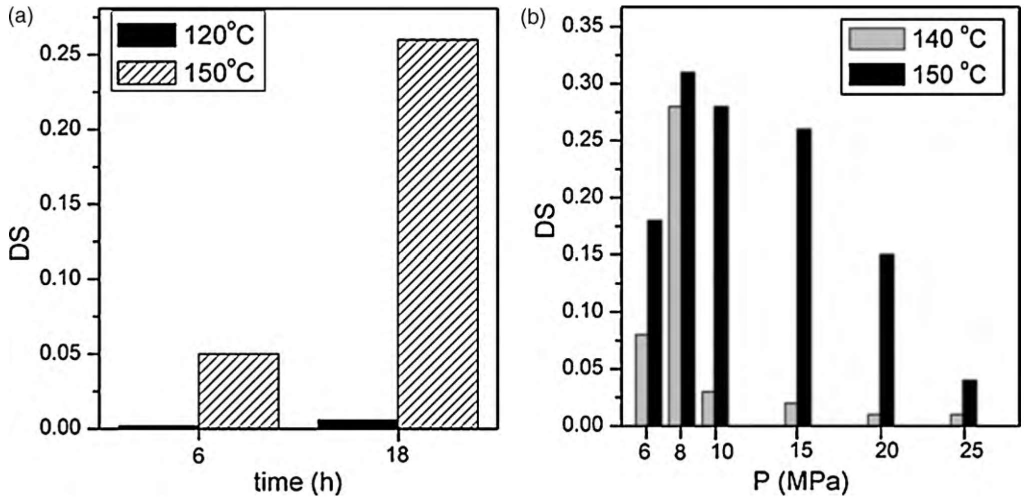


Fig. 3. The DS of starch laurate products at different temperatures (a) and pressures (b).

vinyl laurate and that the work-up procedure involving thorough washing of the product with methanol was successful.

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 h 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 are given in Table 1.

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 investigated for a range of conditions (Table 1, entries 1–19). The effect of the temperature and reaction time at a fixed pressure of 15 MPa is shown in Fig. 3a. 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 6–18 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 on the DS were observed earlier in our group when performing starch acetylation reactions in sub-critical CO_2 (Muljana et al., 2008) and related reactions in DMSO (Junistia et al., 2009).

The effect of pressure on the DS is given in Fig. 3b 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 (Francisco & Sivik, 2002), which may enhance the diffusion rate of the reactants into the starch granules, leading to higher DS values (de Gooijer & Koning, 2005).

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 of the chemical reactions near the critical region of the mixtures, as reported in the literature (da Ponte, 2009). 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 (Lockemann, 1994; Lockemann, Muñoz de Soto-Soliz, & Schlünder, 1995).

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 (Lockemann, 1994; Lockemann et al., 1995). 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 (Knez, Laudani, Habulin, & Reverchon, 2007).

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 (Francisco & Sivik, 2002). 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.

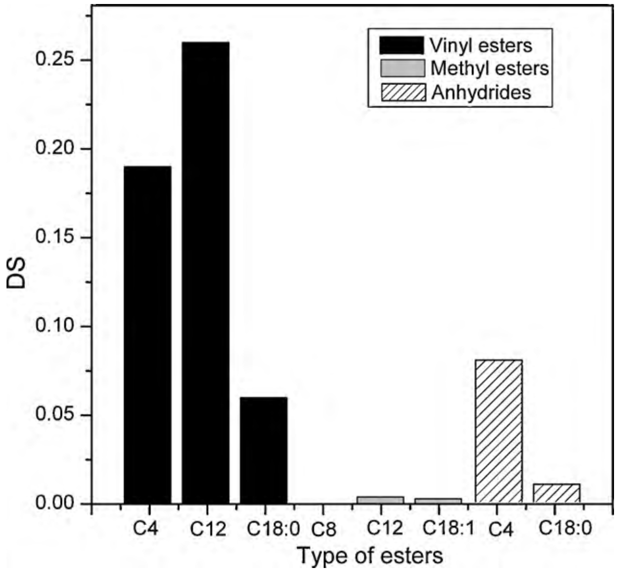


Fig. 4. The effect of different types of esters reagents on the product DS.

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 Fig. 4 and Table 1 (entries 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. These 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 (Fig. 5) (deGraaf, Broekroelofs, Janssen, & Beenackers, 1995; Jarowenko, 1986; Xu et al., 2004).

The nucleophilic substitution reaction involves three steps (Fig. 5). In the first step, a starch alkoxide is formed by the reaction of starch with the base. In a subsequent step, the carbonyl group is reacting with the starch alkoxide, forming a tetrahedral intermediate. Finally, the leaving group (OR'^{-}) is eliminated and the product is formed. According to this mechanism (deGraaf et al., 1995; Jarowenko, 1986; Xu et al., 2004) 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 (Bruice, 2004; Ege, 1994). 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 2).

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 (Bouma, Poppinger, & Radom, 1977). However, the vinyl alcohol acidity has been estimated with *ab initio* molecular orbital (MO) calculations (Wiberg, Ochterski, & Streitwieser, 1996) 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 agree-

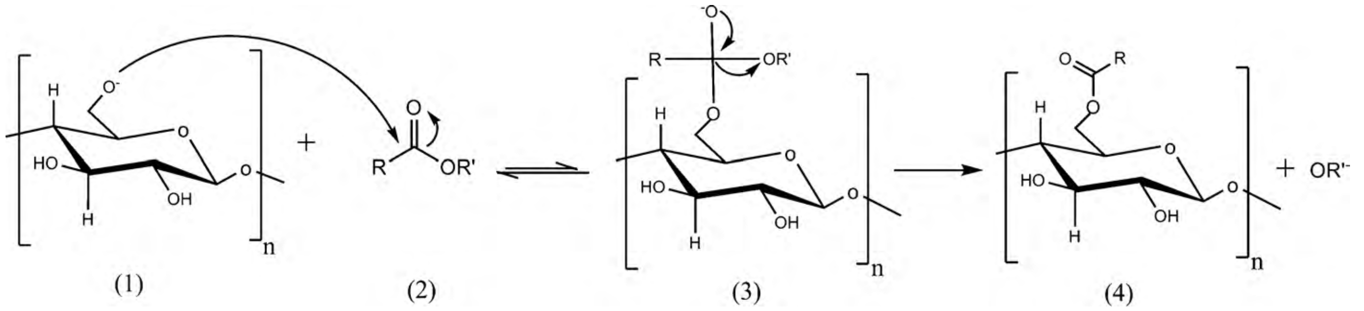


Fig. 5. Proposed reaction mechanism for the starch esterification reaction. R is the fatty acid chain in the starch backbone. OR′⁻ is the leaving group.

ment 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 (Fig. 4). 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 (Junistia et al., 2008). 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 (Aburto, Hamaili, et al., 1999; Junistia et al., 2008).

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 (Fleming & Kazarian, 2005; Francisco & Sivik, 2002) and thus lead to higher DS values (de Gooijer & Koning, 2005). This effect is likely more pronounced for longer fatty acid chains.

3.3.3. *Catalyst screening*

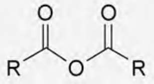
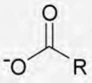
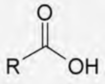
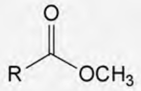
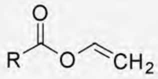
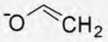
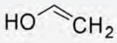
A number of catalysts were tested for the esterification reaction of starch with vinyl laurate. The results are given in Table 1 (entry nos. 4–7). It can be seen that K_2CO_3 (DS 0.26) is more active than the other basic salts (DS < 0.1). As reported in the literature, the reactivity of catalysts for 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 (Junistia et al., 2009). Our data are in agreement with these findings, except for TEA. Despite its low pK_b value (Table 1), the catalytic activity of TEA is very low (DS = 0.01). This may be the result of a different reaction mechanism for the TEA catalysed reaction (Bengtsson et al., 2003; Bruice, 2004). 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 (Bengtsson et al., 2003; Bruice, 2004). The amine–lauric acid complex reacts with the deprotonated starch alcohol group with the formation of a tetrahedral intermediate (Fig. 5). 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.

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 Fig. 6a, and the results for all measurements are given in Table 3.

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. 6a). 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 (Aburto, Alric, & Thiebaud, et al. 1999; Junistia et al., 2009). This is confirmed

Table 2
The p*K*a values of the leaving group of the fatty acid esters/anhydrides.

Fatty acid reagent	Leaving Group	Conjugate acid of the leaving group	pK_a
			4.83[a] 10.15[b]
	$^{-}O-CH_3$	H_3C-OH	15.5[c]
			n.a.[d]

[a] Data for butyric acid, taken from: Lide (1998).
[b] Data for stearic acid, taken from: Kanicky and Shah (2002).
[c] Data taken from: Bruice (2004).
[d] Not available.

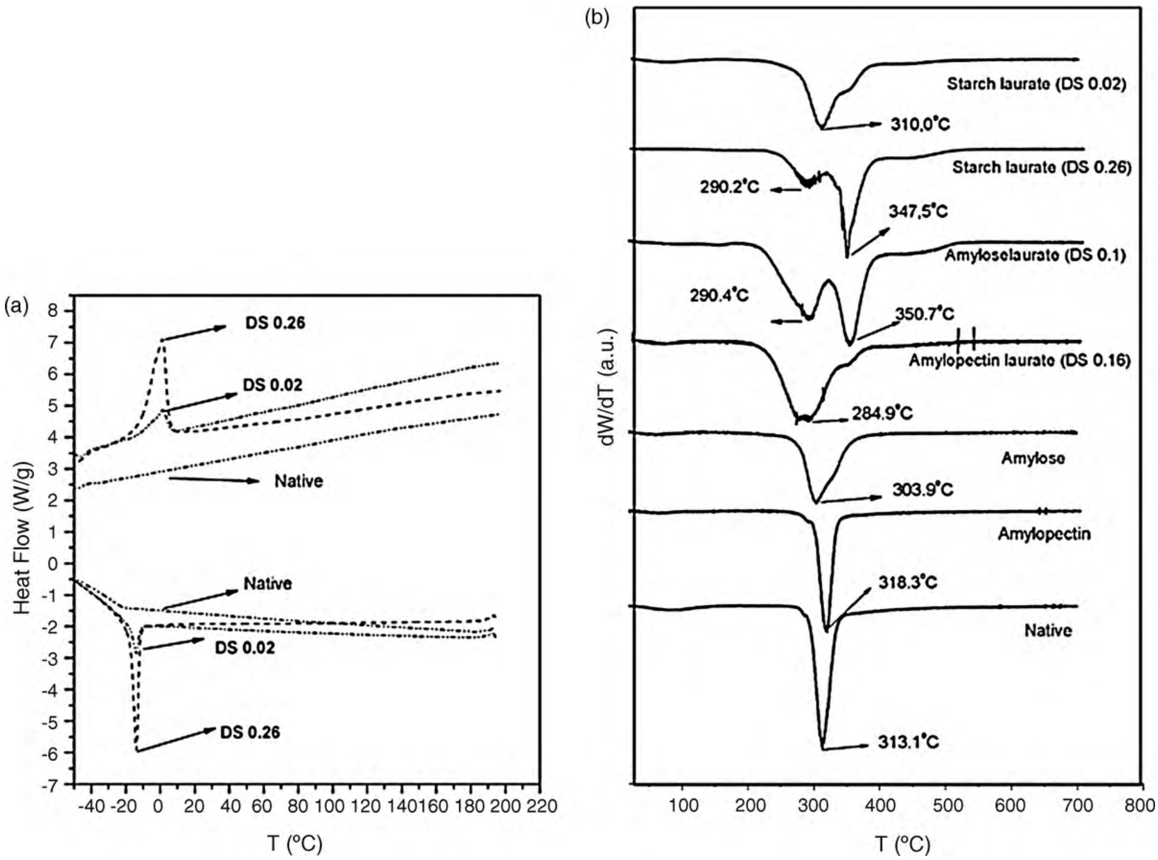


Fig. 6. The thermal properties of the products: DSC results (a) and TGA derivatives (b).

by a lower melting enthalpy (ΔH_m) and a lower crystallization enthalpy (ΔH_c) at higher DS values (Table 3).

In contrast with the trend of the enthalpy values (ΔH_m, ΔH_c), the T_m (−13.7 to −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 (Aburto, Alric, & Thiebaud, et al. 1999). The transition temperatures are not far off for those observed for pure vinyl laurate (Table 3, 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 (Aburto, Alric, & Thiebaud, et al. 1999; Thiebaud et al., 1997). This assumption is further confirmed by the T_m (45.6 °C) and T_c (38.9 °C) values of starch stearate (Table 3) 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) (Junistia et al., 2009).

The first derivatives of the TGA curves for several starch laurates are shown in Fig. 6b. The thermograms of the products (DS range of 0.02–0.26) show a decrease in the initial degradation temperature (230–240 °C) compared to 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 (Aburto, Hamaili, et al., 1999; Ren, Xu, Sun, Peng, & Sun, 2008). Furthermore, two degradation peaks are visible for the starch laurates, one at a value lower than virgin starch (290 °C) and one at a value considerably higher than native starch (347 °C, Fig. 6b). The intensity of particularly the second peak becomes more pronounced for the product with the highest DS value.

As reported in the literature, the two peaks are likely related to different degradation temperatures of the amylose and amy-

Table 3
Hydrophobicity and thermal properties of the products.

No.	Products	DS	Contact angle	T_c (°C)	ΔH_c (J/g$_{laurate}$)	T_m (°C)	ΔH_m (J/g$_{laurate}$)
1	Starch laurate	0.28	90 ± 1.6	−13.8	36.6	1.8	41.6
2	Starch laurate	0.26	94 ± 2.1	−13.8	55.8	1.2	57.8
3	Starch laurate	0.15	104 ± 1.8	−13.9	53.9	1.3	56.1
4	Starch laurate	0.03	102 ± 1.9	−13.9	46.3	1.5	37.3
5	Starch laurate	0.02	96 ± 1.4	−14	99.8	1.5	97.8
6	Starch laurate (6 h)[a]	0.05	n.m.[c]	−13.7	217.2	1.4	230.9
7	Starch stearate	0.06	n.m.[c]	38.9	66.1	45.1	64.8
7	Amylose laurate[b]	0.1	n.m.[c]	−11.5	73.9	1.1	73.5
8	Amylopectin laurate[b]	0.15	n.m.[c]	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]
9	Native potato		45 ± 2.1	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]
10	Vinyl laurate			−10.72	164.4	5.76	166.1

[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.

lopectin fraction in the starch (Mano, Koniarova, & Reis, 2003). This suggests that the two peaks 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. These two samples were prepared using pure amylose and amylopectine as the feed at a temperature of 150 °C and a pressure of 15 MPa using K_2CO_3 as the basic catalyst and vinyl laurate as the reagent. The results confirm the hypothesis of different degradation temperatures for the amylose and amylopectine regions in starch (Fig. 6b).

The area of the peaks from the amylose laurate fraction in the starch laurate sample (at higher DS values) is considerably larger than that of the amylopectine-laurate peak (Fig. 6b). This suggests that reaction in the amylose part of the starch is occurring at a higher rate than in the amylopectine parts. A higher fatty acid substitution in the amylose region is likely due to a higher accessibility of the reactants in the amorphous phase (consisting of amylose) compared with that of the crystalline phase (consisting of amylopectin) (Chen, Schols, & Voragen, 2004; Huang, Schols, Klaver, Jin, & Voragen, 2007). 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 (Francisco & Sivik, 2002).

Contact angle measurements were performed on native potato starch and the starch laurate samples with various DS (0.02–0.28). The results are given in Table 3. Native potato starch had a contact angle of 45° which is in agreement with the reported values for native corn starch (43°) (Chi et al., 2008).

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 (Aburto, Alric, & Thiebaud, et al. 1999; Aburto, Hamaili, et al., 1999). 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 (Karbowiak, Debeaufort, Champion, & Voilley, 2006).

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 $scCO_2$ as the solvent. The occurrence of chemical reaction and the presence of a chemically bound fatty acid chains was verified with ^{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. 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_2CO_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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