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Synthesis of Sago Starch Laurate in Densified Carbon Dioxide

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Fatty acid starch esters are potential candidates for novel biodegradable plastics. This work describes a systematic study on the synthesis of starch laurate using sago starch and vinyl laurate (VL) in densified CO₂ as a green solvent. The phase behavior of the CO₂-VL system was investigated in a high pressure view cell and the critical point of the CO₂-VL mixtures was shown to increase with temperature. Within the experimental window, sago starch laurate with a maximum degree of substitution (DS) of 0.97 is obtained. To the best of our knowledge, such high DS values have never been reported before for reactions in densified CO₂. Moreover, the presence of laurate chains in the starch backbone has a profound influence on the degree of crystallinity, the melt and crystallization temperature, and the degradation temperature of the final products. POLYM. ENG. SCI., 58:291–299, 2018. © 2017 Society of Plastics Engineers

INTRODUCTION

Global demand for plastics is growing with a rate of almost 20% per year, from 204 million tons in 2002 rose to 311 million tons in 2014 [1]. Plastics waste, however, causes serious environmental problems, because of high volume to weight ratio and resistance to degradation. Another environmental issue is related with the availability of crude oils as the major raw material for commercial plastic production [1]. Crude oil is not-renewable and its availability is depleting. To overcome these problems, biodegradable plastics and particularly those based on sustainable renewable resources (mainly natural polymers or polymerisable materials from plants and microbes) are of high interest.

Indonesia is a tropical country with a large potential for the production of commodity bioplastics. Starch, a typical natural biopolymer used for biodegradable polymers applications, can be obtained abundantly in Indonesia from various sources such as tubers (cassava, arrowroot, sweet potato) and grains (job's tears, sorghum, and many types of cereals). However, the application of starch as a raw material for biodegradable plastics is still limited [2, 3] due to its brittleness, low hydrophobicity, and low mechanical strength [4–6]. These drawbacks can be

overcome by chemical modification of the starches to obtain a thermoplastic material as end product.

Among others, the esterification of starch with fatty acid esters such as fatty acid vinyl esters (FAVE), fatty acid methyl esters (FAME), and fatty acid chlorides (see Fig. 1) in organic solvents has resulted in products with improved thermoplastic properties compared to those of their native counterparts [8–10]. However, their synthesis involve the use of organic solvent, with a relatively high and negative environmental impact, and product work-up is often cumbersome [2]. To overcome these problems, supercritical CO₂ (sc CO₂) as a solvent for starch modification with fatty acid esters has been recently reported [7]. The authors reported the successful esterification of potato starch with FAVE, FAME, and fatty acid anhydride. However, the degree of substitution (DS) of the products is still relatively low (DS 0.01–0.3), thus resulting in less than optimal mechanical properties [7].

This work explores the use of sago starch for novel starch esters using vinyl laurate (VL) as the reagent. The application of sago starch, displaying a type C crystallinity [11], was proven to give higher reactivity with FAME compared to potato starch (type B of crystallinity) [12]. However, products with a relatively low DS range (0.034–0.45) was obtained. This work focuses on the use of VL, which is known to be more reactive than FAME, thus targeting final products with higher DS values. A systematic study was conducted to determine the influence of several process variables on the DS. In addition, to gain insights in the phase behavior during the reaction, a number of experiments were performed in a high pressure view cell. The molecular structure and relevant product properties were analyzed using ¹H-NMR, Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM), X-ray diffraction (XRD), thermal gravimetry analysis (TGA), and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Materials

Sago starch was purchased from Bina Sago Lestari (Indonesia). The starch water content was determined by a gravimetric method and shown to be 16.9% wt/wt. Analytical grade VL was purchased from Fluka (Germany). Analytical grade salt catalysts (potassium carbonate, sodium acetate, sodium sulfate) were purchased from Merck (Germany). Dimethyl sulfoxide-d₆ (dimethylsulfoxide [DMSO]-d₆) was obtained from Aldrich. Technical grade methanol was purchased from Bratachem (Indonesia). All chemicals were used as received without further purification. High purity CO₂ (≥ 98% volume) and N₂ (≥ 98% volume) were purchased from Sangkuriang (Indonesia).

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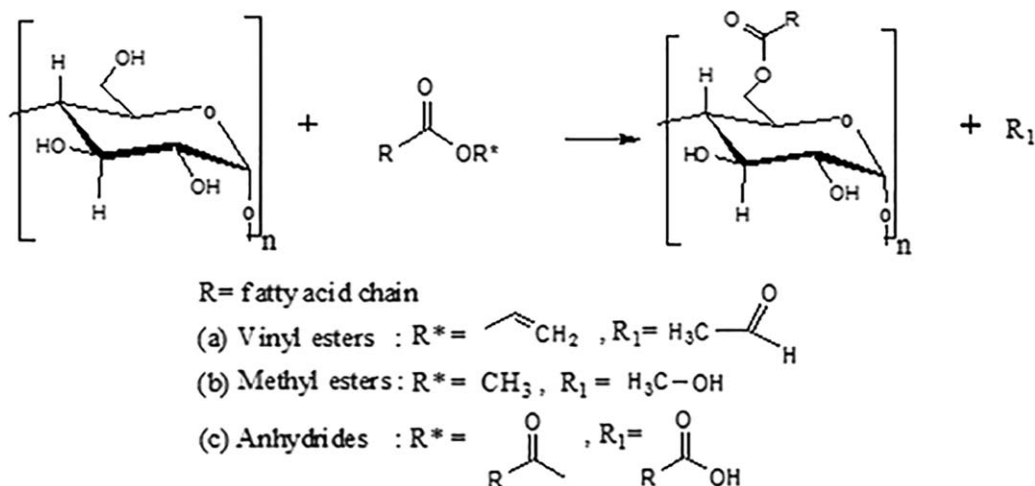


FIG. 1. Esterification of starch with various sources of fatty acid [7].

Experimental Setup

The high pressure reactor setup consists of a stirred reactor, an electrical heating element with temperature controller, a high pressure pump unit, and CO_2 and N_2 storage bottles. The reactor has a capacity of 35 ml and may be operated in a temperature range from 30°C to 300°C and a maximum pressure of 20 MPa. The CO_2 is introduced to the reactor using a positive displacement pump (Chrom Tech) equipped with an integrated cooling system to eliminate cavitation issues in the pump. The pump has a maximum flow rate of 24 ml/min and a maximum pressure of 69 MPa.

A high pressure view cell was used to determine the phase behavior of the system. It consists of a high pressure stirred view cell (NWA GmbH, Lorrach, Germany), equipped with a turbine type impeller, two stainless steel cartridge heaters (Conrad Electronic Benelux), a thermal controller, and a high pressure pump (Lewa) with a capacity of 60 kg/h at a maximum pressure of 35 MPa. The cell has a capacity of 60 ml and may be operated at a maximum pressure of 40 MPa and a maximum temperature of 200°C .

EXPERIMENTAL

Esterification of Sago Starch Using VL

The starch laurates were prepared by reacting native sago starch with VL, using an alkaline salt as the catalyst. Native sago starch (2.5 g, dry basis), VL, and the salt were charged to the batch reactor. After flushing with N_2 to remove air (approximately 5 min), the reactor was pressurized with CO_2 and heated to the desired temperature. CO_2 was added to increase the pressure to the desired level. After reaction, the reactor was cooled to room temperature and depressurized to atmospheric conditions. The solid product was separated from the remaining liquid VL, washed with methanol (approximately 0.5 l), filtered and dried in a vacuum oven at 70°C until constant weight [7].

Phase Behavior Study

To get insights in the reaction with sub/supercritical CO_2 , phase behavior studies of VL- CO_2 mixtures were carried out in

a high-pressure view cell. In particular, the critical points of the VL- CO_2 mixtures were determined. The molar ratio of VL- CO_2 (Eq. 1) used in these experiments was similar to those used in the actual esterification experiments. The critical point of the mixture was visually determined and set at the point when the biphasic mixture became a single (supercritical) phase and at the point when the single phase become biphasic again after depressurization according to a reported procedure. The critical points as determined by both methods are equal within 0.04 MPa. The VL mole fraction (y_{VL}) at the critical point was calculated by Eq. 1.

$$y_{\text{VL}} = \frac{n_{\text{VL},0}}{(n_{\text{VL},0} + n_{\text{CO}_2,0})} \quad (1)$$

where $n_{\text{VL},0}$ is the initial molar intake of VL and $n_{\text{CO}_2,0}$ the molar intake of CO_2 at a given pressure and temperature. To determine the molar intake of CO_2 , the density needs to be known at different pressures and temperatures. These values were obtained from the Span and Wagner Equation of State [13–15].

Analytical Equipment

$^1\text{H-NMR}$ spectra were recorded using a JEOL JNM-ECA 500 spectrometer operating at 500 MHz at an operating temperature of 60°C . Prior to the measurements, the starch sample was dissolved in DMSO- d_6 at a temperature of 90°C for 2 h. FT-IR spectra were acquired on a FTIR Prestige 21 Shimadzu. TGA measurements were performed on a TGA Mettler Toledo Type TGA/SDTA 851. The samples were heated to 900°C in an inert atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. DSC analysis were carried out using a Perkin Elmer DSC 8000. The samples (4 – 5 mg) were heated from 0°C to 200°C with a heating rate of $10^\circ\text{C min}^{-1}$. XRD analyses were done in a diffractometer type PW1710 BASED with Anode Cu. The morphology of native starch and the starch fatty acid esters products were determined using SEM (JEOL T330A).

Determination of the DS Values of the Products

The DS describes the number of substituents per anhydroglucose unit (mole/mole AGU). The DS values can vary from

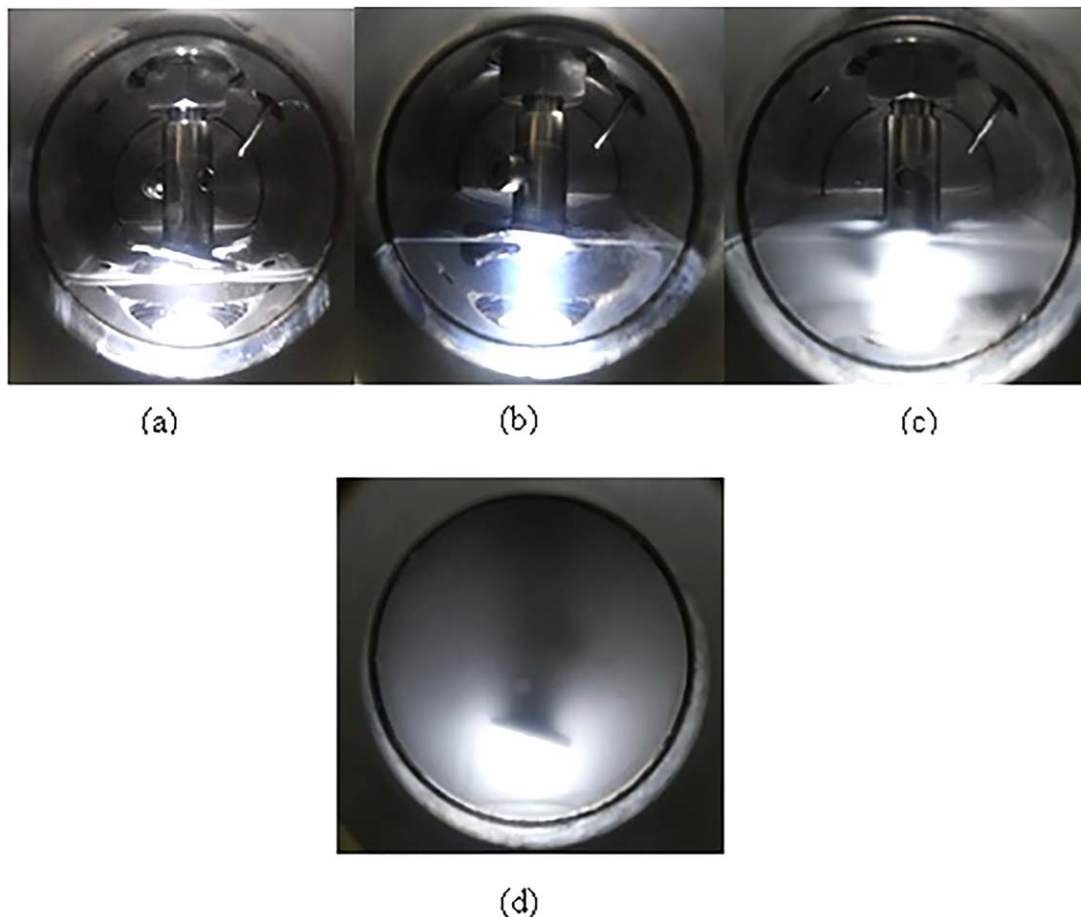


FIG. 2. Phase behavior of VL-scCO₂ mixtures at 50°C with pressure of 5 MPa (a), 12 MPa (b), 14 MPa (c), and 15 MPa (d). [Color figure can be viewed at wileyonlinelibrary.com]

0 to 3 as each AGU contains on average three hydroxyl group [5, 16]. The DS values were determined using a hydrolysis method according to a previously reported procedure [5]. A starch sample (1 g) was placed in a 250 ml erlenmeyer flask with stopper. RO water, that is, water purified through Reverse Osmosis, (10 ml), 0.5 N NaOH (15 ml), and a few drops of phenolphthalein were added. The mixture was subsequently stirred gently at a temperature of 30°C for 4 h. Excess alkali present in the mixture was titrated with 0.1 N (HCl) until the red color of phenolphthalein disappeared. The DS was calculated using Eq. 2.

$$DS = \frac{162 \times (N_{\text{NaOH}} \times V_{\text{NaOH}} - N_{\text{HCl}} \times V_{\text{HCl}})}{(1000 \times W) - 182 \times (N_{\text{NaOH}} \times V_{\text{NaOH}} - N_{\text{HCl}} \times V_{\text{HCl}})} \quad (2)$$

where V_{NaOH} is the volume of NaOH (ml), V_{HCl} is the titration volume of acid (ml), N_{NaOH} is the normality of NaOH solution, N_{HCl} is the normality of the HCl solution, W is the mass of the fatty ester starch sample (g), 162 and 182 are the molecular weight of AGU and laurate as substituent on the starch backbone, respectively.

RESULTS AND DISCUSSION

Starch esterification reactions in CO₂ are known to be affected by the temperature and pressure [7]. CO₂, especially when in

the supercritical state, is known to lead to swelling of the starch granules and possibly act as a solvent for the reagents. Both factors facilitate transfer of substrates into the starch granule and may thus lead to higher reaction rates. In this context, knowledge of the phase behavior of starch, reagents and CO₂ is of high relevance.

As such, the critical point of the VL-CO₂ mixtures at three different temperatures ($T = 50^\circ\text{C}$, 100°C , and 120°C) and with the same molar ratio between VL and CO₂ as used in the reactions, were determined. The changes of the VL-CO₂ system from gas liquid VL-CO₂ to supercritical phase with pressure (from 5 to 15 MPa) at temperature of 50°C is clearly shown in Fig. 2. The supercritical phase at 50°C is reached at critical pressures of about 15–16 MPa with a VL mole fraction (y_{VL}) of about 0.06 (calculated by Eq. 1). It is obvious that the critical

TABLE 1. Critical properties of VL -CO₂ binary mixtures at different temperatures.

No	Reagent	T (°C)	Critical region (MPa)	y_{VL}
1	Vinyl Laurate	50	15–16	0.05
2	Vinyl Laurate	100	21–22	0.06
3	Vinyl Laurate	120	24–25	0.06

TABLE 2. Overview of experiments.

No	T (°C)	P (MPa)	Reaction time (h)	Type of catalyst	VL intake (mol/mol AGU)	K_2CO_3 intake (mol/mol AGU)	DS
1	100	8	1.5	NaOAc	3	0.1	0.06
2	100	8	1.5	NaOAc	5	0.1	0.67
3	100	8	1.5	Na_2SO_4	3	0.1	0.29
4	100	8	1.5	Na_2SO_4	5	0.1	0.81
5	80	8	1.5	K_2CO_3	3	0.1	0.16
6	80	8	1.5	K_2CO_3	3	0.4	0.22
7	90	8	1.5	K_2CO_3	3	0.1	0.31
8	90	8	1.5	K_2CO_3	3	0.2	0.46
9	90	8	1.5	K_2CO_3	3	0.4	0.56
10	100	8	1.5	K_2CO_3	3	0.1	0.52
11	100	8	1.5	K_2CO_3	3	0.2	0.69
12	100	8	1.5	K_2CO_3	3	0.4	0.82
13	100	8	2.5	K_2CO_3	5	0.1	0.85
14	100	10	1.5	K_2CO_3	5	0.1	0.84
15	100	20	1.5	K_2CO_3	5	0.1	0.78
16	100	8	3	K_2CO_3	5	0.1	0.88
17	100	10	3	K_2CO_3	5	0.1	0.97
18	100	20	3	K_2CO_3	5	0.1	0.79
19	120	20	5	K_2CO_3	5	0.1	0.74
20	120	20	10	K_2CO_3	5	0.1	0.95
21	80	10	10	K_2CO_3	5	0.1	0.73

parameters (T and P) of binary VL- CO_2 mixtures are higher than the one of pure CO_2 ($T = 31^\circ C$, $P = 7.38$ MPa).

A similar behavior was observed at $100^\circ C$ and $120^\circ C$ (figures not shown for brevity). However, the critical pressures are somewhat higher compared with the one at $50^\circ C$ (see Table 1). This is not surprising and is related to the fact that the density of CO_2 decreases with temperature and therefore a higher pressure is required at higher temperature to reach a single supercritical phase.

A series of experiments was designed (Table 2) to evaluate the influence of important process variables such as temperature, pressure, K_2CO_3 intake, and various types of alkaline salts (NaOAc, K_2CO_3 , and Na_2SO_4) on the DS of the product. The

experiments span a broad range of conditions and include both the sub-and near-critical regime. After reactions and work-up, products with a range of DS values (0.04–0.97, see Table 2) were obtained.

Three different salt base catalysts (K_2CO_3 , NaOAc, Na_2SO_4) were used in this experiments. The effect of these salts on the DS at two different VL intakes (3 and 5 mol/mol AGU) is shown in Fig. 3a and b. In both cases, the use of NaOAc results in the lowest DS value. It is clear that the salt catalyst plays an important role in the reaction. The reactivity of the catalyst is expected to be a function of its basicity and a maximum DS value is anticipated when using the base with the lowest pK_b value [16].

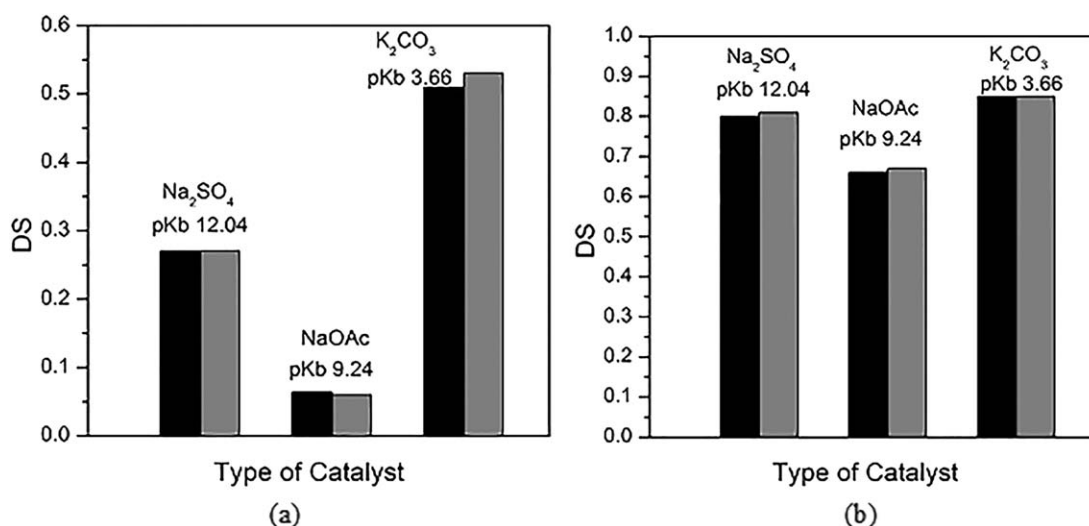


FIG. 3. Effect of different types of catalyst on the DS at a VL intake of 3 mol/mol AGU (a) and 5 mol/mol AGU (b). Conditions: $100^\circ C$, 8 MPa, 1.5 h, and a catalyst intake of 0.1 mol/mol AGU.

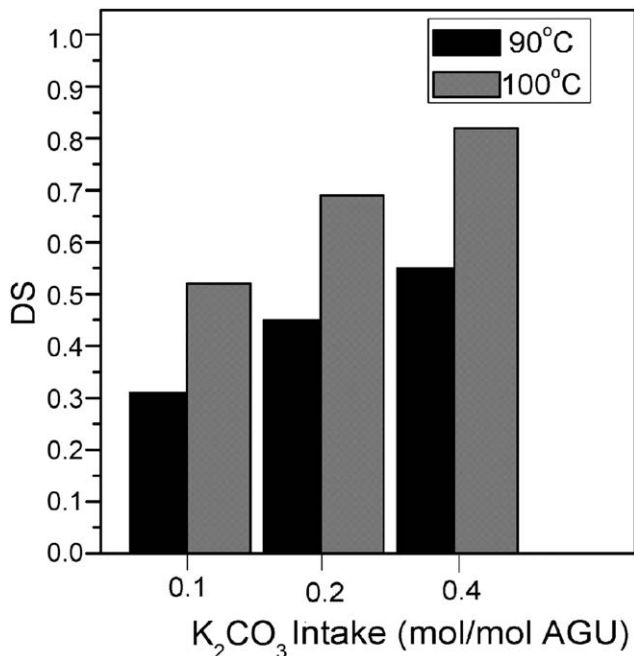


FIG. 4. The effect of K_2CO_3 intake and temperature on the DS. Conditions: 8 MPa, 1.5 h, a VL intake of 3 mol/mol AGU.

As shown in Fig. 3, it is apparent that K_2CO_3 gives products with the highest DS value. This is expected, as this salt has the lowest pK_b value. However, when comparing the performance of Na_2SO_4 and $NaOAc$, this trend is absent and Na_2SO_4 , despite being a weaker base than $NaOAc$, gives products with higher DS values. A possible explanation may be related to different salt effects on the gelatinization behavior of starch at elevated pressures. After being pressurized at 350, 530, and 700 MPa for 15 min at 29°C, the presence of Na_2SO_4 (0.07 M, similar to that

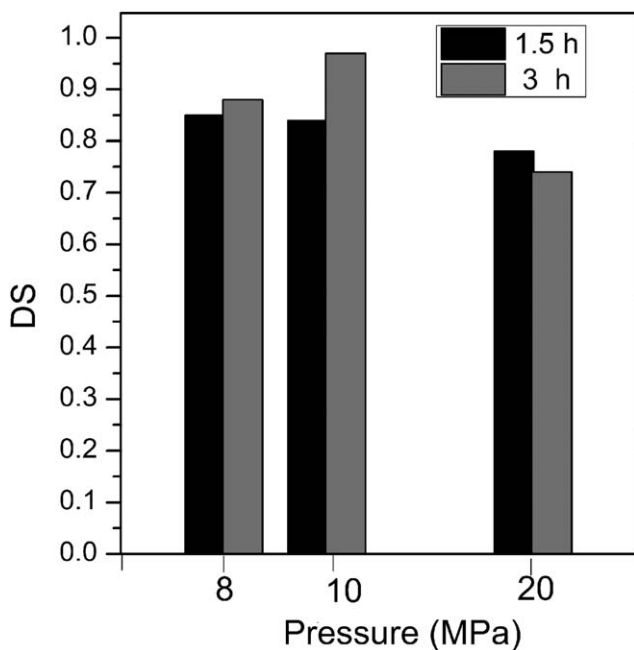


FIG. 5. The effect of pressure on DS at two different reaction time. Conditions: 100°C, VL intake of 5 mol/mol AGU, and a catalyst intake of 0.1 mol/mol AGU.

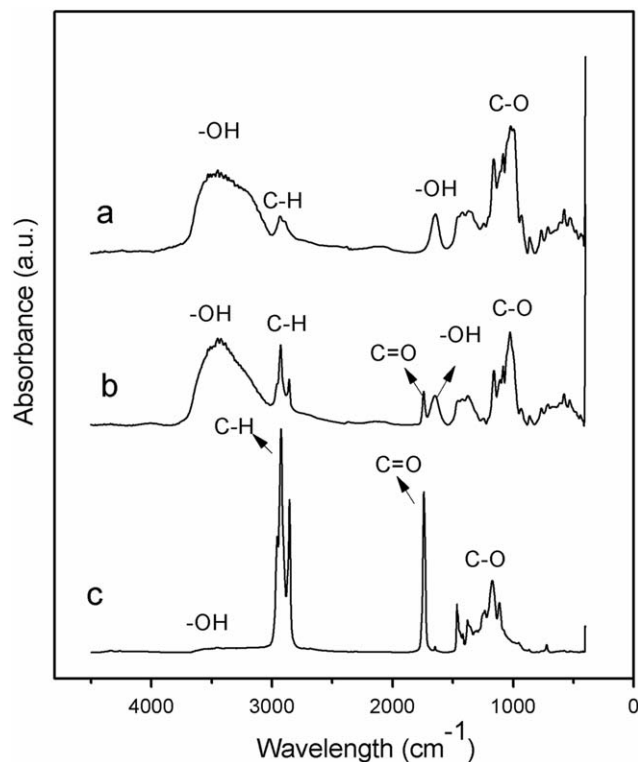


FIG. 6. FT-IR spectra of Native Sago Starch (a), starch laurate with a DS of 0.06 (b), and starch laurate with a DS of 0.81 (c).

in our experiments) is known to result in an increase in the degree of gelatinization (DG) of potato starch to almost 90% [17]. This effect is much more profound for Na_2SO_4 than for other salts such as $NaCl$ and $NaOAc$. Thus, the unexpectedly good performance of Na_2SO_4 may be related to a higher DG, which will lead to higher diffusivities of the reactants in the swollen starch granules.

As K_2CO_3 showed the highest reactivity among the basic catalysts used in the experiments, it was selected for further investigations. The effect of K_2CO_3 on the product DS was investigated for three different feed compositions (0.1 mol/mol AGU, 0.2 mol/mol AGU, 0.4 mol/mol AGU) and at two different temperatures (80°C, 100°C).

The experimental results (Fig. 4) show that the DS values increase with the K_2CO_3 intake until the upper experimental limit of 0.4 mol/mol AGU. These findings are in line with studies on esterification of corn and Hylon VII using DMSO as the solvent [18, 19]. Higher intakes of the base catalyst will lead to a higher concentration of starch alkoxides in the mixture and this will have a positive effect on the reaction rates with VL. As a consequence, higher product DS value is attained at higher catalyst intakes.

The effect of temperature was investigated at 90°C and 100°C (Fig. 4) at a constant pressure of 8 MPa, VL intake of 3 mol/mol AGU and 1.5 h reaction time. The positive influence of temperature on the DS values is clearly shown in Fig. 4. The same observations can be found in the literature, not only reactions in densified CO_2 [7] but also in other solvents such as DMSO [17] and ionic liquids [5].

Pressure has a more complex effect on the DS values (Fig. 5). It is apparent that an optimum of DS is observed at

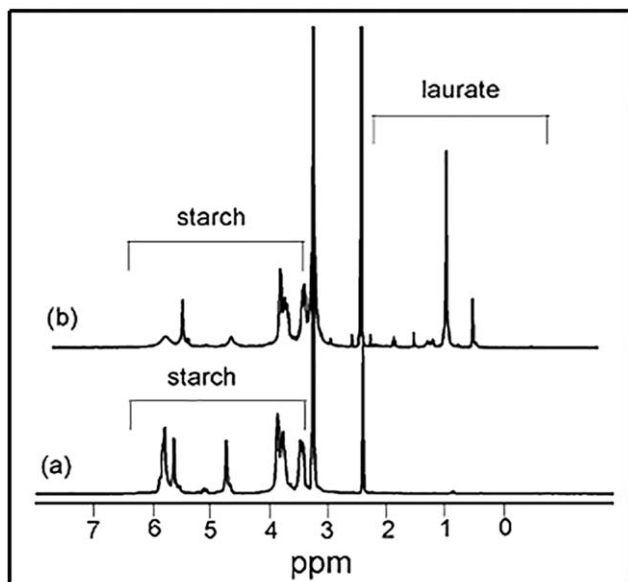


FIG. 7. ¹H-NMR analysis of native sago starch (a), sago starch laurate with a DS of 0.81 (b).

10 MPa for a reaction time of 3 h. This trend is in line with previous results by us for the esterification of potato starch in CO₂ [7]. Moreover, a different trend is shown at 1 h reaction time. Here, the effect of pressure (from 8 to 10 MPa) is limited and the DS values are about constant (Fig. 5).

The trend can be explained by considering two opposite effects. CO₂ is known to be a plasticizer for starch, leading to higher diffusion rates of the VL inside the starch granules, ultimately giving products with higher DS values. This effect is expected to be more profound at higher pressures. However, higher pressures also have a negative effect due to compression of particles, which in turn decreases the free volume in the starch matrices [20] and lowers the diffusion rate and eventually results in products with a lower DS value.

The starch ester products were characterized using FT-IR, ¹H-NMR, SEM, TGA, and DSC and the results will be compared with native sago starch.

The FT-IR spectra of native sago starch, sago laurate with a DS of 0.04, and sago laurate with a DS of 0.79 are given in Fig. 6. All spectra show an absorption band at 3,300–3,600 cm⁻¹ and at 1,235–1,242 cm⁻¹, corresponding to the –OH stretching and bending band of starch, respectively [2, 21].

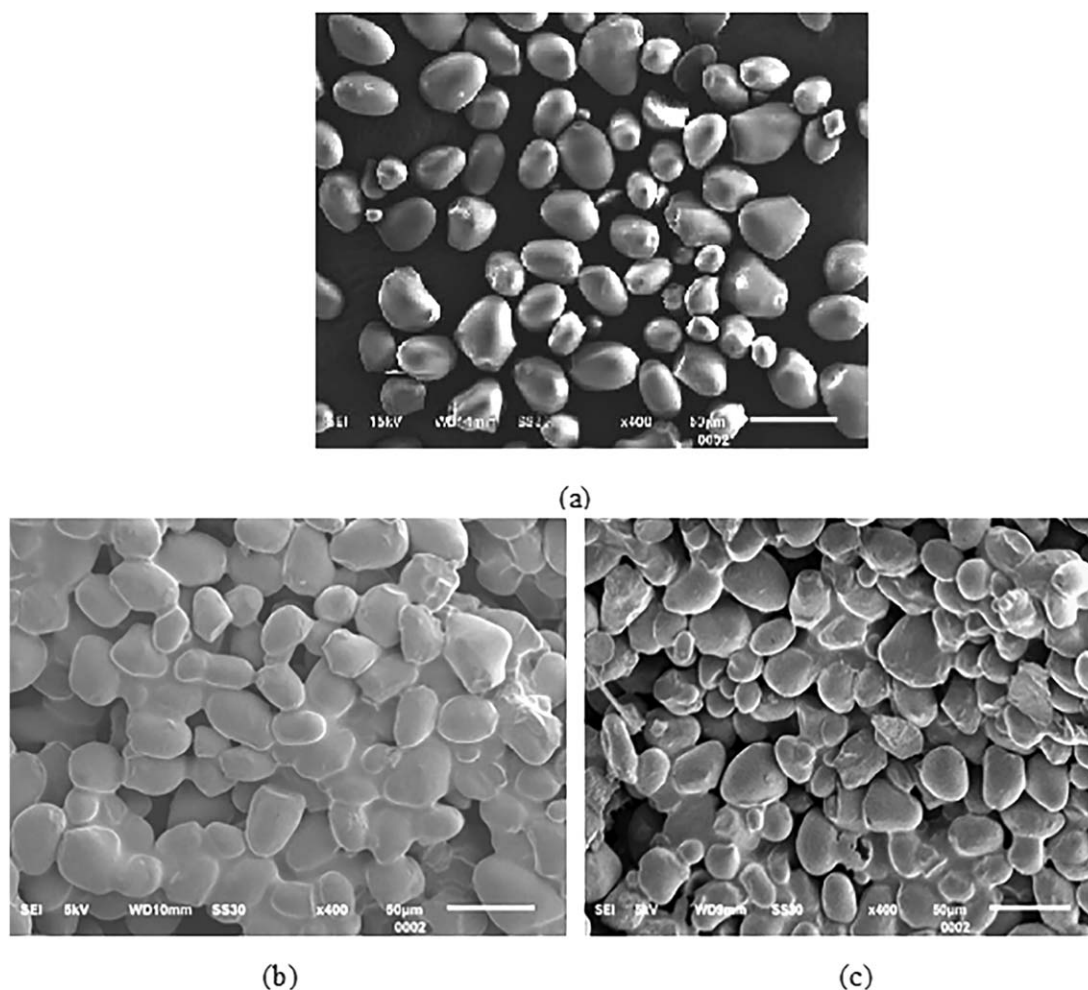


FIG. 8. SEM of native sago starch (a), sago starch laurate with DS of 0.06 (b), and sago starch laurate with DS of 0.16 (c).

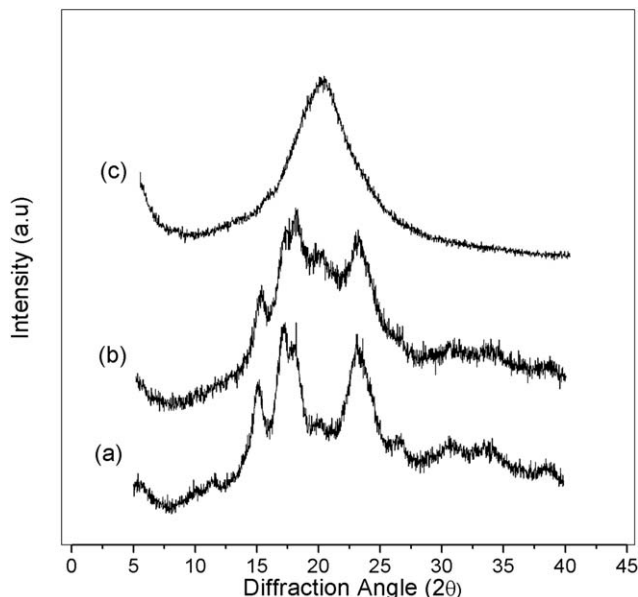


FIG. 9. X-ray diffraction pattern of native sago starch (a), sago starch laurate DS = 0.73 (b), and DS = 0.95 (c).

The peak intensity of the -OH stretching band decreases with higher DS value (Fig. 6) in agreement with the fact that part of the OH groups are substituted by the laurate group. The presence of the laurate group in the products can also be seen from the increase of the peak intensity of -CH stretching band at $2,800\text{--}3,000\text{ cm}^{-1}$ at the higher DS values and the presence of the carbonyl (-C=O) stretching band at $1,738\text{ cm}^{-1}$ [2, 5, 21].

Also the comparison of $^1\text{H-NMR}$ spectra of native sago starch (Fig. 7a) and sago starch laurate with a DS of 0.81 (Fig. 7b) clearly indicates the occurrence of the reaction. Both spectra show peaks at δ 3.6–5.6 ppm that correspond to the seven proton of the starch [19, 22].

The main difference between both spectra is the presence of peaks at δ 0.8–2.5 ppm in the sago starch laurate (Fig. 7b), which correspond to the protons of the fatty acid backbone [19]. This indicates that the reaction was successful. In addition, the absence of peaks at δ 7–7.2 ppm reveals that the products is not contaminated with the unreacted VL [7].

SEM analysis of the native sago starch and the products are given in Fig. 8. It is clear that there is a significant difference between the morphology of the native and the sago laurate products.

The native sago starch granules show an oval shape (Fig. 8a) with different particle sizes, in line with literature data [21]. The granules of the starch laurates appear agglomerated (Fig. 8b) and fused, particularly for the product with the higher DS value (Fig. 8c) [21, 23]. This is not surprising when considering possible hydrophobic (van der Waals) interaction of the aliphatic side chains, especially at relatively high DS values.

On the mesoscopic level, the esterification reaction are expected to have an influence on the crystallinity of the product. The diffraction patterns of three products (native sago starch, sago laurate with a DS of 0.73, and sago laurate with a DS of 0.95), as measured by XRD analysis, are shown in Fig. 9. Typical C-type semi crystalline XRD patterns with a strong

diffraction peak at 2θ values of 5.54° , 15.18° , 17.2° , 18.1° , 23.1° , and 26.96° are obtained for native sago starch and for sago laurate with a DS of 0.73 [11]. Conversely, the sago laurate with a DS of 0.95 only shows a broad single peak at 23.1° , indicating that this product has lost its crystallinity and become fully amorphous.

The decrease in crystallinity of the product can be quantified based on the ratio of the crystalline (A_c) reflections and the overall area (A_t) [24]. The results are given in Table 3. It is obvious that the degree of crystallinity is reduced from 34% for native sago starch to 28% for a product with a DS of 0.73 and with complete loss of crystallinity for a product with a DS of 0.95. This decrease in crystallinity is due a plasticizing effect of CO_2 during reaction, inducing gelatinization of the starch particles and leading to a reduction in the crystallinity of the product [20, 25]. The changes in the molecular as well as meso-structure of the starch on derivatization with laurate chains has a clear influence on the final properties.

The TGA thermograms of native sago starch and the derivatives are shown in Fig. 10a. The curves for the sago starch samples show two distinct decomposition steps. The degradation/decomposition temperature of the sago starch laurate (240°C) is lower than that for native sago starch (290°C). This may be the result of disruption of hydrogen bonds in the starch at higher DS values and loss of crystallinity [2]. Moreover, the sago starch laurates show a second degradation peak at higher values than for native sago starch (Fig. 10a), indicative for higher thermal stability of the starch laurate derivatives.

The TGA data for sago starch and laurate derivatives were compared with those for native potato starch and laurate derivatives (Fig. 10b and c). Both native potato and sago starch show the same degradation profile. The derivatives (Fig. 10c), however, show different degradation profiles. Evidently, sago starch laurate has a slightly lower degradation temperature than that of the potato starch analog. This is possibly related to differences in pressure resistance for both starches [20]. Potato starch, with a B type crystalline structure, is known to be more pressure resistant compared with sago starch (C- type crystalline structure).

Thermal properties of the products and starting material were determined and shown to differ considerably. The melting (T_m) and crystallization temperature (T_c) of native sago starch and the products were measured by DSC and the results are shown in Table 4. The T_m and T_c of the products are not a strong function of the product DS (Table 4). The products have lower transition temperatures (T_m and T_c) compared with native sago starch, suggesting that the crystallinity of native sago starch is significantly reduced. This is in line with the decrease in melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) at higher

TABLE 3. Crystallinity data.

No	Sample	DS	Degree of crystallinity (% xc)	Relative crystallinity (Xrc)
1	Native	—	0.34	1
2	Sago Laurate	0.73	0.22	0.67
3	Sago Laurate	0.95	0	0

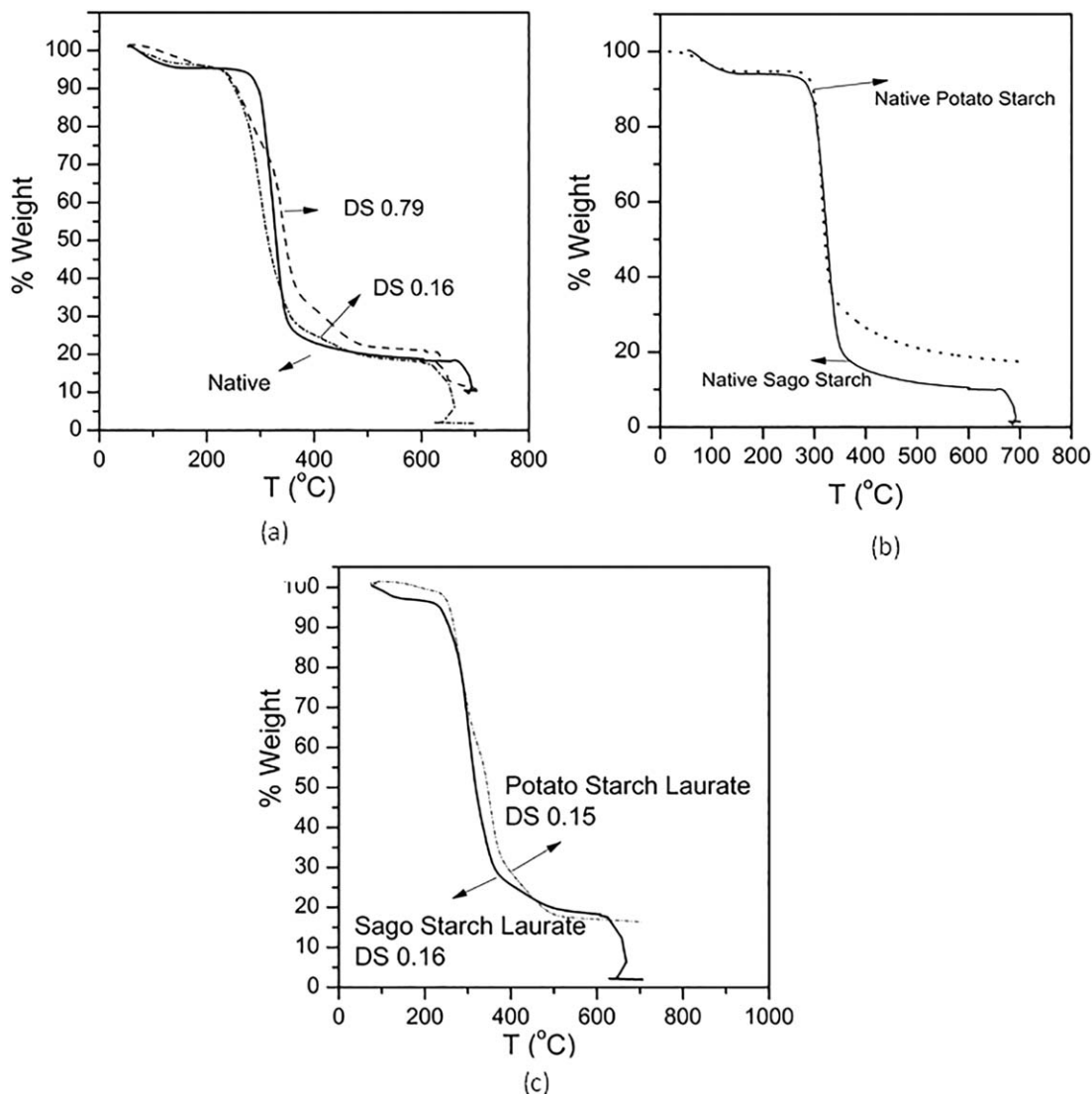


FIG. 10. TGA Analysis on sago starch and sago starch derivatives (a), native sago and native potato starch (b), sago and potato starch laurates (c).

DS values (Table 4). The decrease in crystallinity is also confirmed by the XRD analysis (see above).

Another important finding is that the transition temperatures of the products are mainly determined by the properties of the laurate side chains as the transition temperatures of the products are not far off from the ones of pure VL (T_m of 5.76°C and T_c of -10.72°C).

TABLE 4. Thermal properties of the products as measured by DSC.

No	Sample	DS	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)
1	Native	—	nd ^a	nd ^a	nd ^a	nd ^a
2	Sago Laurate	0.73	-13.57	2.03	14.84	12.23
3	Sago Laurate	0.95	-13.63	2.65	5.44	2.65

^aNot detectable.

CONCLUSIONS

The potential application of densified CO₂ as a solvent for the synthesis of sago starch laurates was investigated. The introduction of fatty acid chains was successful using the selected synthesis method as was evident from changes in the FT-IR and ¹H-NMR of the products compared with to virgin sago starch. The reactivity is a strong function of temperature, the basicity of the catalyst, and the catalyst intake and, within the investigated experimental window, a maximum product DS of 0.97 was achieved. This is prominently higher than found for related esterification reactions in CO₂. The use of reactive fatty acid derivatives as well as fine tuning of the experimental conditions constitutes pivotal elements in achieving this.

In addition, the product crystallinity decreases with the DS as confirmed with XRD and DSC analysis. This indicates that the final product crystallinity may be tuned by the process condition. The thermal properties (degradation temperature, melting and crystallization temperature) of the products are considerably

different from those for native sago starch. The products have a higher thermal stability and a lower melting and crystallization temperature, which will have a positive effect on the suitability of the products to be used as thermoplastic materials.

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REFERENCES

1. E. van Eygen, J. Feketitsch, D. Laner, H. Rechberger, and J. Fellner, *Resour. Conserv. Recycl.*, **117**, 183 (2017).
2. A. Sunita and R.A. Banerjee, *Carbohydr. Polym.*, **150**, 359 (2016).
3. J. Ivanovic, S. Milovanovic, and I. Zizovic, *Starch/Staerke*, **68**, 821 (2016).
4. R.A. de Graaf, A.P. Karman, and L.P.B.M. Janssen, *Starch/Staerke*, **55**, 80 (2003).
5. W. Xie and Y. Wang, *Starch/Staerke*, **63**, 190 (2011).
6. L. Xuanxuan, L. Zhigang, X. Fu, and X. Zhigang, *J. Agric. Food Chem.*, **61**, 9882 (2013).
7. H. Muljana, S. van der Knoop, D. Keijzer, F. Picchioni, L.P.B.M. Janssen, and H.J. Heeres, *Carbohydr. Polym.*, **82**, 346 (2010).
8. A.D. Sagar and E.W. Merrill, *J. Appl. Polym. Sci.*, **58**, 1647 (1995).
9. J. Aburto, I. Alric, and E. Borredon, *Starch/Staerke*, **51**, 132 (1999).
10. J. Aburto, I. Alric, and E. Borredon, *Starch/Staerke*, **57**, 145 (2005).
11. C. Pukkahuta and S. Varavinit, *Starch/Staerke*, **59**, 624 (2007).
12. E. Hermawan, L. Rosyanti, L. Megasari, A.K. Sugih, and H. Muljana, *Int. J. Chem. Eng. Appl.*, **6**, 152 (2015).
13. R. Span and W. Wagner, *J. Phys. Chem. Ref. Data*, **25**, 1509 (1996).
14. Z.G. Lei, H. Ohyabu, Y. Sato, H. Inomata, and R.L. Smith, *J. Supercrit. Fluids*, **40**, 452 (2007).
15. M. Hammer, A. Ervik, and S.T. Munkejord, *Ind. Eng. Chem. Res.*, **52**, 9965 (2013).
16. L. Junistia, A.K. Sugih, R. Manurung, F. Picchioni, L.P.B.M. Janssen, and H.J. Heeres, *Starch/Staerke*, **61**, 69 (2009).
17. B.A. Rumpold and D. Knorr, *Starch/Staerke*, **57**, 370 (2005).
18. R.E. Dicke, *Cellulose*, **11**, 255 (2004).
19. L. Junistia, A.K. Sugih, R. Manurung, F. Picchioni, L.P.B.M. Janssen, and H.J. Heeres, *Starch/Staerke*, **60**, 667 (2008).
20. J.D. Francisco and B. Sivik, *J. Supercrit. Fluids*, **22**, 247 (2002).
21. A.V. Singh, L.K. Nath, and M. Guha, *Starch/Staerke*, **63**, 523 (2011).
22. M. Elomaa, T. Asplund, P. Soininen, R. Laatikainen, S. Peltonen, S. Hyvarinen, and A. Urtti, *Carbohydr. Polym.*, **57**, 261 (2004).
23. L.A. Bello-Perez, E. Agama-Acevedo, P.B. Zamudio-Flores, G. Mendez-Montecalvo, and S.L. Rodriguez-Ambriz, *LWT-Food Sci. Technol.*, **43**, 1434 (2010).
24. S.J. Wang, Y. Jinglin, G. Wenyuan, L. Hongyan, and P.G. Xiao, *Carbohydr. Res.*, **341**, 289 (2006).
25. H. Muljana, F. Picchioni, H.J. Heeres, and L.P.B.M. Janssen, *Carbohydr. Polym.*, **78**, 511 (2009).