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Experimental and Modeling Studies on the Synthesis and Properties of Higher Fatty Esters of Corn Starch

This paper describes a systematic study on the synthesis of higher fatty esters of corn starch (starch laurate and starch stearate) by using the corresponding vinyl esters. The reactions were carried out in DMSO using basic catalysts (Na_2HPO_4, K_2CO_3, and Na-acetate). The effect of the process variables (vinyl ester to starch ratio, catalyst intake, reaction temperature and type of the catalyst) on the degree of substitution (DS) of the starch laurate and starch stearate esters was determined by performing a total of 54 experiments. The results were adequately modeled using a non-linear multivariable regression model ($R^2 \geq 0.96$). The basicity of the catalyst and the reaction temperature have the highest impact on the product DS. The thermal and mechanical properties of some representative product samples were determined. High-DS products (DS = 2.26-2.39) are totally amorphous whereas the low-DS ones (DS = 1.45-1.75) are still partially crystalline. The thermal stability of the esterified products is higher than that of native starch. Mechanical tests show that the products have a tensile strength (stress at break) between 2.7–3.5 MPa, elongation at break of 3–26%, and modulus of elasticity of 46–113 MPa.

Keywords: Starch esters; Esterification; Vinyl laurate; Vinyl stearate; Product properties

1 Introduction

Plastics are very useful materials and are used in large amounts (245×10^6 t per annum) [1, 2]. The largest application area of plastics is the use as packaging material (37%) [1]. However, most of the plastic waste is not biodegradable, and this causes serious environmental problems [1, 3, 4]. The development of novel biodegradable plastic materials capable of decomposing when given an appropriate environment and time is of utmost importance [5].

Starch is an attractive feedstock for the synthesis of novel biodegradable plastics. It is cheap and abundantly available [3]. The global starch production was estimated at 60×10^6 t in 2004 [6]. The use of native starch as a building block for novel biodegradable polymers, however, is rather limited to date. Examples are agricultural mulch [7], packaging material, and food service-ware [8]. The limited use mainly results from a number of unfavorable properties of starch such as low moisture resistance, high brittleness, and incompatibility with hydrophobic poly-

mers [9]. Chemical or physical modification is required for successful applications as biodegradable polymers. Typical examples are blending with polyvinyl alcohol [3], polyethylene [7] and polycaprolactone [10] and chemical modification by esterification with organic acids [11–19].

Esterification is one of the oldest methods used to improve starch properties [11]. Most early studies were mainly focused on the use of short-chain carboxylic acid (C1–C4), and particularly on the synthesis of starch acetate (C2) [11, 12]. *Mullen* and *Pacsu* [11, 12] studied the synthesis and properties of C1–C6 esters of starch. The mechanical properties of products with longer ester chains (C4 and C6) and plasticized acetate esters were considerably improved compared to native starch. *Sagar* and *Merill* [13] studied the synthesis and properties of C4–C6 esters of high-amylose starch. The products were biodegradable, however, their mechanical properties were still not satisfactorily. *Thiebaud* et al. [14] and *Aburto* et al. [15–19] synthesized longer-chain fatty esters (C8–C18) of potato starch and corn amylose using fatty acid chlorides and pyridine. The high DS esters showed interesting properties. The products were hydrophobic and their mechanical properties were considerably improved compared to native starch. Alternative routes to avoid the use of acid chloride/pyridine combinations have been developed. The use of methyl and glyceryl esters to pre-

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pare starch laurate (C12) ester was investigated but only yielded products with relatively low DS values (max. 0.65) [19]. The use of vinyl esters has also been explored [20–22]. However, the research activities were mainly limited to the use of vinyl acetate. Two examples using higher vinyl esters (vinyl laurate) were reported by *Mormann* et al. [20]. Unfortunately, the physicochemical properties of the products were not mentioned.

We have recently performed exploratory studies on the synthesis of starch esters of higher fatty acids using vinyl laurate and vinyl stearate as the reagents [23]. Long-chain fatty esters of corn starch with a broad range in degree of substitution (DS = 0.24−2.96) were prepared by reacting the starch with vinyl laurate or vinyl stearate in the presence of basic catalysts in DMSO. This paper describes systematic studies using Design of Experiments (DOE) to gain insights in the effect of process variables (temperature, vinyl ester to anhydroglucose ratio, catalyst type and intake) on the DS of the products. The experiments were modeled using non-linear multivariable regression. In addition, the thermal and mechanical properties of representative examples of the highly hydrophobic materials are described and discussed.

2 Materials and Methods

2.1 Materials

Corn starch (approx. 73% amylopectin and 27% amylose) was purchased from Sigma (Seelze, Germany). The starch was dried for 48 h at 105°C under vacuum (~0.1 kPa) to reduce the moisture content below 2% before use. Analytical grade vinyl stearate (Aldrich, Tokyo, Japan), vinyl laurate (Fluka, Buchs, Switzerland), and acetic anhydride (Merck, Darmstadt, Germany) were used without further purification. The catalysts for the esterification reaction were analytical-grade potassium carbonate (Boom, Meppel, the Netherlands), sodium acetate, and disodium hydrogenphosphate dodecahydrate (both Merck). Technical-grade dimethyl sulfoxide (DMSO), 4-*N*,*N*-dimethylaminopyridine (DMAP), and tetrahydrofuran (THF) were supplied by Acros (Geel, Belgium). Analytical-grade methanol, pyridine, and toluene were obtained from Labscan (Dublin, Ireland). All these chemicals were used as received.

2.2 Analytical equipment

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a 400 MHz Varian AMX NMR machine (Varian, Palo Alto, CA, USA). The spectra were recorded at 50°C, as recommended by *Laignel* et al. [24]. TGA measurements were performed using a TGA 7 Thermogravimetric Analyzer (Perkin Elmer, Norwalk, CT, USA). The samples were heated to 700°C in a nitrogen atmosphere with a heating rate of 10°C/min. DSC analyses were performed on a TA Instruments DSC 2920 (TA Instruments, New Castle, NJ, USA). The samples (about 10 mg) were placed in sealed aluminum cells. After a first heating run from room temperature up to 200°C to delete the thermal history of the material, each sample was cooled to −50°C and then heated again to 200°C (heating rate 10°C/min). The thermal properties (T_m, T_c, and T_g) of each sample were determined from the spectra related to the cooling run and the second heating one. T-Bones samples (with thickness of 2 mm) for determination of the tensile properties were prepared using a melt press apparatus (Fontijne, Vlaardingen, Netherlands), operated at 150°C and 150 bar for 3 min. The tensile tests were performed using an Instron Series IX Automated Materials Testing System 1.09 (Instron, Norwood, MA, USA) at 20°C and a crosshead speed of 30 mm/min.

2.3 Methods

2.3.1 Typical example of the preparation of laurate and stearate starch esters

The corn starch (0.5 g) was gelatinized in DMSO (5 mL) at 70°C for 3 h. After the mixture became a homogenous, colorless solution, vinyl laurate or vinyl stearate (3–5 mol/mol with respect to the AHG units) and the catalyst (potassium carbonate, sodium acetate, or disodium hydrogenphosphate, 2–5%, w/w, with respect to starch) were added. The reactor content was kept at 80-110°C for 24 h. The product was precipitated using methanol (100 mL), and the liquid phase was removed by decantation. This precipitation-decantation procedure was repeated twice using 50 and 25 mL of methanol, respectively, to purify the reaction product. Finally, the product was dried in a vacuum oven (70°C, 0.5 kPa) for 24 h or until constant weight.

2.3.2 Peracetylation procedure and DS determination

The presence of unsubstituted hydroxyl groups in the products resulted in broad and overlapping starch resonances in ^{1}H-NMR spectra. A peracetylation reaction to substitute all of the remaining hydroxyl groups with acetate groups was therefore applied to obtain reliable DS values. Typically, the starch ester (0.1 g) was added to THF (4%, w/v) and stirred at 55°C until dissolution (typically 3 h). Subsequently, the peracetylating reagent (1 mol DMAP, 10 mol acetic anhydride, and 22 mol pyridine per

mole AHG units) were added. The peracetylation reaction was conducted for 7 h at 50°C. The product was precipitated by the addition of methanol and washed several times with methanol before finally dried overnight in a vacuum oven at 70°C and 0.5 kPa. The DS of the products was calculated using a procedure given in previous work [23].

2.3.3 Experimental design

The experiments were carried out in six blocks. The three variables used in each block were the vinyl ester to AHG starch molar ratio (x_1), catalyst intake (x_2), and reaction temperature (x_3). All experiments in a block were conducted using a three-variable, two-level full-factorial experimental design with one center point, giving a total of $2^3+1 = 9$ experiments per block. For each block, a given type of catalyst (Na_2HPO_4, K_2CO_3 or Na-acetate) and vinyl ester (either vinyl laurate or vinyl stearate) were applied. This gave a total of 54 experiments (two types of vinyl esters × three types of catalysts × nine experiments per block). In a later stage, the type of catalyst was quantified using the pK_b of the catalyst (x_4). The ranges for the individual variables (x_1-x_4) are shown in Tab. 1.

The mathematical analysis of the experimental data was performed with the software package "Matchad 13" (Mathsoft). The response (*y*, DS of the products) was modeled using the following expression:

$$y = b_0 + \sum_i \beta_i x_i + \sum_i \beta_{ii} x_i^2 + \sum_j \sum_{k \neq j} \beta_{jk} x_j x_k \qquad (1)$$

Here, β_i, β_{ii} *and* β_{jk} are the regression coefficients obtained by a multiple regression procedure. One of the terms, namely x_1^2, caused singularity of the matrix used for the modeling, and was therefore excluded. A *t*-statistic was used to rank the individual regression coefficients (β_i, β_{ii}, or β_{jk}) according to their relative importance [25].

An analysis of variance (ANOVA) was performed to check the adequacy of the model. The applied procedure is well described in the literature [25] and consists of calculating the sum of squares (SS) for the model and the error, together with the total sum of squares. In combination with the relative degrees of freedom (DF) it is possible to calculate the mean square (MS) for the model and the corresponding error. On the basis of the latter values, the *F*-value for the model is calculated. With this information the *P*-value for the model is determined. The latter value is related to the statistical significance of the model.

3 Results and Discussion

A schematic representation of the esterification reaction of starch with a vinyl ester is provided in Equation (2). The starch was gelatinized before the addition of the vinyl ester to make the starch OH groups more accessible for reaction. The reactions were carried out in DMSO for 24 h using three different basic salts (Na_2HPO_4, K_2CO_3, or Na-acetate) as the catalysts. The products of the reaction were brownish gels which became lighter in color after product precipitation and washing with methanol. After drying, the products were isolated as transparent, yellowish solids. The products were soluble in organic solvents such as toluene and THF.
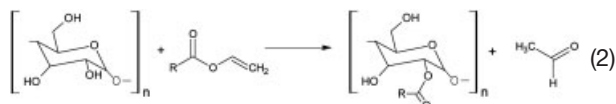
(1) R = laurate (C12)
(2) R = stearate (C18)

The products were characterized by ^{1}H-NMR in CDCl$_3$. The peaks of starch (δ 3–5.5 ppm) and aliphatic hydrogen atoms of the fatty acid chain (δ 0.8–2.5 ppm) were clearly present. The starch peaks were broad and overlapping,

Tab. 1. Experimental design variables.

Variable level	Independent variables			
	Full factorial variables			Additional variable
	Vinyl ester to AHG-starch ratio [mol/mol] x_1	Catalyst intake [%, w/w][a] x_2	Reaction temperature [°C] x_3	Catalyst basicity (pK_b)[b] x_4
Low (−1)	3	2.0	80	K_2CO_3 (3.66)
Middle (0)	4	3.5	95	Na_2HPO_4 (6.8)
High (+1)	5	5.0	110	CH_3COONa (9.25)

[a] In % (w/w) based on starch intake, in the model (Eq. 3) it is transformed to $10^5 \times$ catalyst mole amount.
[b] Taken from ref [26].

and only after the starch esters were peracetylated, the resolution of these peaks was considerably improved. The DS of the products was determined by using ^{1}H-NMR spectra of the peracetylated starch esters.

The effect of three reaction parameters (molar ratio of vinyl ester to AHG units of starch x_1, catalyst intake x_2, and reaction temperature x_3) on the DS of starch was studied using a full factorial experimental design with one center point. The ranges of the values of the independent variables (x_1-x_3) are shown in Tab. 1. An additional variable x_4 (related to the basicity of the catalyst) was also included in order to obtain a general model for starch esterification. A total of 54 experiments were conducted. The results of the experiment are given in Tab. 2.

3.1 Mathematical modeling

Modeling of the DS data for both vinyl esters was performed using non-linear multivariable regression based on the four independent variables (Tab. 1). The type of catalyst was quantified using the basicity constant (pK_b) in water [26, 27]. The experimental data for both starch laurate and starch stearate esterification are best described with a quadratic model including interaction terms (Eq. 3).The modeled values for β_{ij} for the two esters are given in Tab. 3.

$$
\begin{aligned}
DS = {} & \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1 x_2 + \\
& \beta_6 x_1 x_3 + \beta_7 x_1 x_4 + \beta_8 x_2 x_3 + \beta_9 x_2 x_4 + \beta_{10} x_3 x_4 + \quad (3) \\
& \beta_{11} x_2^2 + \beta_{12} x_3^2 + \beta_{13} x_4^2
\end{aligned}
$$

The result of the analysis of variance is given in Tab. 4. The very low *P*-values indicate that the models are statistically significant. The R^2 values for the models are 0.970 (starch laurate) and 0.967 (starch stearate), respectively, and it may be concluded that the models describe the experimental data well. The parity plots of both models are given in Fig. 1 and confirm this statement.

Moreover, the adjusted R^2 values are very close to the R^2 ones, which indicate [25] that all significant variables are included in the model. Finally, we also performed a PRESS analysis [25] (see corresponding R^2 values in Tab. 4), which represents an "internal" validation method for the model. Also in this case the reasonable R^2 values (0.805-0.875) indicate that the model correctly predict the products DS as function of the process variables within the range of experimental variables.

To evaluate the effect of each variable on the product DS, two plots showing the dependence of the DS on reaction temperature and catalyst amount (in %, w/w), for both starch laurate and starch stearate are given in Fig. 2. Of all the variables studied, the type of catalyst has the largest effect on the product DS for both the laurate and stearate esters (Fig. 2). The highest product DS values were

obtained using K_2CO_3. Catalyst performance of CH_3COONa is slightly less than for K_2CO_3 whereas the lowest DS products were produced when using Na_2HPO_4 as the catalyst. These results may be rationalized by considering the role of the catalyst in the modification reaction. It is assumed that the first step in the reaction sequence is activation of the starch OH groups by deprotonation by a base [21, 22]. The resulting anion will react with the vinyl ester to from the product. On the basis of the sequence, it can be rationalized that the rate of the reaction (and thus the product DS) will be higher when using a stronger base. This is indeed the case when comparing the performance of K_2CO_3 with CH_3COONa. K_2CO_3 is a stronger base (pK_b 3.66) than CH_3COONa (pK_b 9.25) and this leads to higher product DS values for K_2CO_3. However, the performance of Na_2HPO_4 does not follow this trend. The pK_b for the latter (6.8) is intermediate between that of the other two catalysts, whereas catalyst performance is considerable lower. A similar trend was observed by *Dicke* [27] for the acetylation of Hylon VII starch using vinyl acetate. The product DS for Na_2HPO_4 was considerably lower (1.00) than for K_2CO_3 (2.18) and CH_3COONa (1.82). A possible explanation of this peculiar behavior of Na_2HPO_4 is the fact that the pK_b values in water are used for quantification whereas the actual solvent for the reaction is DMSO. Unfortunately, the base strengths of the catalysts in DMSO are not known. Another explanation may be related to the regiochemistry of the reaction. *Dicke* [27] showed that Na_2HPO_4 has a strong tendency to selectively deprotonate the OH group at the C2 position of starch leading to C2 substituted acetate esters. This was not the case for alkaline catalysts, such as carbonate or acetate salts leading to higher DS esters. The explanation for the high preference of C2 substitution for the Na_2HPO_4 catalyst is not yet known and needs to be established by mechanistic studies.

Besides the type of catalyst, the catalyst intake and reaction temperature also affect the product DS (Fig. 2), although to a lesser extent. As expected and in line with studies on starch acetates [27], higher reaction temperatures and catalyst intakes lead to higher product DS values. Of all variables studied, the vinyl ester to AHG ratio has the smallest effect on the product DS.

3.2 Product properties

The thermal and mechanical product properties for two starch laurate and stearate samples with medium ($DS_{laurate} = 1.75$, $DS_{stearate} = 1.45$) and high DS values ($DS_{laurate} = 2.26$, $DS_{stearate} = 2.39$) were determined. Representative DSC spectra for the starch stearate are given in Fig. 3 and the results for all samples are summarized in Tab. 5.

Tab. 2. Overview of experimental data.

Experiment	Vinyl ester	Catalyst	Vinyl: AHG[a] [mol/mol]	Catalyst [%, w/w]	Temperature [°C]	DS
1	laurate	Na_2HPO_4	3.00	2.00	80	0.62
2	laurate	Na_2HPO_4	3.00	5.00	80	0.75
3	laurate	Na_2HPO_4	3.00	2.00	110	1.46
4	laurate	Na_2HPO_4	3.00	5.00	110	1.12
5	laurate	Na_2HPO_4	5.00	2.00	80	0.27
6	laurate	Na_2HPO_4	5.00	5.00	80	0.87
7	laurate	Na_2HPO_4	5.00	2.00	110	1.27
8	laurate	Na_2HPO_4	5.00	5.00	110	1.32
9	laurate	Na_2HPO_4	4.00	3.50	95	1.11
10	laurate	CH_3COONa	3.00	2.00	80	2.28
11	laurate	CH_3COONa	3.00	5.00	80	2.44
12	laurate	CH_3COONa	3.00	2.00	110	2.54
13	laurate	CH_3COONa	3.00	5.00	110	2.78
14	laurate	CH_3COONa	5.00	2.00	80	2.24
15	laurate	CH_3COONa	5.00	5.00	80	2.42
16	laurate	CH_3COONa	5.00	2.00	110	2.59
17	laurate	CH_3COONa	5.00	5.00	110	2.67
18	laurate	CH_3COONa	4.00	3.50	95	2.17
19	laurate	K_2CO_3	3.00	2.00	80	2.23
20	laurate	K_2CO_3	3.00	5.00	80	2.52
21	laurate	K_2CO_3	3.00	2.00	110	2.52
22	laurate	K_2CO_3	3.00	5.00	110	2.94
23	laurate	K_2CO_3	5.00	2.00	80	2.54
24	laurate	K_2CO_3	5.00	5.00	80	2.88
25	laurate	K_2CO_3	5.00	2.00	110	2.72
26	laurate	K_2CO_3	5.00	5.00	110	2.84
27	laurate	K_2CO_3	4.00	3.50	95	2.50
28	stearate	Na_2HPO_4	3.00	2.00	80	0.48
29	stearate	Na_2HPO_4	3.00	5.00	80	0.47
30	stearate	Na_2HPO_4	3.00	2.00	110	1.53
31	stearate	Na_2HPO_4	3.00	5.00	110	1.35
32	stearate	Na_2HPO_4	5.00	2.00	80	0.07
33	stearate	Na_2HPO_4	5.00	5.00	80	0.09
34	stearate	Na_2HPO_4	5.00	2.00	110	0.96
35	stearate	Na_2HPO_4	5.00	5.00	110	0.93
36	stearate	Na_2HPO_4	4.00	3.50	95	0.27
37	stearate	CH_3COONa	3.00	2.00	80	1.70
38	stearate	CH_3COONa	3.00	5.00	80	2.12
39	stearate	CH_3COONa	3.00	2.00	110	2.44
40	stearate	CH_3COONa	3.00	5.00	110	2.56
41	stearate	CH_3COONa	5.00	2.00	80	1.41
42	stearate	CH_3COONa	5.00	5.00	80	1.40
43	stearate	CH_3COONa	5.00	2.00	110	1.82
44	stearate	CH_3COONa	5.00	5.00	110	2.79
45	stearate	CH_3COONa	4.00	3.50	95	1.98
46	stearate	K_2CO_3	3.00	2.00	80	2.64
47	stearate	K_2CO_3	3.00	5.00	80	2.21
48	stearate	K_2CO_3	3.00	2.00	110	2.96
49	stearate	K_2CO_3	3.00	5.00	110	2.64
50	stearate	K_2CO_3	5.00	2.00	80	2.24
51	stearate	K_2CO_3	5.00	5.00	80	2.55
52	stearate	K_2CO_3	5.00	2.00	110	2.59
53	stearate	K_2CO_3	5.00	5.00	110	2.90
54	stearate	K_2CO_3	4.00	3.50	95	2.41

[a] Molar ratio of the vinyl ester to AHG units of starch.

Tab. 3. Values for the coefficients of the DS model for starch laurate and stearate.

Coefficient	Starch laurate	Starch stearate
β_0	9.1748	17.1082
β_1	0.2183	−0.1104
β_2	0.0732	−0.0857
β_3	−0.0327	−0.1568
β_4	−2.5650	−2.6939
β_5	0.0027	0.0120
β_6	−0.0008	0.0010
β_7	−0.0249	−0.0470
β_8	−0.0006	0.0001
β_9	−0.0066	0.0017
β_{10}	0.0016	0.0023
β_{11}	0.0011	0.0009
β_{12}	0.0003	0.0008
β_{13}	0.1979	0.1947

The thermal behavior of the products is a strong function of the DS. In particular the behavior at relatively high temperatures ($>0°C$) is further discussed. At moderate DS values the products still display a melting (at 20–30°C) and a crystallization temperature (at 10–25°C). These values are reduced considerably compared to virgin corn starch, which is known to contain crystalline areas, especially in the amylopectin part [15, 22]. Unfortunately the thermal transitions for the virgin material lie above the degradation temperature and can therefore not be accurately determined [2]. In any case, esterification of starch with vinyl laurate and stearate reduces the crystallinity of the starch considerably and lead to a lowering of the transition temperatures. Thermal transitions at relatively high temperature (melting, crystallization, or glass transition above 0°C) were even absent for the high DS prod-

ucts, implying that these products are fully amorphous. To the best of our knowledge, these are the first examples of completely amorphous starch esters.

Changes in the transition temperatures of native starch by esterification have been reported in the literature [13, 14, 17]. For instance a T_m of 32°C was reported for a potato starch stearate ester with a DS of 1.8 [17], close to the value obtained in our study for the medium DS starch stearate (21°C). The melting point of the potato starch stearate was close to that of model compounds for the stearate side chains (methyl stearate, 40-42°C; octadecane, 28-30°C) and the authors concluded that the transition temperatures are solely determined by the side chain without any significant contribution of the starch backbone. However, in the present work, the T_m for the medium DS starch laurate (27°C) is much higher than that of the corresponding side chain model compounds (−10°C for dodecane and 5°C for methyl laurate). This clearly indicates that the observed thermal transitions are not only determined by the side chains but by an interplay between the starch backbone and ester side chains.

TGA analysis was performed to study the thermal degradation behavior of the starch laurate and stearate samples (Fig. 4).

The TGA (Fig. 4) curves clearly show starch esterification with either laurate or stearate results in products with enhanced thermal stability. Native corn starch degrades at lower onset temperatures (250–300°C) than the corresponding esters (300–350°C). The difference in thermal stability between the laurate and stearate sample is limited. Similar trends were reported for amylose octanoate-stearate-laurate esters [17] and potato starch octanoate-laurate esters [14]. The mechanical properties (stress at break, elongation at break and elasticity modulus) of the products were determined (Tab. 6). All materials generally

Tab. 4. Analysis of variance for DS models for starch esterification.

|	SS	DF	MS	F	*P*-value	R^2 values	
			Starch laurate				
Model	16.3399	13	1.2569	35.2903	1.96×10^{-8}	R^2	0.970
Error	0.4986	14	0.0356			$R^2_{adjusted}$	0.945
Total	16.8386	27				R^2_{press}	0.875
			Starch stearate				
Model	20.9531	13	1.6118	27.629	1.026×10^{-7}	R^2	0.967
Error	0.8167	14	0.0583			$R^2_{adjusted}$	0.939
Total	21.7699	27				R^2_{press}	0.805
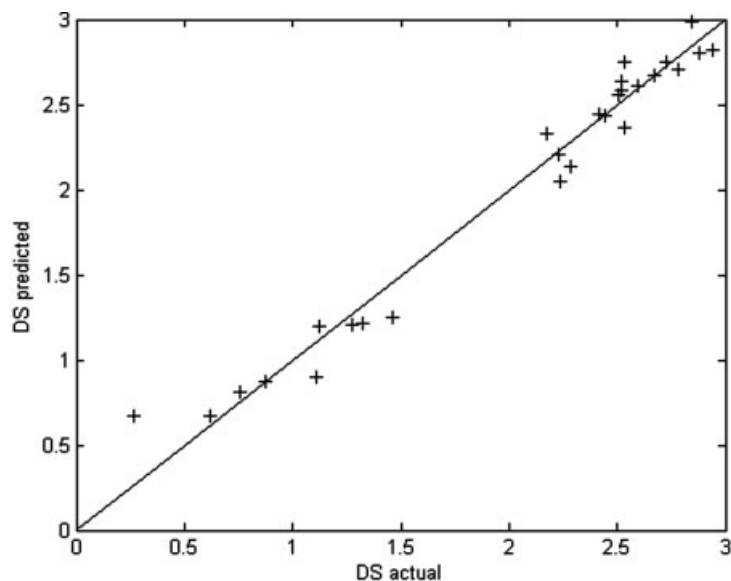
a. starch laurate
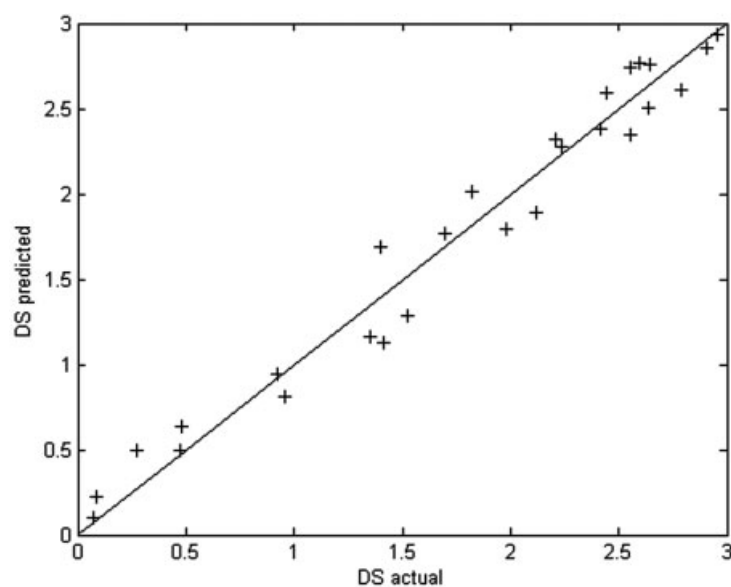
b. starch stearate

Fig. 1. Parity plots of the DS models for starch laurate and stearate 317×132 mm (96×96 DPI).

Tab. 5. Melting point (T_m) and crystallization temperature (T_c) of representative starch laurate and stearate samples.

Starch ester	DS	T_m [°C]	T_c [°C]
Starch laurate	2.26	n.d.[a]	n.d.[a]
Starch laurate	1.75	27	22
Starch stearate	2.39	n.d.[a]	n.d.[a]
Starch stearate	1.45	21	12

[a] n.d.= not detectable.

show tensile strengths between 2.7–3.5 MPa, elongation at break between 3-26%, and modulus of elasticity between 46–113 MPa. For starch laurate an increase in product DS results in lower tensile strengths and modulus of elasticity, but higher elongation at break. This is in agreement with previous studies regarding the mechanical properties of starch esters with different chain length of the fatty acid moiety [13, 17]. An inverse behavior is, however, observed for the high DS starch stearate sample. This product is more rigid than the product with medium DS value (higher tensile
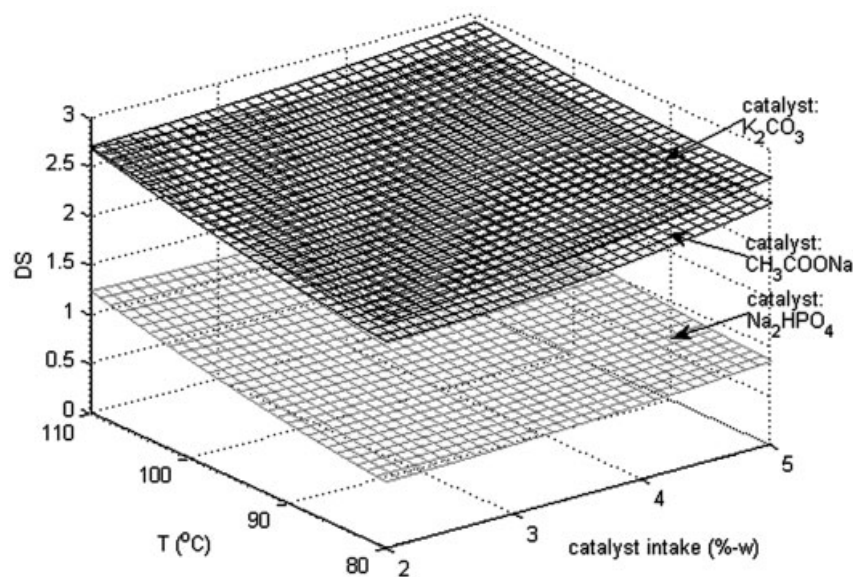
a. starch laurate
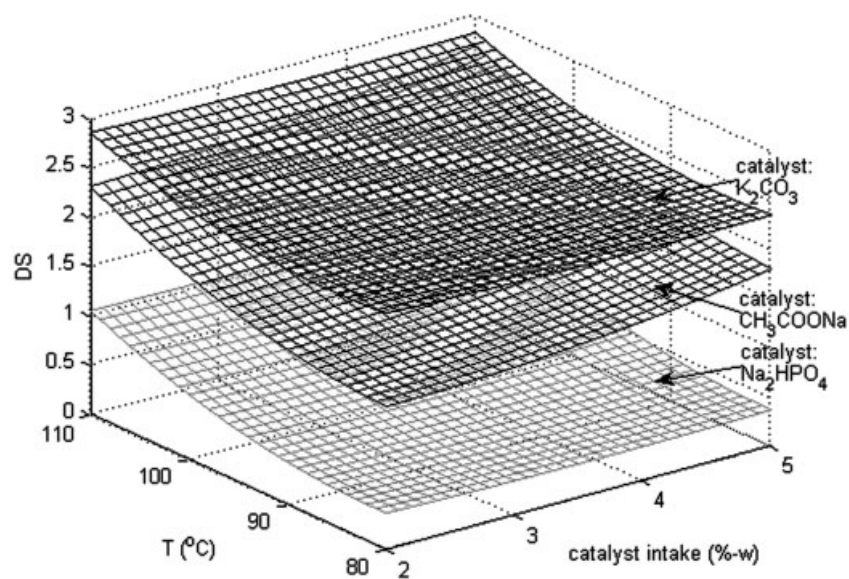
b. starch stearate

Fig. 2. 3D contour plot of the DS as a function of reaction temperature and catalyst intake (at constant vinyl ester to AHG molar ratio of 4) 185×251 mm (96×96 DPI).

strength and elasticity modulus, and lower elongation at break).

A deeper understanding of the mechanical behavior can be gained by investigating the shape of the stress-strain curves (typical examples in Fig. 5). Both starch laurate samples display, independently of the DS values, a clear plastic behavior with a maximum in the stress-strain curves. The values of the yield strain, calculated as the

ratio between the stress at yield (σ_y, determined from the stress-strain curves as the stress at which the material ceases to be linearly elastic) and the modulus, is roughly 0.05 for both laurate samples. This indicates that their mechanical behavior is comparable to that of typical engineering polymers [28]. Starch stearate with a relatively low DS (1.45) displays a very similar behavior as the laurate samples (i.e. plastic deformation and yield strain of about 0.05). On the other hand, starch stearate at rela-
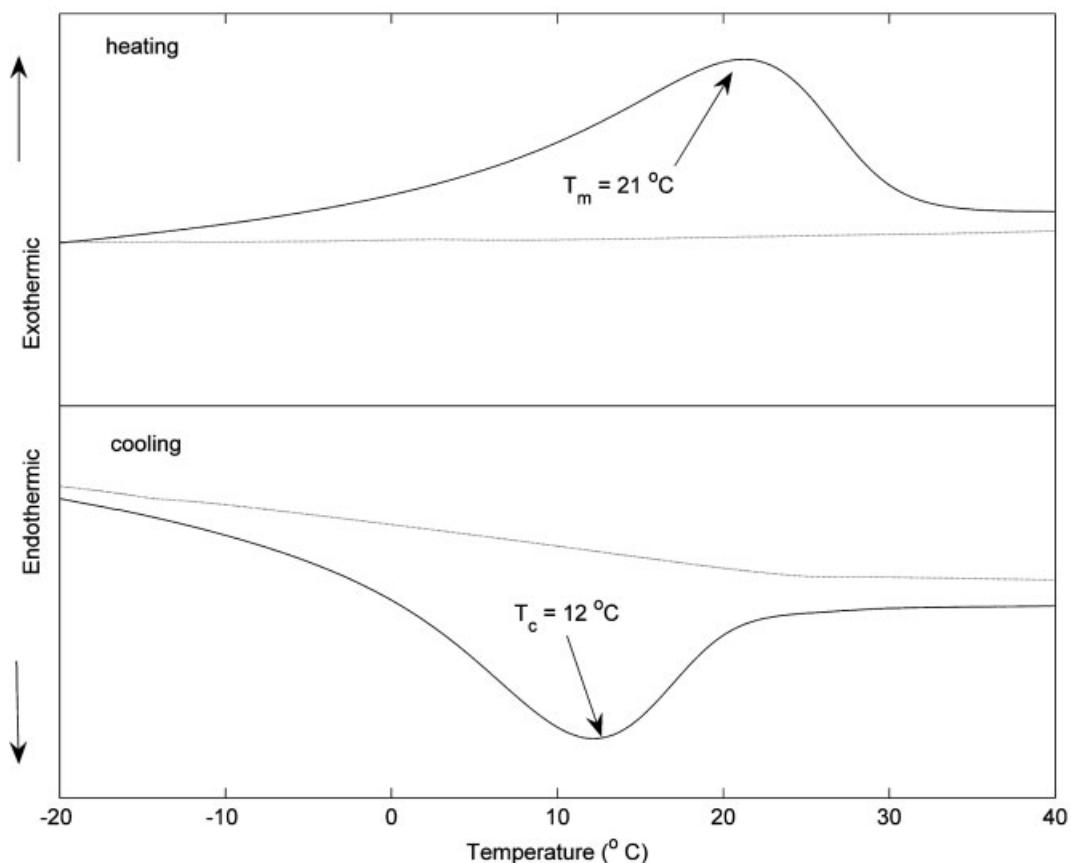
Fig. 3. DSC analysis of starch stearate esters (—): DS 1.45; (· · ·): DS 2.39. 152 × 114 mm (600 × 600 DPI).
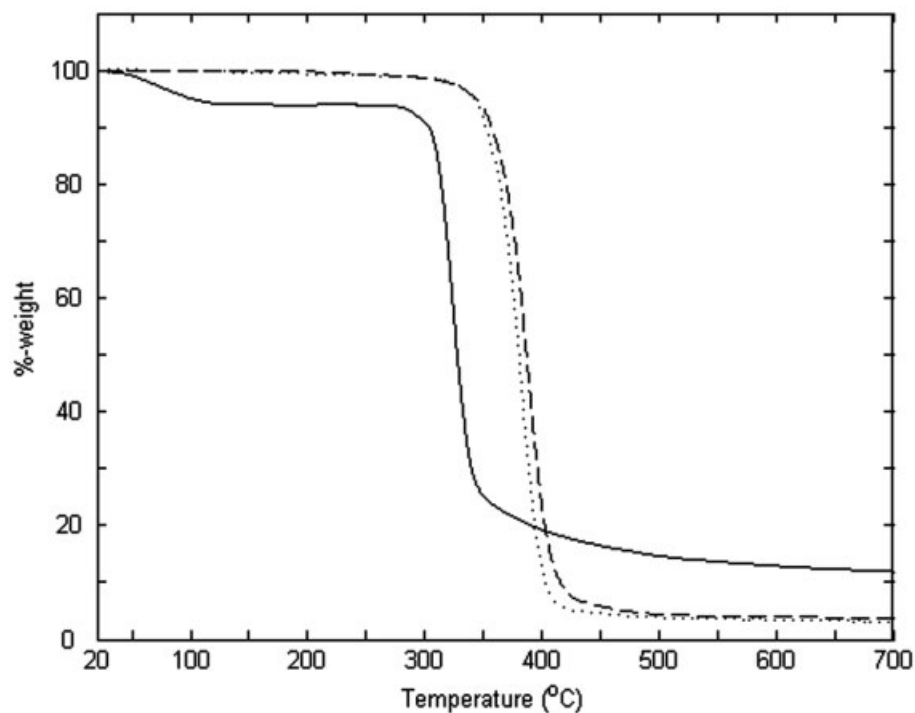

Fig. 4. TGA analysis of various starch samples. (—): native starch; (– – –): starch laurate (DS 2.26); (· · ·): starch stearate (DS 2.39). 148 × 111 mm (96 × 96 DPI).
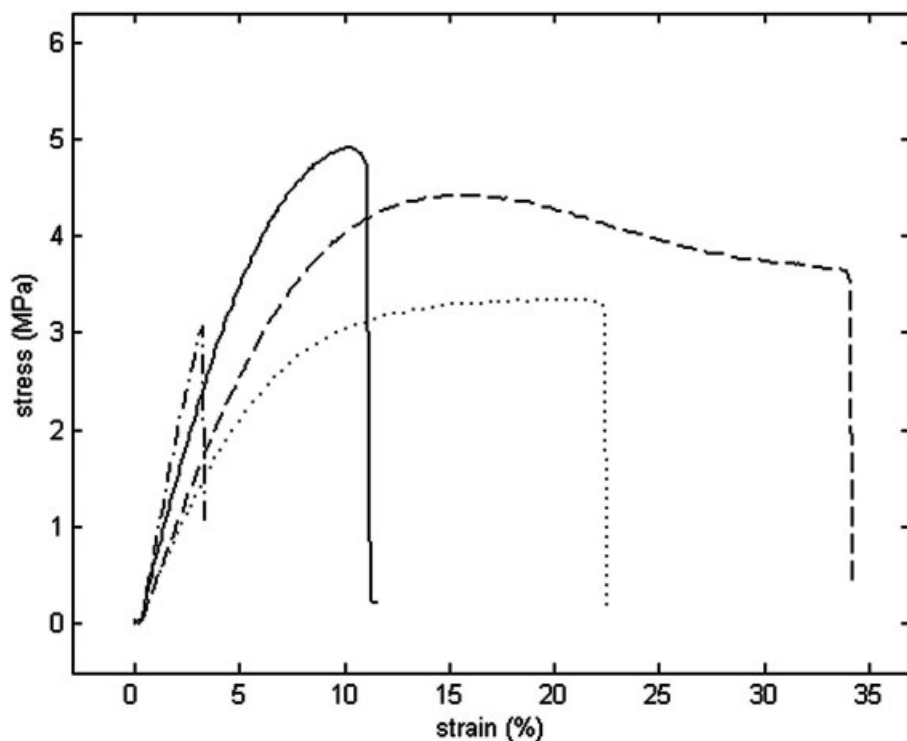
Fig. 5. Stress-strain curves for starch esters. (—): starch laurate (DS 1.75); (– – –): starch laurate (DS 2.26); (· · ·): starch stearate (DS 1.45); (– · –): starch stearate (DS 2.39). 148 × 111 mm (400 × 400 DPI).

Tab. 6. Mechanical properties of the starch esters.

Starch ester	DS	Stress at break [MPa]	Elongation at break [%]	Modulus [MPa]
Starch laurate	2.26	3.5 ± 1.0	26.1 ± 15.2	59.9 ± 14.1
Starch laurate	1.75	3.0 ± 2.2	8.7 ± 3.3	82.7 ± 4.0
Starch stearate	2.39	2.7 ± 1.0	3.1 ± 1.3	112.7 ± 14.9
Starch stearate	1.45	3.2 ± 0.1	21.7 ± 4.1	46.3 ± 2.8

tively high DS values (2.39) does not show any plastic behavior but only an elastic one. The corresponding yield strain (roughly 0.025) lies still in the typical range of engineering polymers but also close to that typical of composite materials [28], thus indicating a relatively more rigid material with respect to all other samples. These considerations strongly point out the fact that the mechanical behavior can be coarsely (plastic vs. elastic behavior) but also finely (stress and strain at break but also modulus values) tuned by the chemical structure of the fatty acid chains as well as the DS values.

Although there are many differences in the synthetics methods as well as in testing conditions and procedures, a rough comparison can be made between the mechanical properties of the esters described in this paper and those reported for related starch esters synthesized with alkanoyl chloride as reagent and pyridine as catalyst [17] (Tab. 7). Inspection of the mechanical properties of the starch esters as shown in Tab. 7 confirms that the corn starch esters synthesized in our research are relatively rigid materials as compared to the potato starch esters. In this respect the difference in stress and elongation at break for the high-DS starch laurate sample is striking. While for corn starch (DS 2.26) relatively high stress at break (3.5 MPa) is coupled with a low elongation (26%), for potato starch exactly the opposite is observed: relatively low stress (0.7 MPa) coupled with a significant (1500%) elongation. The same considerations are valid for starch stearate at high DS values (higher stress and lower elongation when using corn instead of potato starch). On the other hand at low DS values comparable stresses at break (3.2 MPa for corn starch, 3.7 MPa for potato starch esters) are coupled with significant differ-

Tab. 7. Comparison of the mechanical properties of corn starch ester (this study) with potato starch ester [17].

Property	Corn starch laurate ester		Potato starch laurate ester		Corn starch stearate ester		Potato starch stearate ester	
	Low DS (1.75)	High DS (2.26)	Low DS	High DS (2.7)	Low DS (1.45)	High DS (2.39)	Low DS (1.8)	High DS (2.7)
Stress at break [MPa]	3.0 ±2.2	3.5 ±1.0	n.a.[a.]	0.7 ±0.4	3.2 ±0.1	2.7 ±1.0	3.7 ±0.6	1.9 ±0.3
Elongation at break [%]	8.7 ±3.3	26.1 ±15.2	n.a.[a.]	1500 ±8.6	21.7 ±4.1	3.1 ±1.3	9 ±2	10 ±2

[a] n.a. = not available.

ences in the elongation (22% for corn starch esters, 9% for potato starch). In agreement with our own data, an unexpected behavior was also observed for the mechanical properties of the esters from potato starch. The medium or high DS stearate esters of potato starch are more rigid than the starch esters from lower-chain fatty acids (octanoate and laurate) [17]. The authors related this inverse property of starch stearate to crystallization of C18 side chains, as confirmed by DSC. Here, we show that although no crystallization of C18 occurred (see DSC data of the high DS material in Tab. 5), the high DS material is still more rigid, merely because of the structural property of the C18 side chain with respect to the starch backbone.

Comparison with the literature data implies that the mechanical behavior of starch esters of higher fatty acids is also a clear function of the type of starch used. Moreover, this comparison also confirms our conclusion derived from the analysis of thermal properties (*vide supra*): it is not only the individual factors (kind of starch and fatty acid, DS) which mainly determines the thermal and mechanical behavior, but the interplay between those factors.

4 Conclusions

A systematic study, including statistical modeling, on the synthesis of corn starch esters with long chain fatty acids is described. The starch esters were synthesized by reacting gelatinized starch with vinyl laurate or vinyl acetate in DMSO in the presence of basic catalysts (Na$_2$HPO$_4$, K$_2$CO$_3$, and Na-acetate). Statistically adequate ($R^2 \geq 0.96$ and *P*-value of $\leq 10^{-7}$) second-order mathematical models correlating the effect of process variables (vinyl to AHG-starch molar ratio, reaction temperature, catalyst intake, and catalyst basicity) to the DS of the starch ester products were developed. The DS of the products is a strong function of the basicity of the catalyst. The use of K$_2$CO$_3$ and CH$_3$COONa catalysts resulted in medium-high DS prod-

ucts (2.1-2.9 for starch laurate, 1.4-3 for starch stearate), while the use of Na$_2$HPO$_4$ resulted in low-medium DS products (0.3-1.5 for starch laurate, 0.07-1.5 for starch stearate). Reaction temperature and catalyst intake also affect the product DS although to a lesser extent than the type of catalyst. The models may be used to determine the appropriate process conditions to obtain a product with a pre-defined DS.

Thermal and mechanical behavior of the samples of different DS values clearly show that the DS represents one of the crucial factors affecting the final product properties. Comparison with literature data indicate that the properties may be (fine) tuned also by the starch source. Thus, the chemical composition of the starting materials (either starch or the ester precursor) as well as the processing parameters affect the final product DS values and as such provide an effective toolbox to modulate the desired product properties for a given application.

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