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Thermal and mechanical properties of fatty acid starch esters

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ABSTRACT

The current study examined thermal and mechanical properties of fatty acid starch esters (FASEs). All highly soluble esters were obtained by the sustainable, homogeneous transesterification of fatty acid vinyl esters in dimethylsulfoxide (DMSO). Casted films of products with a degree of substitution (DS) of 1.40–1.73 were compared with highly substituted ones (DS 2.20–2.63). All films were free of any plasticizer additives. Hydrophobic surfaces were characterized by contact angle measurements. Dynamic scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) revealed thermal transitions (T_g, T_m) which were influenced by the internal plasticizing effect of the ester groups. Thermal gravimetric analysis (TGA) measurements showed the increased thermal stability toward native starch. Tensile tests revealed the decreasing strength and stiffness of the products with increasing ester-group chain length while the elongation increased up to the ester group laurate and after that decreased. Esters of the longest fatty acids, palmitate and stearate turned out to be brittle materials due to super molecular structures of the ester chains such as confirmed by X-ray. Summarized products with a DS 1.40–1.73 featured more "starch-like" properties with tensile strength up to outstanding 43 MPa, while products with a DS >2 behaved more "oil-like". Both classes of esters should be tested as a serious alternative to commercial starch blends and petrol-based plastics. The term C_{number} is attributed to the number of total C-Atoms of the fatty acid (e.g. C_6 = Hexanoate).

1. Introduction

Several different strategies have been developed in the field of bio-based materials. On the one hand, the usage of bio-based monomers e.g. dilactide to produce polylactide (PLA) (Jacobson, Fritz, Degée, Dubois, & Jérôme, 1999) and, on the other hand, the blends of starch with bio-based or synthetic polyesters. The usage of functionalized starch in bio-plastic processing has not yet been commercially established. With its low market price and worldwide availability, starch is a highly attractive feedstock. Serious studies ~~on~~ using starch as a material have been conducted since the 1960s, mostly as a co-component (Belgacem & Gandini, 2008). So-called thermoplastic starch (TPS) is produced by extrusion of native starch with plasticizers e.g. water, sorbitol or glycerol (Mitrus, 2009). Inter alia, TPS is used as a component in blends with hydrophobic polyesters like PLA or Ecoflex® (Fleche, Gosset, & Videau, 1994). Important drawback is the limitation of the starch-amount in bio-plastics because of its hydrophilicity and strong brittleness. Many studies have been conducted to improve the compatibility between these blend components and enhance the amount of starch.

One approach to overcome the drawbacks of TPS was the synthesis of starch triacetate, leading to hydrophobic and thermoplastic processable material (Whistler & Hilbert, 1944). However, it also showed a high brittleness even when plasticizers were applied. Another approach was to use fatty acids (long-chain carboxylic acids) as esterification agents (Karrer & Zega, 1923). Strongly hydrophobic, film-forming, flexible materials with lowered glass transition temperatures were obtained without using any further plasticizers (Wolff, Olds, & Hilbert, 1951). Comparable with other polymeric systems e.g. polymethacrylates (Rogers & Mandelkern, 1957), covalently bound fatty acid groups show an internal plasticizing effect. Successful molding experiments with fatty acid esters of starch, amylose and amylopectin with DS ~3 were made by Wolff et al. (1951). In this context, studies on casted films showed decreasing strength with increasing ester group chain length by tensile tests. Conversely, the elongation increased to a maximum ester chain length and after that decreased while the materials became brittle. A further study on a homologous series on esters of amylose (DS 2.0–2.7) revealed decreasing softening points of materials with increasing ester chain length, reaching a minimum value for starch myristate (C_{14}) (Gros & Feuge, 1962). Tensile tests on these casted films again revealed the decreasing tendency of the strength with a minimum value for starch

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laurate (C_{12}). In accordance to prior studies, elongations increased to a maximum value while esters while the longest fatty acid esters became brittle again. The hydrophobicity of fatty acid starch esters was shown by water vapor adsorption, confirming the earlier contact angle measurements tendencies (Scholz, Roger Ray, & Anderson, 1958) of all fatty acid starch esters being hydrophobic materials. Recent studies complemented the characterization of the products with DSC-, DMTA and TGA-measurements (Aburto, Alric, Borredon, & Cedex, 1999; Aburto, Alric, Thiebaud, et al., 1999; Liebert et al., 2011; Sager & Merrill, 1995). Glassy transitions in DSC measurements appeared mostly undefined and broad; in many cases, no defined transitions were detected. Due to the variety of starch types and approaches of synthesis, the data are sometimes contradictory and not directly comparable. Approaches of blending fatty acid starch esters with PE were also made but resulted in a low compatibility of the blend components due to their thermodynamic immiscibility (Bikiaris et al., 1999). Besides the often used heterogeneous fatty acid chloride-esterification procedure using pyridine (Aburto, Alric, et al., 1999; Aburto, Alric, Thiebaud, et al., 1999), fatty acid vinyl esters/DMSO (Junistia et al., 2009; Winkler, Vorwerg, & Wetzel, 2013), fatty acid chlorides/imidazole (Liebert et al., 2011) and the use of ionic liquids (Xie, Shao, & Liu, 2009; Xie & Wang, 2011) are mentioned as possible homogeneous methods of synthesis for fatty acid starch esters.

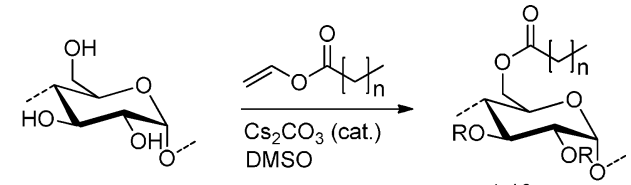
To sum it all up, many studies have been dealing with the thermal and mechanical properties of fatty acid starch esters with a high degree of substitution (2.0–3.0), revealing the thermoplastic, hydrophobic character of the materials. Only very view data is available for fatty acid starch esters with a medium DS of ~1.5. However, a higher "starch content" in the product is desirable due to the much higher price of fatty acid derivatives. Apart from that, the processability without the use of further plasticizers is highly attractive and should be retained. Furthermore, a high elongation at break besides a low tensile strength, as shown for most of the fatty acid esters of starch in literature, is not useful for the majority of applications in packaging or material fields. The main problem in view of an application e.g. as a packaging material is the low tensile strength of all FASEs. With ~10MPa, starch hexanoate showed the highest value, which is still lower than commercial available polymers (e.g. LDPE) and should be at least 25 MPa. An improvement is strongly necessary and one successful approach is given in the current study. The esterification procedure is based on the homogeneous transesterification of vinyl esters in DMSO (Junistia et al., 2009; Winkler et al., 2013). Since a whole series of fatty acid vinyl esters has become commercial available, this method became a powerful tool in laboratory scale esterification of carbohydrates beyond starch, e.g. cellulose (Cao et al., 2013), wood (Jebrane & Sèbe, 2008) and maltodextrin (Shogren, Biswas, & Willett, 2010). Due to the high costs of reagents and synthesis, there is no industrial scale application up to now. The actual study shows the potential of fatty acid starch esters (C_6–C_{18}) with a medium DS of 1.40–1.67 as hydrophobic film-forming materials with thermoplastic properties. Characteristic material properties such as thermal transitions and specific mechanical parameters of films are compared with high-DS fatty acid starch esters (DS 2.20–2.63). FASEs with DS 1.40–1.73 have the potential to be a serious alternative toward industrial bioplastics due to their high tensile strength up to 43 MPa as well as a high stiffness with moderate elongation. In view of an application as packaging materials, one general possibility is the surface modification of hydrophilic starch films (Bengtsson, Koch, & Gatenholm, 2003) to obtain interactions of the starch backbone inside and retain the high barrier properties toward, e.g. oxygen. Different from that, the homogeneously produced materials in the actual study are more suitable as a thermoplastic and completely softening material for e.g. injection molding experiments or extrusion processes. To obtain high barrier properties, multi-layer films would be preferable.

2. Materials

Gelose 80, a starch with 80% amylose content was supplied by *Penford Corp*. It was dried prior to use (16 h at 105 °C) in order to obtain a moisture content of <1.5%. The botanical origin of the starch was maize. Since it is known that high amylose starches give better mechanical material properties compared to amylopectin (Wolff et al., 1951), a high amylose starch was used in the current study. All reagents were used as received. *Sigma-Aldrich* supplied vinyl laurate (99%), vinyl stearate (95%) and dimethylsulfoxide (DMSO, 99.7%); *TCI Europe* supplied vinyl hexanoate, -decanoate, -octanoate (99%) and -palmitate (96%); *Alfa Aesar supplied* Cs_2CO_3 (99%). THF (>99%) was supplied by Merck, chloroform (>99%) by AppliChem and ethanol (99%) by Carl Roth.

3. Methods

3.1. Synthesizing FASES through homogeneous transesterification



Anhydro glucose unit (AGU)

Prior to esterification, a homogeneous dispersion of starch in DMSO (10%, w/w) was formed by stirring 2 h at 95 °C and 200 rpm. Subsequently, an aliquot of 40 g, containing 4.0 g starch (25 mmol anhydroglucose units = AGU) was added by the fatty acid vinyl ester (3.5/AGU for high-DS >2, 0.1 mol/AGU excess of vinyl ester if the desired DS was <2) and heated to 110 °C. Then, Cs_2CO_3 was added (3 mol% based on AGU) and the reaction mixture was stirred for 2 h at 110 °C. After cooling the suspension, it was added with 150 mL ethanol.[1] Then the raw product was dissolved in chloroform or THF and precipitated via dropwise addition to ethanol.[1] After subsequent washing, the product was dried in vacuum (85 °C, 16 h) to obtain moisture content <1%, which was determined by using a Sartorius moisture analyzer based on the weight loss of the sample at 130 °C.

A blind sample was obtained by applying the same procedure as described above but with the absence of the fatty acid vinyl ester. Though film forming was not possible, the corresponding analytical methods (e.g. contact angles) could not be applied.

3.2. Determination of the DS via elementary analysis

Being an often used standard method for DS-determination of fatty acid starch esters (Aburto, Alric, et al., 1999; Grote & Heinze, 2005), elementary analysis was applied for DS-determination. Measurements were performed using the combustion technique on a FlashEA 1112 CHNS/O automatic elemental analyzer with 2 auto samplers MAS200R (Thermo Scientific). Every sample was measured at least twice.

For the evaluation, the software ChemBioDraw Ultra 12.0 (CambridgeSoft) was applied to calculate the percentages of C, H and O for a starch ester molecule. The best fit for a starch macromolecule of 30 AGUs with a modifiable number of fatty acid ester groups gave the desired DS (Winkler et al., 2013). The accuracy of this method (values obtained by the supplier) is given in Table 1.

Table 1
Accuracy of elementary analysis.

Theoretical value	experimental value
100 ppm	100 ± 10 ppm
0.10%	0.10 ± 0.01
1.00%	1.00 ± 0.02
10.00%	10.00 ± 0.1
50.00%	50.00 ± 0.3
90.00%	90.00 ± 0.3

3.3. SEC-MALL spectroscopy

Size exclusion chromatography (SEC) with multi angle laser light scattering (MALLS) was used to determine the molar mass weight average M_w and the molar mass distribution *MMD*. Polymer molecules were separated on columns with porous gel according to their molecular hydrodynamic volume.

The SEC-MALLS system that was used to investigate native starch in DMSO consisted of a Waters 515 HPLC pump, 717 autosampler, a Waters in-line degasser DG2 and a Waters 2414 refractive index detector (RI). The column series PSS Suprema S30000, S1000 and S100 was used for sample fractionation. Elution of the starch sample was carried out using dimethyl sulfoxide (DMSO) containing 0.09 m $NaNO_3$ at a flow rate of 0.5 mL/min and a temperature of 70 °C. A Wyatt Dawn HELEOS MALLS detector (λ = 658 nm) was used to detect the scattering light intensity.

In order to prepare the starch laurate samples, about 8 mg were dissolved in 4 mL THF (2 mg/mL) and stirred for 24 hours. Before the measurement, the solutions were filtrated using 1 μm PTFE membranes. Subsequently, the starch ester samples were measured at 25 °C using an SEC-MALLS system which consisted of a Waters 2695 separation module, a DAWN DSP-F laser photometer (Wyatt, 488 nm), a dual λ absorbance detector 2487 (Waters) and a refractive index detector 2414 (Waters, 35 °C). The column system PLgel 10 μm precolumn, 3× Plgel 20 μm Mixed-A; 2000–40,000,000 and 1× Plgel 20 μm Mixed-A LS; 2000–40,000,000 (supplied by Polymer Laboratories) was used. A flow-rate of 1 mL/min was applied.

The evaluation was conducted with Astra-software (Wyatt) using a refractive index increment dn/dc of 0.070 (THF) (Lang, 2000) and 0.068 (DMSO).

3.4. Film preparation

Solutions of the samples in chloroform (DS 2.20–2.63) or THF (DS 1.40–1.67) with a minimum concentration of 7.5% (w/w) were casted on a 100 mm × 20 mm PTFE-coated glass plate and stroked with a 1 mm squeegee. Afterwards, the films were dried on air and under vacuum.

3.5. Contact angle measurements (CAM)

Contact angles against a water drop on the casted films were measured using a Krüss DSA 100 Video-Goniometer. The advancing contact angles were compared for evaluation. The given contact angles are the result of two measurements.

3.6. Differential scanning calorimetry (DSC)

DSC measurements were performed on a DSC 7 (PerkinElmer). An amount of 5–10 mg starch ester was measured in two heating circles of minus 20–200 °C with a heating and cooling rate of 10 K/min. For a comparable determination of thermal transition temperatures, the second heating curves were evaluated. For a verification of the results, selected samples were measured at least twice. As a reliable deviation for the given temperatures, ±0.2 °C was the average result.

3.7. Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were performed on a 2980 (TA Instruments) with a film strip of 10 mm × 20 mm and a thickness of ~20–60 μm, cut from a solution casted film. The heating rate was 5 K/min at different frequencies: 0.01 Hz, 0.1 Hz, 10 Hz and 100 Hz at the same sample strip. For a verification of the results, selected samples were measured at least twice. Though the values were taken in steps of 5 K, some resulting temperatures fluctuated between two steps. As a result, ±2.5 °C was taken as average deviation.

3.8. Thermal gravimetric analysis (TGA)

All measurements were performed on a Q500 thermogravimetric analyzer (TA instruments). An amount of the starch ester sample was heated up to 500 °C in steps of 5 K/min. The degradation was measured by weight loss of the sample. The point of intersection of the elongated lines before and after the first drop of the curve was applied for evaluation. For a verification of the results, selected samples were measured at least twice. As a reliable deviation for the given temperatures, ±0.1 °C was the average result.

3.9. Tensile tests

Tensile tests of films were performed using a Zwick 1445 universal testing machine. According to DIN EN ISO 527, the samples were conditioned at 23 °C and 50% relative humidity during 24 h before each testing. The casted film was cut into 100 mm × 10 mm strips, which were measured in the direction of striking out the film with a speed of 20 mm/min. All resulting data were an average of 5 tensile tests.

4. Results

4.1. Structural features of the starch ester samples

The investigated starch ester samples were subdivided into two classes: medium-substituted esters (DS 1.40–1.73) and highly substituted ones with a DS of 2.20–2.63. Due to the higher hydrophobicity of longer fatty acids (e.g. stearate) and with that earlier precipitation from the polar DMSO-medium, the obtained maximum DS showed a slightly decreasing tendency with increasing chain length. As revealed in Table 2, the obtained DS-values by a reproduction of a certain synthesized starch esters differed slightly (e.g. starch decanoate with high DS). However, the differences in the product properties inside the respective groups were negligible. The key differences in the product properties were found to be between products with medium vs. high DS. In Table 2, the used samples are listed concerning the most important properties, namely mechanical properties of the films as well as glassy transitions (DSC, pure sample and DMTA, film). While the (mass) degradation temperatures of the two product class were similar concerning varying ester chains, the differences in the contact angles were low over all fatty acid starch esters.

In the prior study (Winkler et al., 2013) it came out that a disintegration of the starch backbone chains occurred during synthesis, shown in detail for starch laurate (DS 2.3–2.4). Prior to the esterification, the amylopectin seemed to be not completely disintegrated to give a molecular dispersion and consequently the recovery rate was only 77–85%, as shown by SEC-MALLS. After the subsequent

Table 2
Overview analyzed starch ester samples with exact DS-values.

Ester	DS	σ_{max} [MPa]	*E*-Mod. [MPa]	ε_{max} [%]	T_g-DSC [°C ± 0.2]	T_g-DMTA [°C ± 2.5]
Hexanoate	1.40 ± 0.06				124	160
	1.73 ± 0.07	43.2 ± 0.7	1401.8 ± 49.8	30.8 ± 8.1	114	
	2.43 ± 0.11	10.6 ± 0.2	315.1 ± 9.9	58.6 ± 25.7	68	70
	2.63 ± 0.11	9.3 ± 0.3	289.8 ± 12.9	110.4 ± 41.0	71	
Octanoate	1.50 ± 0.06				148	170
	1.60 ± 0.06	17.6 ± 0.4	516.6 ± 11.8	29.1 ± 4.7		
	2.50 ± 0.10	6.2 ± 0.0	156.4 ± 5.5	86.8 ± 18.7	66	65
Decanoate	1.60 ± 0.06				n.d.	180
	1.57 ± 0.06	18.6 ± 0.9	483.1 ± 26.6	31.4 ± 9.3		
	2.33 ± 0.09				n.d.	70
	2.60 ± 0.11	4.2 ± 0.1	86.7 ± 6.4	181.2 ± 66.7		
Laurate	1.60 ± 0.06	15.5 ± 0.4	382.2 ± 10.6	30.2 ± 12.5	n.d.	185
	2.30 ± 0.10				81	85
	2.43 ± 0.11	3.0 ± 0.2	52.3 ± 10.1	133.4 ± 15.8	78	
Palmitate	1.57 ± 0.06	4.6 ± 0.1	89.6 ± 6.8	30.5 ± 7.7	n.d.	185
	2.23 ± 0.10	3.2 ± 0.1	57.3 ± 2.1	27.2 ± 12.3	100	110
Stearate	1.60 ± 0.07	5.7 ± 0.3	139.5 ± 9.4	16.3 ± 5.1	156	149
	2.20 ± 0.11		Too brittle		n.d.	n.d.

Table 3
Changes in the chemical structure of the model compound starch laurate.

Step	M_W [10^6 g/mol]	Recovery rate [%]
Before transesterification (Gelose 80)	1.90	85
Blind sample (Gelose 80)	1.84	72
Starch laurate, DS 1.60	2.68	87
Starch laurate, DS 2.43	5.90	93

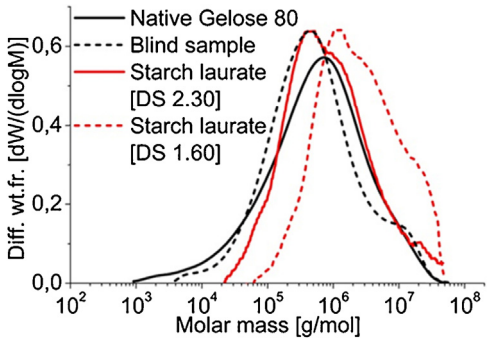


Fig. 1. Molar mass distributions.

transesterification procedure, the recovery rate, which represents the solubility, was increased to 93% (DS 2.4).

As shown in Table 3, for the blind sample (Gelose 80/DMSO in the presence of Cs_2CO_3) no significant reduction of Mw was measured via SEC-MALLS, the brownish color implied traces of degradation or side reactions.

In Fig. 1, the MMDs of the samples are revaled. Summarized, the specific properties of the starch esters obtained by homogeneous transesterification are reasoned by a disintegration of the starch backbone chains during synthesis. As a result, an increased solubility with the lack of aggregated structures was obtained.

4.2. Contact angles of FASE

Contact angle measurements against a water drop are a reliable method to classify a material's hydrophobicity. Plasticized TPS typically possess values of 40–60° (Sreekumar, Leblanc, & Saiter, 2013), revealing its hydrophilic character. Casted films of starch acetate (DS 2.5) + 30% triacetin showed an enhanced contact angle

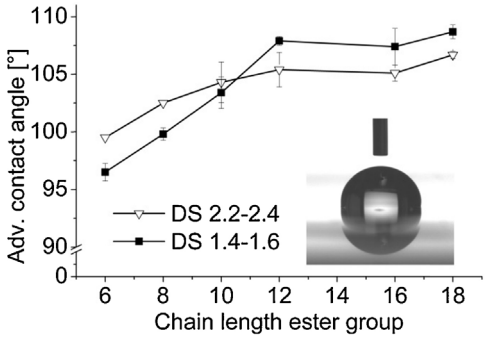


Fig. 2. Contact angles of casted films.

of 82°, revealing the increased hydrophobic character after the acetylation procedure (Gust, 2011).

Fig. 2 shows a comparison of plasticizer-free casted films of different fatty acid starch esters. It became apparent that the hydrophobicity increased with an increasing chain length of the fatty acid ester group.

Products with a DS of 1.40–1.60 revealed a linear increase of the contact angles with increasing ester chain length of overall 10° in the case of C_6-C_{12}. No further significant change was observed for the longer ester groups (C_{12}–C_{18}). It seemed that the remaining OH-groups of the starch are somewhat accessible for the water up to a "critical length" of the fatty acid ester group (C_{12}), after that the starch backbone is most widely shielded. From that critical length, the hydrophobicity of the surface of the films is almost exclusively defined by the fatty acid groups.

In the case of high DS (2.2–2.4) samples, the differences between the types of fatty acid ester groups are quite smaller. Similar to products with DS 1.4–1.6, an increase of the contact angles in the case of C_6–C_{12} was observed, but less well-marked (5°). This can be reasoned by the enhanced degree of esterification of the OH-groups and with that a higher fatty acid ester group-content in the product leading to materials with more "oil-like" than "starch-like" properties. Also, there are no remarkable differences in the contact angles of the starch esters C_{12}–C_{18}.

The higher contact angles of products with DS 1.4–1.6 compared to highly substituted products could be reasoned by differing morphologies of the surfaces of the casted films. However, the disparity was not in a significant range. To sum it all up, a strong increase of

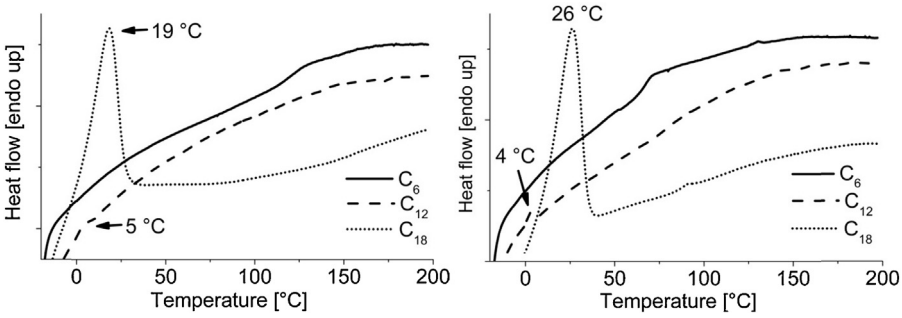


Fig. 3. DSC of starch hexanoate, laurate and stearate/blind sample with marked melting endotherms; DS 1.6–1.7 (a) and DS 2.2–2.4 (b).

the hydrophobicity of all films was observed compared to starch acetate (DS 2.5 + 30% triacetin). An influence of the chain length was shown for the shorter fatty acids C_6–C_{12}. For C_{12}–C_{18} esterified products, the surface seemed to be completely dominated by the long-chain ester groups. However, all products came out to be hydrophobic bio-plastic materials with a remarkable hydrophobicity showing >95° contact angles.

4.3. Thermal behavior

4.3.1. DSC

Native starch consists of crystalline and amorphous domains. In a previous study (Winkler et al., 2013) the disintegration of the starch structure during the homogeneous esterification procedure in DMSO was revealed. In the current study, DSC measurements were applied to study the thermal behavior of the starch esters and obtain important information about the processing temperatures, which are necessarily above T_g (glassy transition temperature) and below T_d (degradation temperature).

Fig. 3 shows the (2nd) heating curves of starch hexanoate, -laurate and -stearate for medium- and highly substituted products. It came out that starch hexanoate had one distinct glassy transition as typical for an amorphous polymeric material. Its T_g-value decreased with an increasing amount of ester groups, which are acting as internal plasticizers. This can be reasoned by the ester groups widening the compact and strong starch structure with its lots of OH-group interactions. The same dependency of the well-marked glassy transitions on the DS was observed for starch octanoate and decanoate (not shown). Consequently, C_6–C_{10} FASEs can be classified as completely amorphous polymers, whose softening temperatures can be easily adjusted by the DS. For this class of materials, no further melting endotherm was detected, which indicates that esters with shorter fatty acids act mainly as an amorphous material. Nevertheless, these materials showed no glassy behavior at room temperature (23 °C), which lies above their detected T_gs. Especially in tensile testings, they rather behaved like ductile polymers above their glassy transitions (see below). Obviously, there seemed to be a second phase in the material with a separate glassy transition. In accordance to fatty acid esters of cellulose, the second phase is ascribed to the fatty acid ester groups (Vaga-Garcia, Gozzelino, Glasser, & Borredon, 2003).

A somewhat different thermal behavior was detected for esters with longer fatty acid groups (C_{12}–C_{18}). In this case, a distinct melting endotherm was detected at lower temperatures. According to interpretations made before (Aburto, Alric, et al., 1999; Aburto, Alric, Thiebaud, et al., 1999), these peaks can be ascribed to the phase dominated by the fatty acid ester groups. In contrast to the amorphous esters with shorter fatty acid chains, the phase consists of crystalline structures. A model of stacked and orientated long-chain ester groups was given by Sealy, Samaranayake, Todd, and Glasser (1996). Proofing the concept of two phases in the examined materials, in the case of starch laurate, both, a melting endotherm at 4 °C and a glassy transition at 79 °C are present. As further shown in Fig. 3, the intensity of the melting endotherm increases dramatically from C_{12} to C_{18} and with minor extent, by enhancing the DS from about 1.6 to about 2.3.

Summarized, two phases are present the FASEs: one dominated by the fatty acid ester groups (at low temperatures, amorphous and/or crystalline) and one dominated by the "backbone" starch chains. Depending on its amount in the final material, which in turn depends on DS and chain length of the fatty acid, every phase has a more or less strong influence on the properties. Starch stearate with a DS of 2.2 for example consists of 78 wt% fatty acids and is a waxy, brittle polymer with a melting point similar to pure stearic acid. Lastly, a DSC-measurement of the pure blind sample showed as expected neither a glassy transition nor a melting endotherm in the absence of external plasticizers.

4.3.2. X-ray measurements

The assumption of two different phases lead to two types of polymers: completely amorphous products with esters of shorter fatty acids and semicrystalline materials in the case of longer ones. To confirm the presence of these two classes of FASEs, X-ray measurements were applied.

In Fig. 4, the X-ray pattern of the blind sample, which implies a disintegrated high amylose starch, is compared with three types of fatty acid ester of starch: Completely amorphous starch hexanoate, semicrystalline starch laurate and semicrystalline starch stearate, while the latter is dominated by the fatty acid ester groups in its properties. The blind sample showed a typical pattern of an amorphous material. Furthermore, a weak signal in the range of 19.5° 2θ is detected, which is the characteristic peak of a disintegrated starch (Aburto, Alric, et al., 1999; Aburto, Alric, Thiebaud, et al., 1999; Liebert et al., 2011). This circular pattern gets more marked in the case of fatty acid starch esters, which was reasoned by Liebert et al. (2011) in the case of starch palmitate by an influencing effect of the orientated palmitate chains on the orientation of the polymer backbone. On the contrary, Aburto et al. attributed this effect to inclusion-complexes of (in their case) amylopectin and fatty acids.

In this context, 2D-X-ray diffraction patterns gave further insight in the structure of the starch esters. Both works, Liebert et al. and Aburto et al. just revealed X-ray patterns to a minimal value of 10° 2 2θ. As shown in this work, an interesting effect was detected at about 4° 2θ. This well-marked signal was detected (in a further measurement) in the case of starch hexanoate at 5° 2θ, for starch laurate indicated at 3.2° and for starch palmitate, as shown by the beginning of the peak, further shifted downwards to 2.7°. Both, the detection of this signal and the downward shift with increasing length of the fatty acid ester group was reasoned in the case of fatty acid esters of cellulose with an increasing intermolecular distance of the backbone chain due to

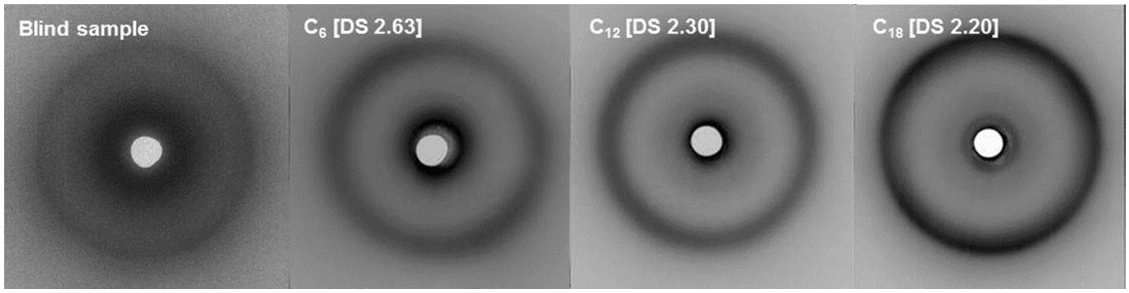


Fig. 4. X-ray diffraction films of the blind sample and starch esters with high DS.

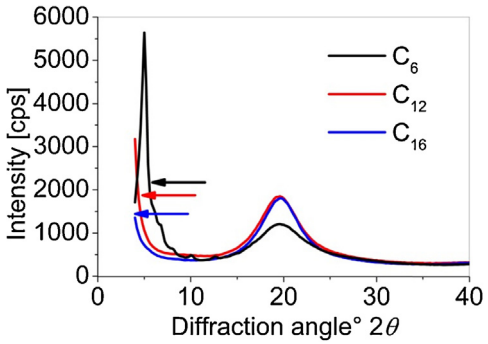


Fig. 5. X-ray diffraction patterns of starch esters with DS >2.

Table 4
Evaluation of the X-ray patterns.

Starch ester (DS >2)	Maxima [° 2θ]
Hexanoate	5.0
	19.6
Laurate	3.2
	19.6
Palmitate	2.7
	19.6

the increasing length of the fatty acid, which are ordered between these chains (Crépy, Miri, Joly, Martin, & Lefebvre, 2011). Though cellulose chains are most widely linear, in the current work, the non-crosslinked amylose chains are assumed to show a similar behavior and the intermolecular distance between the starch backbone chains is increased with increasing length of the fatty acid ester chain.

A second effect, an ordering effect of the long-chain fatty acid phase, is revealed in Fig. 4: with increasing length of the fatty acid, the circular pattern gets more defined an with this narrow, an evidence for a higher ordering level. It is ascribed to layered ordered structures of the long-chain fatty acid chains. Based on the work of Crépy et al., this effect also is visible in Fig. 5. The second peak at ~20° 2θ is a superposition of an amorphous peak disintegrated starch, amorphous fatty-acid ester group phase) and a crystalline peak reasoned by the already mentioned ordering of the long-chain fatty acids. Indeed, in the actual work, the full width half maximum (fwhm) of the peaks was increased with increasing ester chains length. All data are summarized in Table 4.

4.3.3. DMTA

DMTA measurements were applied on casted films to give further information about the thermal behavior of the FASE-materials since glassy and melting transitions can be obtained. Fig. 6 reveals the storage modulus (E') as well as the dissipation factor ($\tan\delta$) of different FASEs.

T_g-values can be detected by a significant drop of the storage modulus (E'), an increase of the loss modulus (E'') and with that an increase of $\tan\delta$, resulting in a peak. The dissipation factor $\tan\delta$ is defined as E''/E'. In the current study, the measurements were automatically stopped before the T_g-peak fully was passed, so only the increasing part of the peak area is visible.

All samples were measured at 0.1, 1, 10 and 100 Hz. At 100 Hz, the curves were differing and showed some peaks, which could not precisely be classified as reasoned by the material's structure or artifacts. For that reason, curves of 10 Hz-measurements are discussed.

As shown in Fig. 6, results of the DMTA-measurements correlate with the conclusions obtained by DSC and X-ray. In the case of starch hexanoate, the curves show only one sudden drop of E' accompanied by an increase of $\tan\delta$, which can be ascribed to the glassy transition. Furthermore, the material possesses the highest strength of the FASEs, which is in common with its mechanical properties obtained by tensile tests (see Section 4.4). The glassy transition of starch hexanoate DS 1.40 is higher than of starch hexanoate with 2.40 DS as well.

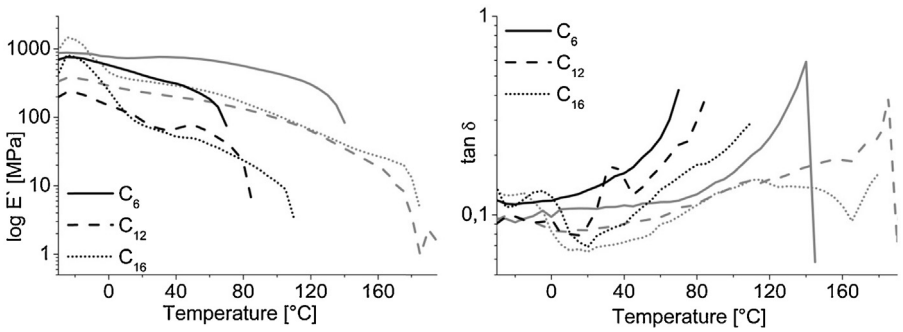


Fig. 6. DMTA measurements (10 Hz): E-mod (a) and tan δ (b) [DS 2.2–2.4 = black, DS 1.4–1.6 = gray].

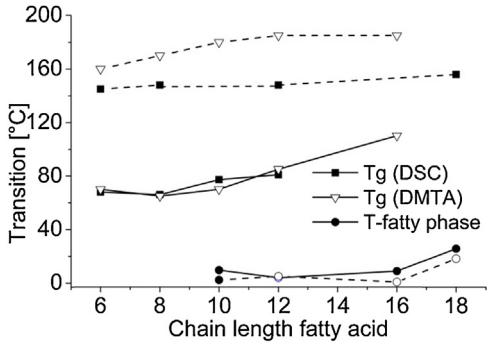


Fig. 7. Thermal transitions [DS 1.4–1.6 = - - -, DS 2.2–2.4 = —], some values were could not be detected.

Esters with the longest fatty acid groups (C_{12} and C_{16}) showed a somewhat different DMTA-curve with a second transition at lower temperatures, which can be ascribed to crystalline structures in the fatty acid ester phase. This melting transition is most distinct in the case of the longer fatty acid ester groups with a higher degree of substitution, because the fatty acid phase has a stronger influence on the material properties in these cases. Furthermore, materials with increasing fatty acid ester chain length and increasing DS show decreased E'-values and with that, possess a minor stiffness, which can be ascribed to the more "oil-like" behavior with increasing fatty acid content in the product.

Fig. 7 compares the detected thermal transitions of all FASE-materials obtained by DSC and DMTA. For FASEs with a DS of 2.2–2.5, the glassy transition temperatures of both methods are concurrent and reveal a minimum value for C_8 (octanoate) respectively between C_6–C_{10}. After that, the T_g-values enhance again. This trend was confirmed and discussed for fatty acid esters of cellulose (Malm, Mench, Kendall, & Hiatt, 1951). For these esters up to the ester group octanoate, the interactions between the starch backbone chains are more and more hindered and the enhanced plastifying effect leads to a decrease of T_g. When the ester chains become too long (>C_8), there is a strong filling of the space in the material, which hinders the motion of the macromolecules and shifts the T_g toward higher temperatures.

For FASEs with a medium DS, the progress was similar but shifted to higher temperatures. Furthermore, both classes of materials reveal a similar trend for the softening temperatures of the fatty acid phase. In the case of C_{12}–C_{18}, melting points were detected while in the case of C_{10}, a peak was detected in DMTA measurements, ascribed to an amorphous transition of the fatty acid phase.

4.3.4. Thermal stability (TGA)

For the usage as a thermoplastic processable material, another important characteristic is the thermal stability at the processing temperature, which must be remarkably higher than T_g or T_m and lower than T_d to avoid a degradation of the polymer. In the case of pure starch with low water content, the polymer degrades before reaching a glassy transition. Plasticizers are applied to obtain thermoplastic starch, which softens at higher temperatures, without degradation of the starch backbone. Typical degradation mechanism for starch at higher temperatures is the decomposition of chemical bonds in the starch chain, oxidation and dextrinisation (Zhang, Golding, & Burgar, 2002). DSC and DMTA measurements revealed the internal plasticizing effect of the fatty acid ester groups by lowered glass transition temperatures. Nevertheless, medium substituted starches obtain a higher content of free OH-groups and relatively high T_g-values compared to products with a DS >2. In Fig. 8 (a), TGA-curves reveal the weight loss during heating and according thereof the degradation of the starch ester samples.

It can be concluded that the esterification of the OH-groups leads to increased stability due to the suppression of the starch degradation mechanisms. Fig. 8(b) shows a comparison of the onset T_d-values (at the first drop) in relation to DS and chain length of the fatty acid.

For every fatty acid, there was a nearly linear increase of the T_d related to the DS. Compared to pure Gelose 80 (T_d = 291 °C), the stability of FASEs with DS 2.2–2.4 was increased by more than 50 °C. The type of fatty acid by keeping a constant DS has minor influence. To sum it all up, all degradation temperatures are remarkably higher than the melting or glass transition temperatures enabling a softening at processing temperature without structural alteration of starch fatty esters even for materials with a medium DS.

4.4. Mechanical properties

Due to their outstanding film-forming ability, mechanical properties of FASEs could be easily characterized by tensile tests with strips of casted films. Fig. 9 reveals typical stress-strain curves for some FASEs with medium and high DS. FASEs with a DS of about 1.6 behaved more like stiff materials while FASEs with DS >2 showed

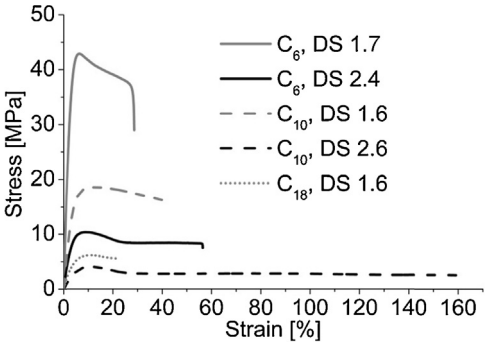


Fig. 9. Stress–strain curves.

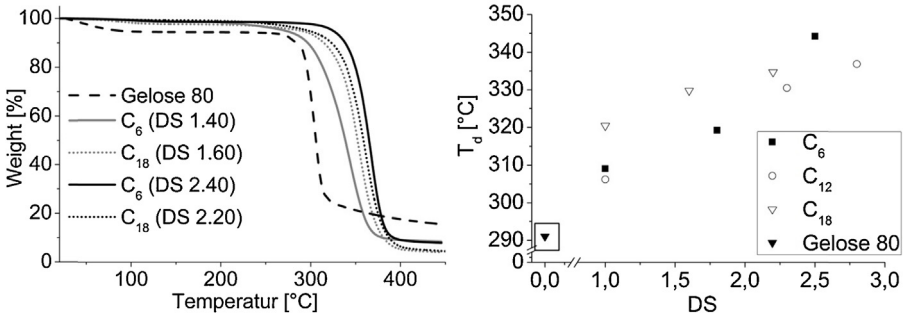


Fig. 8. TGA curves (a) and T_d vs. DS (b).

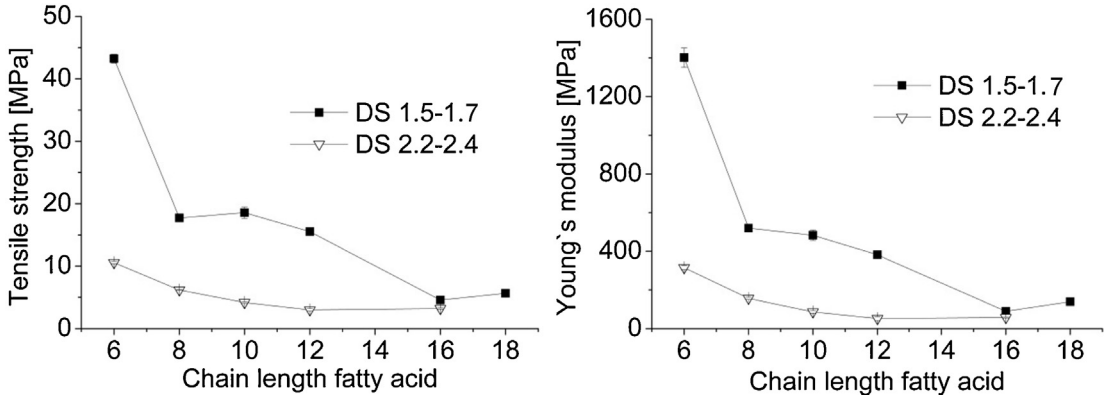


Fig. 10. Tensile strength (a) and Young's modulus (b) related to the type of fatty acid.

a more ductile behavior. A typical characteristic of these ductile material's stress strain curves is the existence of a well-marked upper yield limit. This progress is typical for polymers above their T_g and reasoned by the "cold" flowing-behavior and irreversible orientation of polymer chains, associated with a necking of the sample. Though the measured strength in the stress–strain curve is always related to the initial width of the sample at the beginning of the test, the true material strength is higher. The upper yield limit only exists in the nominally stress–strain curves with a fixed width. Furthermore, compared to the stiff materials, the maximum elongation is increased for highly esterified starches. This behavior became more marked with increasing length of the fatty acid ester-group.

It turned out that, depending on the fatty acid ester chain and DS, materials with completely different mechanical behavior were obtained. With that, a broad range of product properties could be adjusted and enables a wide field of possible applications.

As shown in Fig. 10, strength and stiffness of the materials were decreased with increasing chain length of the fatty acid ester group. This was already explained by the increased distance of the starch backbone chains accompanied by less reinforcing OH-group interactions. A further remarkable effect was obtained by changing the DS from 2.2–2.4 to about 1.6. In the case of starch hexanoate with a DS of 1.73, an outstanding strength of 43 MPa was obtained, which is higher than many industrial packaging polymers. The most remarkable difference between the materials turned out to be between starch hexanoate and octanate (Fig. 10). This indicates that FASEs with ester groups $>C_6$ are more dominated by the plasticizing behavior of the fatty acid groups. The stiffness of the materials revealed a similar trend. While starch hexanoate (DS 1.73) possessed a high value of 1401 MPa, longer fatty acid ester groups lead to strongly reduced values <500 MPa.

The elongation at break revealed a different behavior (Fig. 11) by reaching a maximum and subsequent decreasing values. This decrease can, as already mentioned, be explained with the increasing extent of crystalline structures of the fatty acid ester chains C_{12}–C_{18}. Though in this case the fatty acid groups represent the main part of the material by weight, the influence of their crystalline structures dominates the whole product properties. Starch stearate appeared as a waxy, colorless and brittle material which broke abruptly. Though the influence of the fatty acid chain crystallinity was less-marked for reduced DS (1.6), starch stearate was able to form ductile and flexible films.

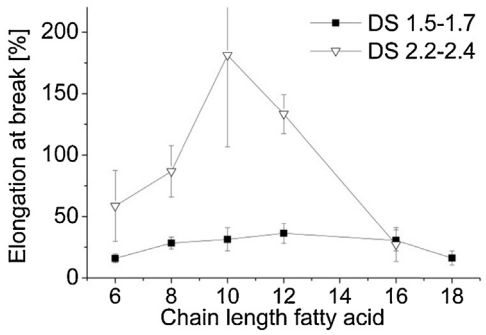


Fig. 11. Elongation at break vs. DS.

Summarized, the type/length of the fatty acid ester group as well as the DS were both important parameters for the properties of the products. In the case of a DS >2, the fatty acid phase represents the main weight part in the final products and determines its character. The DS of ~1.6 came out to be a threshold: In the case of the shorter hexanoate ester chains, strong starch backbone interactions seemed to be enabled, resulting in high strength/stiffness. At the same DS, the long stearate groups resulted in higher distances of the starch backbone chains an less OH-interactions were possible: Strength and stiffness were reduced.

5. Conclusion

In view of a usage as thermoplastic processable materials without plasticizer-additives, a systematic characterization of FASEs with a DS of 1.40–1.73 and 2.20–2.63 was performed concerning their hydrophobic, thermal and mechanical properties.

Obviously, both classes of materials were hydrophobic, softening at higher temperatures and showed increased stabilities of >250 °C. Concerning the mechanical properties of casted films without any further plasticizer-additives, products with a DS of 1.40–1.73 possessed more "starch-like" properties with high stiffness and, in the case of starch hexanoate, an excellent strength of up to 43 MPa. The fatty acid phase dominated products with a DS >2 concerning their mechanical properties and lead to decreased strength and stiffness while increasing the elongation of >200%.

Furthermore, the type of fatty acid ester group turned out to have a strong influence on the structure of the materials. While the esters C_6–C_{10} were completely amorphous materials with at least one glassy transition, the esters C_{12}–C_{18} possessed crystalline structures in the fatty acid phase with a weakening influence of the material revealed in tensile tests. Furthermore, X-ray measurements revealed the growing intermolecular distance of the starch backbone chains with increasing length of the esterified fatty acid, which had a strong influence on the macroscopic properties.

To sum it all up, the class of FASEs with DS of 1.40–1.73 was introduced in the current study and systematically compared with highly substituted FASEs (DS 2.20–2.63). This new product class showed superior properties concerning industrial applications e.g. as a packaging material: high strength up to 43 MPa, high stiffness,

moderate elongation, $T_g < T_d$, a well-marked hydrophobicity and being a completely bio-based product.

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References

Aburto, J., Alric, I., Borredon, E., & Cedex, T. (1999). Preparation of long-chain esters of starch using fatty acid chlorides in the absence of an organic solvent. *Starch/Stärke*, *4*, 132–135.

Aburto, J., Alric, I., Thiebaud, S., Borredon, E., Bikiaris, D., Prinos, J., et al. (1999). Synthesis, characterization, and biodegradability of fatty-acid esters of amylose and starch. *Journal of Applied Polymer Science*, *74*, 1440–1451.

Belgacem, M. N., & Gandini, A. (2008). *Monomers, polymers and composites from renewable resources* (1st ed). Amsterdam: Elsevier (chapter 15).

Bengtsson, M., Koch, K., & Gatenholm, P. (2003). Surface octanoylation of high-amylose potato starch films. *Carbohydrate Polymers*, *54*, 1–11.

Bikiaris, D., Aburto, I., Alric, E., Borredon, E., Botev, M., Betchev, C., et al. (1999). Mechanical properties and biodegradability of LDPE blends with fatty-acid esters of amylose and starch. *Journal of Applied Polymer Science*, *71*, 1089–1100.

Cao, X., Sun, S., Peng, X., Zhong, L., Sun, R., & Jiang, D. (2013). Rapid synthesis of cellulose esters by transesterification of cellulose with vinyl esters under the catalysis of NaOH or KOH in DMSO. *Journal of Agricultural and Food Chemistry*, *61*, 2489–2495.

Crépy, L., Miri, V., Joly, N., Martin, P., & Lefebvre, J.-M. (2011). Effect of side chain length on structure and thermomechanical properties of fully substituted cellulose fatty esters. *Carbohydrate Polymers*, *83*, 1812–1820.

Fleche, G., Gosset, S., & Videau, D., inventors; Roquette Freres, assignee. Thermoformable composition, process for its preparation and its use for obtaining thermoformed articles. EP 579546. Jan 19, 1994.

Gros, A. T., & Feuge, R. O. (1962). Properties of fatty acid esters of amylose. *Journal of the American Oil Chemists Society*, *39*, 19–24.

Grote, C., & Heinze, T. (2005). Starch derivatives of high degree of functionalization 11: Studies on alternative acylation of starch with long-chain fatty acids homogeneously in N,N-dimethyl acetamide/LiCl. *Cellulose*, *12*, 435–444.

Gust, S. (2011). *Synthese und Eigenschaften von Stärkeester*. Merseburg (Master thesis).

Jacobson, S., Fritz, H. G., Degée, P., Dubois, P., & Jérôme, R. (1999). Polylactive (PLA) – A new way of production. *Polymer Engineering & Science*, *7*, 1311–1319.

Jebrane, M., & Sèbe, G. (2008). A new process for the esterification of wood by reaction with vinyl esters. *Carbohydrate Polymers*, *72*, 657–663.

Junistia, L., Sugih, A. K., Manurung, R., Piccioni, F., Janssen, L. P. B. M., & Heeres, H. J. (2009). Experimental and modeling studies on the synthesis and properties of higher fatty esters of corn starch. *Starch/Stärke*, *60*, 667–675.

Karrer, P., & Zega, Z. (1923). Zur Kenntnis der Fettsäure-ester von polymeren Kohlenhydraten. *Helvetica Chimnica Acta*, *6*, 822–826.

Lang, J. (2000). Untersuchungen zu Synthese, Charakterisierung und Applikation von hochsubstituierten Stärkefettsäureester. *Dissertation*.

Liebert, T., Nagel, M. C. V., Jordan, T., Heft, A., Grünler, B., & Heinze, T. (2011). Pure, transparent-melting starch esters: Synthesis and characterization. *Macromolecular Rapid Communications*, *32*, 1312–1318.

Malm, C., Mench, J., Kendall, D., & Hiatt, G. (1951). Aliphatic esters of cellulose – Properties. *Industrial and Engineering Chemistry*, *43*, 688–691.

Mitrus, M. (2009). TPS and its nature. In L. Janssen, & L. Moscicki (Eds.), *Thermoplastic starch* (pp. 77–102). Weinheim: Wiley-VCH.

Rogers, S., & Mandelkern, L. (1957). Glass formation in polymers. I. The glass transitions of the poly-(*n*-alkyl methacrylates). *The Journal of Physical Chemistry*, *61*, 985–991.

Sager, A. D., & Merrill, E. W. (1995). Properties of fatty-acid esters of starch. *Journal of Applied Polymer Science*, *58*, 1647–1656.

Scholz, J. J., Roger Ray, B., & Anderson, J. R. (1958). Wetting of polymer surfaces. II. Contact angles of liquids on esters and ethers of amylose and amylopectin. *The Journal of Physical Chemistry*, *62*, 1227–1230.

Sealy, J. E., Samaranayake, G., Todd, J. G., & Glasser, W. G. (1996). Novel cellulose derivatives. IV. Preparation and thermal analysis of waxy esters of cellulose. *Journal of Polymer Science Part B: Polymer Physics*, *34*, 1613–1620.

Shogren, R. L., Biswas, A., & Willett, J. L. (2010). Preparation and physical properties of maltodextrin stearates of low to high degree of substitution. *Starch/Stärke*, *62*, 333–340.

Sreekumar, P. A., Leblanc, N., & Saiter, J. M. (2013). Effect of glycerol on the properties of 100% biodegradable thermoplastic based on wheat flour. *Journal of Polymers and the Environment*, *21*, 388–394.

Vaga-Garcia, C., Gozzelino, G., Glasser, W. G., & Borredon, M. E. (2003). Dynamic mechanical thermal analysis transitions of partially and fully substituted cellulose fatty esters. *Journal of Applied Polymer Science: Part B: Polymer Physics*, *41*, 281–288.

Whistler, R. L., & Hilbert, G. E. (1944). Mechanical properties of films from amylose, amylopectin, and whole starch triacetates. *Industrial and Engineering Chemistry*, *36*, 796–798.

Winkler, H., Vorwerg, W., & Wetzel, H. (2013). Synthesis and properties of fatty acid starch esters. *Carbohydrate Polymers*, http://dx.doi.org/10.1016/j.carbpol.2013.05.086

Wolff, I. A., Olds, D. W., & Hilbert, G. E. (1951). Triesters of corn starch, amylose and amylopectin. *Industrial and Engineering Chemistry*, *43*, 911–914.

Xie, W., Shao, L., & Liu, Y. (2009). Synthesis of starch esters in ionic liquids. *Journal of Applied Polymer Science*, *116*, 218–224.

Xie, W., & Wang, Y. (2011). Synthesis of high fatty acid starch esters 1-butyl-3-methylimidazoliumchlorid as reaction medium. *Starch/Stärke*, *63*, 190–197.

Zhang, X., Golding, J., & Burgar, I. (2002). Thermal decomposition chemistry of starch studied by ^{13}C high-resolution solid-state NMR spectroscopy. *Polymer*, *43*, 5791–5796.