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A comparison of different synthesis routes for starch acetates and the resulting mechanical properties

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ABSTRACT

Starch acetate based on a sustainable native polymer can be used as a thermoplastic substance to produce e.g. commodity material. This work investigates the influence of the synthesis routes and starch species on the mechanical properties of starch acetate with 20 w% triacetin as a plasticizer after thermoplastic processing. For better comparison, acetic acid anhydride was used both as a reactant and a solvent for all reactions. Three activators, acetic acid, aqueous sodium hydroxide and potassium carbonate, were applied in order to compare the esterification of the polysaccharide. The activators strongly determine parameters like reaction time and molecular degradation of the starch backbone. The modification of starch into starch acetate in acetic acid anhydride with potassium carbonate as an activator was analyzed in detail. To reach highly substituted starch acetates ($DS_{Acetate} > 2$), the addition time of potassium carbonate, as well as the penetration of the acetic acid anhydride into the starch granule was of great importance. The analytical methods of titration, SEC-MALLS, ^{13}C NMR, X-ray and FT-Raman spectroscopy were applied and the mechanical parameters of tensile strength, elastic modulus and elongation at break were determined in the resulting specimens. A strong correlation between the mechanical data and the synthesis route was found.

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1. Introduction

Starch is one of the most abundant natural polymers. It is composed of the linear amylose and highly branched amylopectin. In the last 15 years, many papers have been published describing the modification of starch to turn it into a thermoplastic material. Starch itself can be plasticized with different low molecular weight organic compounds (Borchers, Dake, Dinkelaker, Sachetto, & Zdrahala, 1993) to produce, for example films (Thunwall, Kuthanova, Boldizar, & Rigdahl, 2008; Walenta, Fink, Weigel, Ganster, & Schaaf, 2001), foams or plastic parts (Qiao, Jiang, & Sun, 2005). The advantage of using native starch to produce thermoplastic material is, of course, that it biodegrades better and is lower in cost. But compared to synthetic polymers, starch often exhibits poor mechanical properties. The main reasons for this are its hydrophilic nature and therefore its relatively huge water uptake, as well as the brittleness (Shogren, 1992) of the resulting material. Chemical modifications are necessary to significantly improve the mechanical properties. Acetylation of starch results in good thermoplastic processing, enhanced mechanical properties (Gonzalez & Perez, 2002; Xu & Hanna, 2005) and increased hydrophobicity. Esterification reactions of starch are very well documented. The first starch acetates were already described in literature in 1865 (Schuetzenberger, 1865). Around the middle of the last century, a lot of work in this field was done by various groups in the US (Mullen & Pascu, 1942; Whistler & Hilbert, 1944). An important step and also a common synthesis of starch acetates were mentioned by Mark and Mehltretter (1972). They described using acetic acid anhydride as a reactive solvent and induced the acetylation of untreated starch using an aqueous sodium hydroxide solution. This meant that over the years, the reaction time could be decreased more and more. Biswas et al. (2008) describe the acetylation of starch in 2 min in a microwave using iodine as a catalyst. But in order to use starch acetate on an industrial scale, synthesis has to be kept as simple as possible. This requires low reactant excess, a short reaction time, moderate reaction temperature as well as an economical working up. The simplest way would be to esterify starch using acetic anhydride. But even the reaction of starch with acetic anhydride for 15 h at 140 °C only results in starch acetate with low substitution and an acetyl content of 8.7% (Seiberlich, 1941). An activator is imperative in order to achieve highly substituted starch acetates that are necessary for good mechanical properties. This current paper compares the chemical and mechanical properties of starch acetates depending on the synthesis route. Therefore an acetylation method of starch induced with acetic acid (Kakuschke, Rapthel, Stoye, & Schmoz, 1998) and one with potassium carbonate are compared with the procedure carried out by Mark and Mehltretter.

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2. Experimental

2.1. Materials

Acetic acid, acetic acid anhydride, sodium hydroxide, and potassium carbonate with an analytical grade of ⩾96 percent (Riedel de Haën) were used. 1,2,3-triacetoxypropane (triacetin or glycerin triacetate), supplied by Sigma Aldrich, was used as the plasticizer. Dellite® LVF (unmodified nano clay), with cation exchange capacity (CEC) =105 mequi/100 g, was supplied by LAVIOSA, S.p.A Co., Italy.

High amylose maize starch (HAMS, content of amylose: 51 percent; M_w: 6.2×10^6 g/mol), maize starch (MS, content of amylose: 19 percent; M_w: 31.1×10^6 g/mol), and waxy maize starch (WMS, content of amylose: <5 percent; M_w: 46.1×10^6 g/mol) were obtained from Cargill, while potato starch (PS, content of amylose: 22 percent; M_w: 28.3×10^6 g/mol) was purchased from Emsland Stärke.

2.2. Preparing starch acetate using different methods

For comparison, starch acetates were synthesized by the methods described by Mark and Mehltretter (M&M), Kakuschke and Rapthel (K&R) and additionally, a method of acetylation of starch induced with potassium carbonate. The latter was already mentioned by Reinisch, Radics, and Roatsch (1995) but could not be repeated with larger amounts of starch, so that a modification of this synthesis was necessary. The following methods were used for the esterification of all mentioned starch species.

2.2.1. Representative esterification starch using the method of M&M

Here, acetic acid anhydride was used as a reactive solvent. For example, 130 g (0.71 mol; water content 11%) of starch were put into a glass reactor with a mechanical stirrer and a reflux condenser, followed by 437.2 g (4.3 mol; 6 moleq/AGU) of acetic acid anhydride. 22.4 g of 50 w% aqueous sodium hydroxide solution (0.28 mol; 0.4 moleq/AGU) was added drop by drop. The temperature of the oil bath was set to 115 °C for 5 h before the brownish, transparent and viscous mixture was precipitated and washed several times with distilled water. The esterified starch was dried at ambient temperature.

$DS_{Acetate}$: 2.71 (titration).

Yield: 87%.

2.2.2. Representative synthesis of starch acetate using the K&R method

Ninety-one grams of starch (0.5 mol; water content of 11%) were put, along with 360 ml of acetic acid (6 mol; 12 moleq/AGU) and 78 g of acetic acid anhydride (0.75 mol; 1.5 moleq/AGU), into a reactor with a reflux condenser and a mechanical stirrer. The mixture was stirred at a temperature of the oil bath of 115 °C for 8 h before adding 230 g (2.25 mol; 4.5 moleq/AGU) of acetic acid anhydride. Then the mixture was stirred for another 16 h before being cooled down to room temperature. The homogeneous, brownish, slightly viscous and transparent solution was cast into distilled water to precipitate the product using an ultra turrax. The working up was done as mentioned before.

$DS_{Acetate}$: 2.50 (titration).

Yield: 91%.

2.2.3. Representative synthesis of starch acetate with potassium carbonate

A kneader was used as a reactor for the starch acetate synthesis with potassium carbonate. Thus, 306 g of acetic acid anhydride (3.0 mol; 6 moleq/AGU) were placed together with 91.1 g of waxy maize starch (0.5 mol; water content 11%). The temperature of the thermostat was set to 95 °C for up to 0.75 h. Afterwards, 34.5 g of potassium carbonate (0.25 mol; 0.5 moleq/AGU) were added portion by portion within 5 min. The kneader was closed and the thermostat temperature was heated up to 115 °C for 1 h before cooling to room temperature and to precipitate starch acetate by adding distilled water to the kneader. The working up was done as mentioned above.

$DS_{Acetate}$: 2.90 (titration).

Yield: 89%.

2.3. Measurements

2.3.1. Determining the average degree of substitution

^{13}C NMR, titration and FT-Raman spectroscopy were applied to determine the $DS_{Acetate}$. If not specified further, the DS was determined through titration.

2.3.1.1. Titration. For the starch acetates, the acetyl content was determined using the method of Klemm, Philipp, Heinze, Heinze, and Wagenknecht (1998). Esterified starch (150 mg dry sample) was allowed to swell by placing it in 10 ml of an acetone–water mixture (1:1 by volume) for 24 h at room temperature. Five milliliters of a 1 M ethanolic potassium hydroxide solution were added to the suspension to start the complete deacetylation for 24 h at ambient temperature. The same procedure was done for 2 blank values without starch ester. Excess potassium hydroxide was titrated with 0.5 aqueous hydrochloric acid back to a pH of 7.0. The consumption of hydrochloric acid was ascertained and the DS was calculated as follows:

$$\%\mathrm{Sub} = \frac{(BV - V_{HCl}) \times M_{Sub} \times c_{HCl} \times 100\%}{E} \quad (1)$$

$$\mathrm{DS} = \frac{162 \times \%\mathrm{Sub}}{M_{Sub} \times -(M_{Sub} - 1) \times \%\mathrm{Sub}} \quad (2)$$

BV, blank value [ml] (consumption of HCl for blank values, average value),
V_{HCl}, volume of hydrochloric acid [ml],
E, weight of esterified starch [mg],
c_{HCl}, molarity of hydrochloric acid [mol/l],
M_{Sub}, molar mass of substituent [g/mol] (acetat: 43 g/mol).

2.3.1.2. ^{13}C NMR spectroscopy. ^{13}C NMR spectra were measured using a Varian Unity Inova 500 spectrometer. The esterified polysaccharides were measured after dissolution in d_6-DMSO (125 MHz; 80 °C). The chemical shift was related to the signal of d_6-DMSO (δ = 39.5 ppm relative to TMS δ = 0 ppm). All signals in the region of δ = 102–94 ppm were caused by $C1_{AGU}$ carbons and were therefore normalized to 1. The total DS was then obtained from the integrals of the methyl group signals ($\delta \sim 20$ ppm) of the acetate function.

2.3.1.3. Raman spectroscopy. Raman spectra were recorded on a BRUKER RFS 100/S from the pure product with 128 scans at a laser power of 300 mW and in the range of wavelength between 3500 and 50 cm^{-1}.

2.3.2. Determining molecular weight distribution

Molecular weight averages were determined using SEC-MALLS. The SEC-MALLS system consisted of a 515 pump, DRI detector (2414 der Fa. Waters), MALLS detector (Dawn HELEOS, Wyatt Technologie Inc.) and columns from SUPREMA. Esterified samples were saponified under mild conditions, so that no degradation of the polymer was observed. The procedure for this was to disperse

starch esters in water and to saponify by adding 1 N NaOH. The mixture was stirred for 24 h at room temperature before it was neutralized with 1 N HCl. The deacetylated starch was then precipitated with 60 w% aqueous methanol. After centrifugation, the starch was washed several times with 60 w% aqueous methanol and dried under reduced pressure. 0.5 w% of this starch was dissolved in DMSO to analyze the molecular weight average via SEC-MALLS.

2.3.3. UV–VIS spectroscopy

The UV–VIS measurements were carried out using a UV–VIS-NIR spectrophotometer (Perkin Elmer Lambda 950) with a slit width of 2 nm. The determined UV–VIS spectra are recorded from the bare thin polymer films. To prepare the film, the synthesized starch acetate powders were dissolved in CH_2Cl_2 in order to obtain solutions with 1 w% polymer content. 2 ml of each solution was cast onto cleaned glass slides (5 × 5 cm), covered with a petri dish and dried for 24 h at room temperature. The films were removed from the glass slides by submerging them into distilled water for 10 min and detaching them with a razor blade. The resulting thickness of the bare polymer films is about 10 μm.

2.3.4. Extrusion and injection die molding of starch acetates

Samples of starch esters were mixed with triacetin and left to set overnight to equilibrate. If 5 w% Dellite LVF as montmorillonite was used to reinforce starch acetate, it was dispersed in the plasticizer and then dispersed in starch acetate through melt intercalation at 180 °C. The samples were then extruded on a twin-screw extruder (MiniLab Haake) at a temperature between 160 and 170 °C and at screw speed of 250 rpm before injection die molding (Minijet Haake) into specimens at 230 °C.

2.3.5. Mechanical testing of the specimens

The mechanical testing (Zwick Z020) was performed on a series of 6 pieces according to ISO 527, type 5 A after storing the specimens in standard atmosphere (23 °C; 50% relative humidity) for 24 h.

3. Results and discussion

3.1. Synthesis of starch acetates and the results of three different synthesis routes

Under the reaction conditions given in Table 1, starch acetates of maize starch with different amylose content were prepared using the K&R procedure.

Firstly, it can be said that highly substituted starch acetates can always be achieved no matter what the amylose content is of the starch used. Chen, Schols, and Voragen (2004) and Huang, Schols, Klaver, Jin, and Voragen (2007) reported that the acetic acid anhydride penetrated better into the crystalline regions of amylopectin in the starch granules than in the amorphous ones with amylose when esterifying with small amounts of acetic acid anhydride. This may result in the highest DS value for waxy maize starch when compared with the other starch species. But it should be recognized that with the progression of acetylation to higher DS values, the structure of the starch granule is destroyed and the native A-type crystalline structure of the starch is lost after acetylation (Shogren, 1996). Evidently this influences the molecular degradation as well. The molecular weight average indicates a high degradation of the starch backbone up to the factor of ~100, especially when waxy maize starch is used as a starting material. For high amylose maize starch, only a factor of ~3 for degradation is noticeable.

Mark and Mehltretter's procedure is a very common synthesis of starch acetates. Compared to the method of Kakuschke et al., starch esters with high DS values can be achieved after 5 h using a highly concentrated aqueous sodium hydroxide solution as an activator. Starch acetates thus obtained exhibit all high DS values and higher molecular weight averages (see Table 2) compared to the synthesis method of K&R.

A not very well described possibility of obtaining starch acetates with high DS values is to use various alkali carbonates. The most important work in this field was carried out by Reinisch et al., who replaced the aqueous sodium hydroxide solution as an activator, known from M&M, with different organic bases and with different alkali carbonates. Particularly the use of potassium carbonate results in highly substituted starch acetates within 2 h and thus 2.5 times faster than the M&M procedure. For better comparison with the first two mentioned methods, the applied temperature was decreased to 115 °C instead of 150 °C, as was written in the paper by Reinisch. This caused several problems, so that only the idea of using potassium carbonate as an activator could be retained but the synthesis steps had to be changed completely. The most important change is to let acetic acid anhydride penetrate the air dried starch granules for 0.75 h at 95 °C in the reactor before adding potassium carbonate. After adding the potassium carbonate it takes just 1 h to get highly substituted starch acetates.

Another advantage of using potassium carbonate as an activator is the much better water solubility of potassium acetate as a byproduct instead of sodium acetate as in the M&M procedure. Hence the working up can be done more economically. Table 3 describes the influence of the molar ratio of acetic acid anhydride to AGE (consistency) as well as potassium carbonate to AGE.

The progress for the degree of substitution and the reaction temperature in relation to the reaction time were recorded for the synthesis of **VIII**, **IX**, **X**, and **XI** (Fig. 1).

Table 1
Preparation of starch acetates using the K&R procedure.

Sample	Starch	moleq Ac_2O per AGU	moleq AcOH per AGU	t [h]	$DS_{Acetate}$	$M_w \times 10^6$ [g/mol]
I	WMS	6	12	24	2.91	0.42
II	MS	6	12	24	2.50	2.61
III	HAMS	6	12	24	2.73	2.01

Table 2
Preparation of starch acetates using the M&M procedure.

Sample	Starch	moleq Ac_2O per AGU	moleq $NaOH_{aq\ 50\ w\%}$ per AGU	t [h]	$DS_{Acetate}$	$M_w \times 10^6$ [g/mol]
IV	WMS	6	0.46	5	2.89	28.77
V	HAMS	6	0.46	5	2.72	2.69
VI	PS	6	0.46	5	2.63	16.28

Table 3
Preparation of starch acetates with potassium carbonate as activator.

Sample	Starch	moleq Ac_2O per AGU	moleq K_2CO_3 per AGU	t [h]	$DS_{Acetate}$	$M_w \times 10^6$ [g/mol]
VII	HAMS	6	0.5	1[#]	0.54	2.74
VIII	HAMS	6	0.5	1.75	2.74	1.65
IX	HAMS	4.5	0.5	1.75	2.70	2.13
X	HAMS	4	0.5	1.75	2.20	1.81
XI	HAMS	4	0.25	1.75	2.63	1.95
XII	HAMS	6	0.25	1.75	1.14	2.04
XIII	PS	4.5	0.25	1.75	2.17	12.43
XIV	WMS	6	0.5	1.75	2.87	18.76

[#] All reactants were added to the reactor from beginning, without premixing.

Fig. 1 demonstrates the premixing effect of starch granules with acetic acid anhydride up to 0.75 h at 95 °C.

During the premixing step the temperature of the reaction mixture exceeds the temperature given by the thermostat. This exothermic behavior is caused by the dewatering of the starch with acetic acid anhydride, resulting in acetic acid, which is important for the reaction. The same synthesis of **VIII** with dried starch, for example, only resulted in starch acetate with low substitution (**XVIII**, see Table 7) even after 5 h of reaction time. Up until this point of the reaction, no acetylation could be detected by titrimetrically determining the degree of substitution. This was true for all four samples discussed. When potassium carbonate is added to the slurry, the reaction temperature immediately increases, caused by acid–base reaction between the acetic acid and the potassium carbonate. Accordingly, the reaction mixture temperature is raised by heating the thermostat. The reaction temperature rises further depending on the molar ratio of the acetic acid anhydride and the potassium carbonate to the anhydro glucose unit. For low ratio of acetic acid anhydride to starch (**IX** and **X**) the temperature of the reaction mixture already reaches its maximum of ~150 °C after ~10 min after the addition of potassium carbonate. For higher ratio of acetic acid anhydride to starch and lower potassium carbonate concentration, the maximum of the reaction temperature occurs later and lower but more expandedly (**VIII**).

Taking both the characteristics of reaction mixture temperature and DS value into consideration, it can be seen that when the maximum reaction temperature is reached, the DS is always around 2.0. At this time the reaction mixture becomes homogeneous and transparent and the viscosity increases immediately. This indicates a very homogeneous distribution of the acetic acid anhydride within the starch granule before potassium carbonate is added. The temperature curves of **IX** and **X** are nearly the same but result in different DS values. A detailed observation of the reactions, which occurs until the esterification happens, shows that there is a major difference in the remaining acetic acid anhydride that can esterify the starch and limit the resulting DS value.

In the premixing phase, acetic acid anhydride reacts with the water from the air dried starch resulting in additional acetic acid. This reacts with potassium carbonate and is added to the slurry after 0.75 h at 95 °C (Fig. 2). This produces potassium acetate and water. The water can react with acetic acid anhydride to form acetic acid while increasing the reaction temperature. These reactions

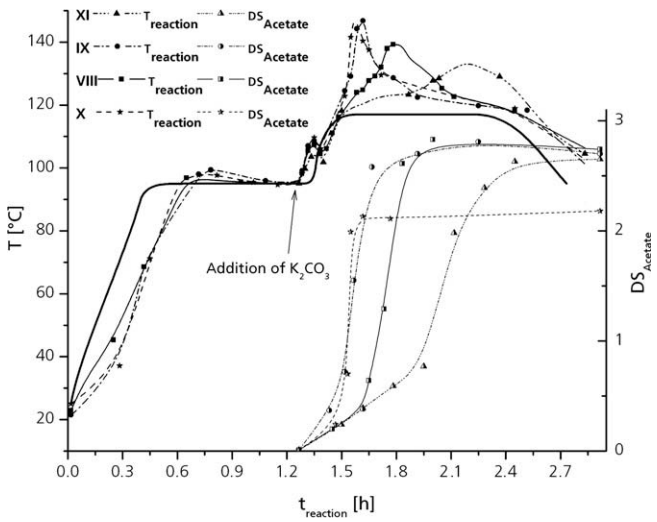

Fig. 1. Temperature and DS development behavior curves in relation to reaction time as a function of molar ratio of acetic acid anhydride and potassium carbonate per AGU for **VIII**, **IX**, **X** and **XI**; bold line is the thermostat temperature.

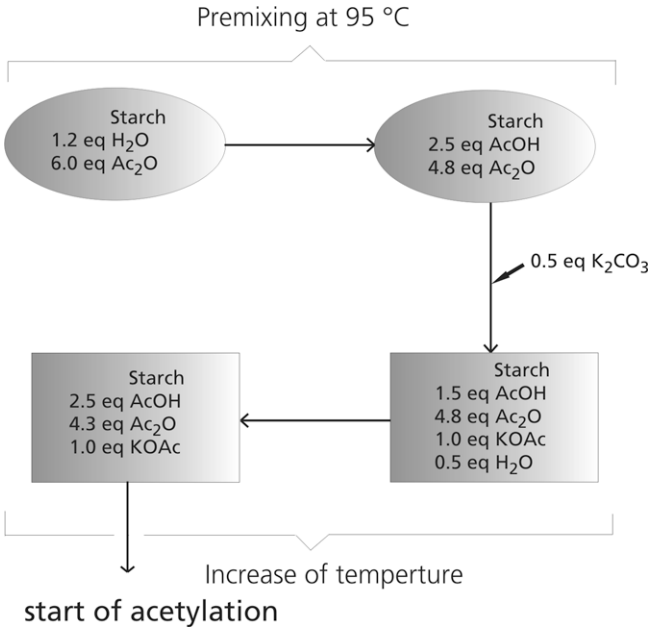

Fig. 2. Reactions before the start of acetylation when using 6 moleq of Ac_2O and 0.5 moleq of K_2CO_3 per AGU.

limit the amount of acetic acid anhydride for the esterification of starch. It limits the degree of substitution depending on the molar ratio used (Table 4).

The degree of substitution is limited because with **X** there are only 2.3 moleq of acetic acid anhydride per AGU left for esterification instead of 2.8 moleq acetic acid anhydride for **IX**. These calculations also explain the later and lower temperature maximum as well as the higher degree of substitution of **XI** compared to **X**. Using less potassium carbonate means there is more acetic acid anhydride left to esterify the starch. The kinetic of the reaction is, of course, also influenced by the molar ratios.

3.2. Influence of the reaction conditions on molecular weight average depending on the synthesis method

As seen before, the molecular weight average of the starch acetates is strongly dependent on the synthesis route. Using waxy maize starch as a starting material demonstrates this very well. The two starch acetates from WMS produced with alkaline activators (**IV**: 28.8×10^6 g/mol and **XIV**: 18.8×10^6 g/mol) exhibit much higher molecular weight averages than the one synthesized with acetic acid as an activator (**I**: 0.4×10^6 g/mol). As mentioned before, the strong degradation is caused by the use of an acid as well as the long reaction time. The highest molecular weight average for starch acetate from WMS was achieved using the M&M method. The same result can be seen when using HAMS; compare **III** (2.0×10^6 g/mol), **V** (2.7×10^6 g/mol) and **VIII** (1.7×10^6 g/mol). For both starch types, it seems that the M&M method results in the highest molar mass average. There may be two reasons for this. The first one is the use of sodium hydroxide, which is more alkaline

Table 4
Molar ratio of molequivalents of reactants per AGU after adding the potassium carbonate in the reaction medium.

Reactant	VIII	IX	X	XI
Ac_2O	4.3	2.8	2.3	2.6
AcOH	2.5	2.5	2.5	2.5
KOAc	1.0	1.0	1.0	0.5

than potassium carbonate. The second one is the use of different reactors, which has to be considered. The M&M procedure was performed in a glass reactor with a mechanical stirrer instead of a kneader using K_2CO_3 as an activator. This creates much more shear stress on the starch chains. For a detailed analysis the synthesis procedure for **VIII** to produce high amylose maize starch acetate was repeated by using a glass reactor (**XVI**) and a kneader (**XV**). In contrast to the synthesis of **VIII,** the premixing time was 1 h.

Both reactions lead to nearly completely substituted starch acetates. When a kneader is used, the molecular weight average is nearly half of that of when a glass reactor is used. This demonstrates that the lowest degradation of the starch backbone is achieved by using potassium carbonate as an activator, when the same reactor type (glass reactor) is used. This also shows the major influence of the reaction time on the molar mass average. High molar degradation can be prevented when shorter reaction times are used. The biggest impact this has on the mechanical properties is with elongation at break. Apparently a more degraded starch backbone causes better elongation behavior (Table 5).

Not only does the synthesis decrease the molar mass average, the thermoplastic processing is also responsible for degradation. It is known that high temperatures and shear forces cause degradation of biopolymers during extrusion and injection molding. To analyze this for a starch acetate rather than for a starch backbone, the material was measured using SEC-MALLS after each processing step, beginning with the synthesis and ending with the resulting specimen. The resulting molecular weight average curves can be seen in Fig. 3. The result is a degradation of the starch backbone of ~50% from the synthesized product to the specimen. Here, the extrusion has the biggest influence on the degradation of the starch backbone. The subsequent injection molding into a specimen does not really influence the molar mass average. This has to be considered by discussing molecular weight averages of starch esters after thermoplastic processing.

Table 5
Comparison of the influence on the molecular weight average depending on the type of reactor and resulting thermoplastic properties with HAMS as a starting material with 20 w% triacetin.

Sample	DS_{Acetat}	$M_w \times 10^6$ [g/mol]	Strength [MPa]	*E*-modulus [GPa]	ε [%]
XIX (glass reactor)	2.88	4.1	17.3 ± 1.2	1.74 ± 0.03	1.07 ± 0.4
XV (kneader)	2.97	2.1	15.6 ± 0.9	1.12 ± 0.05	3.98 ± 0.6

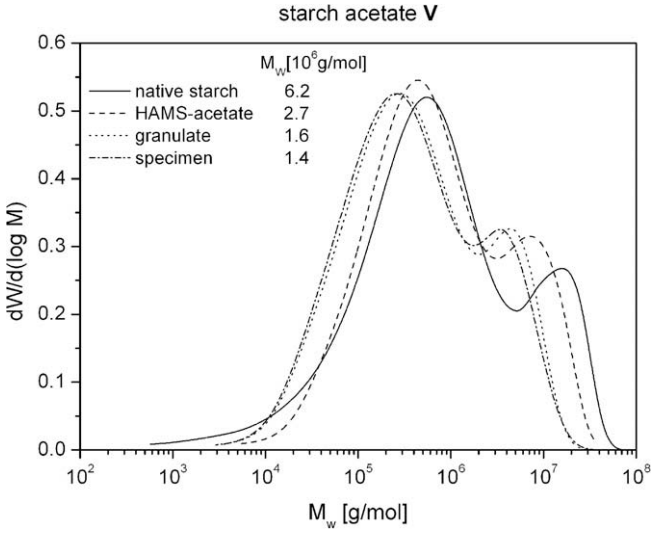

Fig. 3. SEC curves for molecular weight average of starch backbone from starch acetate **V** for each processing step during thermoplastic processing.

3.3. Mechanical properties

Starch acetates achieved using the K&R method clearly reveal, as is known from literature, that using HAMS as a starting material for acetylation results in the best mechanical properties compared to WMS and MS. No specimen for **I** could be produced due to the high brittleness of the material. Acetate from maize starch (**II**) produced a specimen with a tensile strength of 10 MPa, *E*-modulus of 0.8 GPa and elongation at break of 1.3%.

Only high amylose maize starch was used to compare the three methods mentioned based on the knowledge obtained from literature and the experiments with starch acetates which were produced using the K&R method. The highest values for all measured mechanical properties can be found for starch acetate (**V**) produced by the M&M method (Fig. 4). The tensile strength increases to 30 MPa instead of around 20 MPa for the other two starch acetates (**VI** and **XI**). Equally, the behavior for elastic modulus shows the highest value for **V**.

When the values for the degree of acetylation, as well as the molecular weight average of the synthesized starch acetates are considered, it seems that a higher molecular weight average is advantageous in terms of tensile strength and elastic modulus in the resulting plasticized material. It should be taken into consideration that further degradation happens during thermoplastic processing.

Examples of the application of layered silicates to improve the mechanical properties are described in literature (Dean, Yu, & Ma, 2007). An experiment to enhance the mechanical properties of starch acetate with 5 w% Dellite LVF (**XI**) was accomplished. After storage, the thermoplastic processing was carried out and resulted in a composite material which has nearly the same mechanical properties as starch acetate **V**. This demonstrates an easy way to reach good mechanical properties in starch acetates by an even faster synthesis route.

3.3.1. Potato starch as a starting material

Potato starch was one of several tested starches, in addition to the maize starches, which exhibits interesting properties compared to high amylose maize starch. Despite the relatively low content of amylose (22%), it is possible to nearly achieve the same mechanical properties like with HAMS acetate (**III** and **XI**) through alkaline induced acetylation (Table 6).

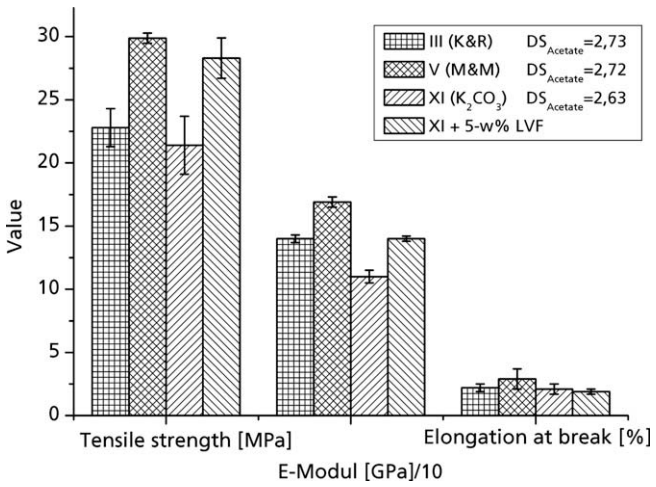

Fig. 4. Mechanical properties of acetates from HAMS depending on the synthesis route after processing with 20 w% triacetin.

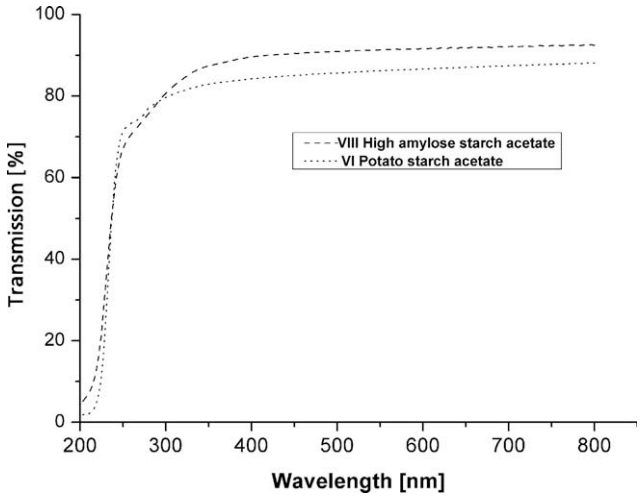

Fig. 5. Transmission measurement for casted films of a thickness of 10 μm from mentioned starch acetates.

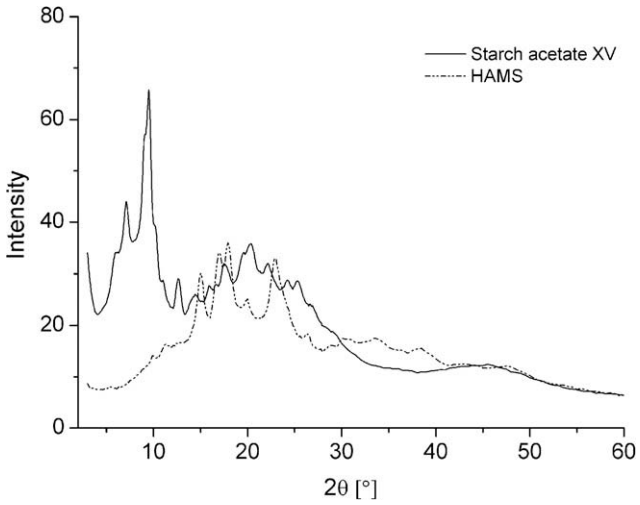

Fig. 6. Comparison for WAXS measurements of High amylose starch and nearly full substituted starch acetate **XV**.

Table 6
Mechanical properties of the described potato starch acetates with 20 w% triacetin.

	Tensile strength [MPa]	*E*-modulus [GPa]	Elongation at break [%]
VI	19.8 ± 1.5	1.52 ± 0.02	1.6 ± 0.3
VIII	20.2 ± 1.3	1.70 ± 0.04	1.3 ± 0.1

If the potato starch was acetylated under acidic conditions, the resulting mechanical properties were poor due to the much higher degradation. Amylose in potato starch exhibits a higher degree of polymerization compared to maize based starches (Avgenaki, 2002). This may equalize the lower content of amylose in potato starch compared to high amylose maize starch in terms of the mechanical properties. Furthermore, it was very surprising to compare the color of the specimens from maize starch based acetates and the acetate from potato starch. While the color is always brownish in the former, specimens made from potato starch acetate with the same amount of plasticizer are nearly colorless and transparent. The lower protein content in potato starch, indicated by the nitrogen content (0.018% for potato starch, 0.096% for high amylose maize starch), causes a minor maillard reaction during thermoplastic processing and with it, less discoloration (Fig. 5).

The UV–VIS measurement shown in Fig. 5 demonstrates that high transparent films from starch acetates are even possible from potato starch acetate.

3.4. Investigations on crystallinity of starch acetates

Comparison of the tensile strength of the starch acetates in Fig. 4 with the ones from Table 5 shows major differences. A specimen of fully substituted starch acetate resulted in lower mechanical properties than starch acetate with remaining hydroxyl groups. This behavior is known from cellulose acetate. Cellulosetriacetate (CTA) exhibits lower mechanical properties than cellulose-2,5-acetate (CA). In contrast to CA, CTA is not amorphous and shows a diffraction peak of (1 1 0) plane, corresponding to a crystallinity of 25–30% (Sata, Murayama, & Shimamoto, 2004). This crystallinity influences the mechanical properties significantly. For this we performed investigations on the crystallinity of starch acetate **XV**. So far, crystallinity of starch acetates could only be observed for amylose triacetate (ATA, Takahashi & Nishikawa, 2003; Wolff & Olds, 1951). Wolff et al. recognized crystallinity after heating ATA for 15 min at 185 °C, which also increased the solubility in chloroform. WAXS measurements were performed (Fig. 6) in order to analyze this more in detail.

The typical pattern of a native A-type starch was found for the high amylose maize starch (Buléon, Colonna, Planchot, & Ball, 1998). The main difference to that of a fully acetylated starch acetate can be seen in the new reflexes in the range of $2\theta = 5–13°$. From this it can be assumed that the signals in Fig. 6 occur from fully acetylated amylose and not amylopectin. Flat film photographs measurements proof, that starch acetates discussed in Fig. 4 (III, V, IX) owns no crystallinity at all. This explains the lower mechanical properties of a starch-3-acetate compared to lower substituted starch acetates.

3.5. Using FT-Raman spectroscopy to determine the average degree of acetylation in starch acetates – multivariate calibration models

Over the past few years FT-Raman spectroscopy has become more and more important in polymer chemistry. It is a fast and non-destructive qualitative and quantitative analytical tool. The Raman peak in a spectrum directly correlates with the amount of substance in the sample (Phillips, Pan, Liu, & Corke, 1998). Phillips et al. described the DS determination using FT-Raman for starch acetates with very low substitution (up to 4% of acetylation) by integrating the signal of C═O stretch at 1732 cm^{-1} and the peak of a C–C stretch at 941 cm^{-1} whose intensity does not change during acetylation. They plotted the ratio of the 1732 cm^{-1} peak and 941 cm^{-1} peak versus the DS of acetylation determined titrimetrically ($R^2 = 0.996$). Fischer, Schenzel, Fischer, and Diepenbrock (2005) described the determination of the DS value for highly substituted cellulose acetates ($DS_{Acetate}$ 1.25–2.90) by applying the PLS algorithm of the BRUKER software OPUS/QUANT 2 to the FT-Raman spectral data of the calibration samples. Thus it was possible to get a highly accurate calibration model ($R^2 = 0.959$). This method was also used to develop a calibration model to determine the DS value of high amylose maize starch acetates in the DS range 0.1–3.0.

For 23 samples of variously substituted starch acetates in the DS range mentioned, the acetyl content was determined using the Klemm et al. method and all were measured using FT-Raman spectroscopy. The best congruence between determined and calculated DS values was found by calculating the first derivatives together with multiplicative scatter correction (MSC). After final cross validation, a highly accurate calibration model ($R^2 = 0.988$) and also

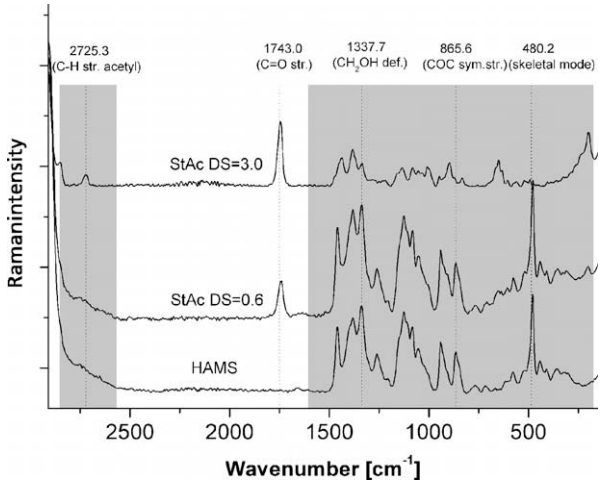

Fig. 7. Exemplary Raman spectra of starch acetates from high amylose maize starch with different DS values.

Table 7
$DS_{Acetate}$ of different substituted starch acetates determined by FT-Raman spectroscopy and ^{13}C NMR.

Sample	$DS_{Acetate\text{-}Raman}$	$DS_{Acetate\text{-}13C\ NMR}$
XV	3.00	2.97
X	2.24	2.20
XII	1.27	1.19
XVIII	0.62	0.78

with low Root Mean Square Error of Cross Validation (RMSECV = 0.092) was the result.

Interestingly, the wavenumber ranges used for this calibration are 2869–2566 cm^{-1} (C–H stretch caused by methyl group of acetyl substituent) and 1666–200 cm^{-1} without the characteristic C=O stretch (Fig. 7). In the latter range, several bands of the anhydro glucose unit can be found (Cael, Koenig, & Blackwell, 1975; Fechner, Wartewig, Kleinebudde, & Neubert, 2005), which are influenced by the derivatization process. Therefore the band of deformation vibration of C6–OH at 1337 cm^{-1} from AGU decreases with an increasing DS value. This behavior is even stronger for the band at 480 cm^{-1}, however there is a high consistency between the DS values of samples which are not used for the calibration determined by ^{13}C NMR and with FT-Raman spectroscopy (Table 7).

4. Conclusion

A strong correlation between the mechanical properties of starch acetates and the synthesis route was evident. Starch acetates from high amylose maize starch synthesized under the conditions of Mark and Mehltretter have the highest mechanical properties compared to the other two discussed synthesis routes. Mechanical properties of starch acetate prepared using potassium carbonate as an activator, can easily be enhanced through melt intercalation by using a layered silicate. Under certain synthesis conditions (alkaline), potato starch acetate demonstrates similar mechanical properties as are found in high amylose maize starch acetates produced with acetic acid as an activator despite the much lower amylose content. Furthermore, a fast method for determining the degree of substitution for starch acetates using FT-Raman spectroscopy was developed.

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