Potato starch stabilized synthetic latexes
Terpstra, Karsjen

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2015

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
CHAPTER 5

Extruded octenyl succinylated starch stabilized polyvinyl acetate latexes: A comparison between regular and waxy potato starch
Abstract
Hydrophobic starches are suitable to replace synthetic protective colloids in free radical polymerizations. Octenyl succinylated waxy potato starch exhibits distinct reversible thixotropic behaviour after dissolution in water and this makes it an interesting protective colloid for polyvinyl acetate based latexes. The effect of degree of substitution (0 to 0.04) on preparation and product characteristics was evaluated for latexes protected with both regular and waxy potato starch. The starch products were extruded before use to introduce a modest degree of degradation and to make them cold-water soluble. The selected polymerization conditions (dry matter = 53 wt %, starch on polyvinyl acetate = 10 wt %, polymerization temperature = 80 °C) allow the use of starch derivatives with a degree of substitution up to 0.02 with respect to coagulation and fouling of the reactor. The substitution degree of potato starch influenced the volume mean diameter (0.6 – 2.9 μm) and the level of polydispersity of the particle size distribution. Latex viscosities in the range of 1 000 – 3 000 mPa·s were achieved with the regular potato starch based products whilst counterparts based on waxy potato starch range from 1 000 to over 10 000 mPa·s. The increased latex viscosity of the latexes stabilized with octenyl succinate waxy potato starch can be tentatively explained by the associative behaviour between waxy potato starch and the octenyl succinate groups.

Introduction
Starch is found in cereal grains (maize, rice, wheat, barley, oat, sorghum), stems (sago palm), legume seeds (beans, peas), roots (sweet potatoes, cassave, arrow roots, yam) and tubers (potatoes). Considerable structural differences are present between the varieties. D-glucose molecules are bound to each other mostly by α-D-(1,4) linkages and with a α-D-(1,6) bond at a branching point. Differences in polymer chain length, number and structure of branches and triple substituted D-glucose units give rise to a large number of polymer configurations. Starch molecules belong to either the subgroup amyllopectin (high degree of polymerization; branched structure) or amylose (lower degree of polymerization; mainly linear chains), with starch granules typically containing 0 to 30% of the latter [1]. The shape and size of the starch granules varies from 1 to 100 μm and their lipid content ranges from 0.1 to 1.2%. Disintegration of starch granules in water requires shear and temperatures in the range of 60 to over 100°C depending on the botanical origin of the starch used. The obtained solution forms a gel upon cooling to room temperature and the degree and speed of this process is strongly correlated with the amylose content and structure. Dissolved amylose chains are present as double helical coils that tend to line up in bundles (retrogradation) and form tightly bound structures, the latter being not easily dissolved in water anymore [1].
The use of amyllopectin (commonly referred to as waxy) starch-based products is recommended in applications were the occurrence of retrogradation after dissolution is undesirable (e.g. wallpaper adhesives). The absence of amylose also improves the dissolution characteristics of the starch granule considerably. Amylose containing granules start to swell after the amylose is leached out and it usually takes some time to completely dissolve the granule remnants. On the contrary, waxy potato (WP) starch based granules immediately transform into a macromolecular dispersion after the gelatinization temperature is reached. The gelation temperature of WP starch is slightly higher than that of regular potato (RP) starch but the disintegration of the swollen granules take place at a lower temperature [2]. This type of starch
Extruded octenyl succinylated starch stabilized polyvinyl acetate latexes

is therefore preferred in those applications in which swollen starch granules, or remnants thereof, are unwanted [3].

A change in the amylose content of a formulation is expected to affect the influence of amphiphilic additives considerably. The interior of the amylose helix coil is slightly hydrophobic and tends to capture linear hydrocarbon chains [4]. Furthermore, the fine-stranded amylose network tends to aggregate into thicker strands when emulsifiers are added [5]. Starches with a low amylose content are therefore usually recommended when a reduction in ingredients of the formulation (e.g. in latexes applicable as adhesives) is desired.

Potato starch has the lowest lipid and protein content and the highest level of bound phosphate groups of the starches available. These properties ensure efficient processing, increase the stability of the formulation obtained and result usually in a final product with the lowest level of reactor fouling during processing. The phosphate groups are, however, mainly present in the amyllopectin fraction and solutions based on RP starch are therefore still prone to considerable retrogradation [1]. Unexpected high levels of viscosity can be achieved if WP starch based products are mixed with molecules containing hydrophobic groups (e.g. fatty acids) and this behaviour is not observed (to the same extent) if other waxy varieties are used [6,7]. This is often explained (on a molecular level) by the association between the amyllopectin side chains and the hydrophobic groups. The corresponding mixtures display reversible thixotropic (shear thinning and formation of reversible gels) behaviour and this is frequently a desired property in those cases in which a fluid material needs to be applied on a surface (e.g. adhesive, coating, cream, etc) [6-8]. This ability of WP starch to associate with hydrophobic groups makes it a less suitable ingredient for formulations in which small size emulsifiers (i.e. detergents) need to be present in the water phase during preparation or application.

Latexes based on octenyl succinic anhydride (OSA) modified starch are already marked as interesting ingredients for making adhesives and paints (Figure 1) [9,10].

Figure 1: The chemical structure of OSA starch.

The combination of the hydrophobic octenyl group and the hydrophilic characteristic of starch confers the OSA starch fragments an amphiphilic nature and renders them “green” alternatives for detergents or emulsifiers. WP starch stabilized latexes are recommended, though a systematic comparison of WP with RP is still lacking in the open literature [11]. This comparative evaluation was the main aim of the present work. Moreover, potato starch with different maximum degrees of substitution (DS max) of OSA (DS max 0.01, 0.02, 0.03 and 0.04) was used and the actual need of derivatization was verified by evaluating the unmodified counterparts. The starches were physically modified by extrusion in order to minimize differences in dissolution characteristics between RP and WP starch [12,13]. The impact of different DS max on the protective colloid characteristics of extruded RP and WP starch was evaluated in a polyvinyl acetate (pVAc) based free radical polymerization (in absence of a detergent, emulsifier and anti-foaming agent) [14,15].
Experimental Materials

Octenyl succinic anhydride (OSA) from Milliken Chemicals was used to synthesize regular potato (RP) and waxy potato (WP) starch (AVEBE U.A.; Food grade) derivatives with a maximum degree of substitution (DS_{max}) of 0.01, 0.02, 0.03 and 0.04 on potato starch in suspension at pH 8.5 [16]. This is the optimal pH for this type of derivatization [17]. However, NaOH can also react directly with OSA or saponify the OSA starch formed [18]. The NaOH consumption during processing was therefore used to get an impression of the efficiency of the esterification. The average efficiency turned out to be 70 % for RP starch and 85 % for WP starch based products. The actual degree of substitution (DS_{act}) is calculated from efficiency and DS_{max}.

The obtained products were extruded (Continua C37; 2 co-rotating axes; 16D with scissor at 10.2; mold: 2 times 3.2 mm; 300 RPM; jacket: 125°C; moisture level 26%; feed: 15 kg/hrs) and subsequently milled (Peppink mill 2.0 mm and 0.5 mm sieve). The vinyl acetate monomer (VAM) was purchased from ACROS and contains 3-30 ppm hydroquinone as inhibitor. Analytical reagent grade sodium persulfate (SPS) was supplied by VWR International. Sodium bicarbonate (SBC) and sodium thiosulfate pentahydrate (STS) were both of analytical quality and obtained from Merck Germany. STS was added as a 0.3 M solution and SPS and SBC were added together as a mixture in water with 3 % SPS and 4 % SBC on weight in total. All ingredients were used without additional purification. The solvent was demineralised water in all cases.

Equipment

A jacketed stainless steel (316) reactor (1 l) equipped with a stainless steel (316) spiral ribbon stirrer (2 cycles with a width of 1 cm and an outer dimension of 10.5 x 7 cm (height x diameter)) was applied. A lid made of borosilicate glass with several connection points was placed on top and the reactor was completely insulated with a radiator foil. A reflux cooler was placed on top together with a pt-100 probe for measuring the headspace temperature (HST). The feeding lines of VAM and the SPS/SBC mixture were placed outside the reflux region with the aid of an accessory to minimize the contamination of VAM with water and premature dissociation of SPS (Figure 2).

Figure 2: Schematic representation of the polymerization reactor used.
VAM was dosed with a peristaltic pump equipped with polytetrafluoroethylene tubing (4 mm) and the volume removed from the storage bottle was replaced by dry nitrogen. The actual VAM dosage was also monitored with a balance. One syringe pump was used to add a premix of SPS and SBC and a second syringe pump was used to add 0.3 M STS after the actual polymerization was finished.

**Procedure**

A 10 wt % starch mixture was prepared by slowly adding the starch derivative to a demi-water containing beaker while thoroughly mixing (3-bladed impeller; 1000 RPM; 10 minutes). The polymerization reactor was filled with 262.5 g of this mixture and automatic mixing (120 RPM) was started. The applied water bath temperature of the reactor (WTR) and dosage protocols of VAM, SPS/SBC and STS are given in Figure 3. Oxygen removal from the reaction mixture as pre-polymerization step was omitted because a pre-dosage of VAM already results in a considerable reduction in amount of dissolved oxygen. The initial reaction mixture temperature (RMT) is around 76°C at the selected reaction conditions. This is even higher than the boiling point of VAM (72 °C) and the added VAM will therefore immediately shift from the liquid to the gas phase. The phase transition will induce a volume expansion of VAM which will lower the oxygen content of the reactor considerably [15]. VAM was used without inhibitor removal in order to ensure close resemblance to experimental conditions applied at industrial level. A total of 0.27 kg VAM was added in all cases with a pre-dosage level of 15 g. The actual dosage was monitored in time and the amount of VAM added was used for mass balance calculations. 1.5 g SPS and 2.0 g SBC were dissolved together in 46.5 g demineralised water and 36 ml of this mixture was added during the polymerization. The actual addition of the mixture starts after 104 minutes with a pre-dosage of 4.5 ml in 1 minute followed by 31.5 ml with a dosage speed of 5.25 ml/hr. 2.7 ml 0.3 M STS ml was added with 2.7 ml/hr after the WTR dropped significantly below 65°C during cooling down. Agitation was continued for at least one hour after the WTR reaches 20°C. The dispersion was transferred into a storage container without any additional treatments and stored at room temperature.

![Figure 3: WTR profile and dosage protocols of SPS/SBC, VAM and STS.](image-url)
**Characterization**

Viscosity, pH and dry matter were determined with the help of a Brookfield DV-II+(20 RPM), WTW pH 320 and Mettler Toledo PM100/LP16 (80°C), respectively. Ethanal and residual VAM were determined with a Perkin Elmer gas chromatograph equipped with a headspace sampling device, a Poraplot Q fused silica column (25 m x 0.32 mm) gas and a flame ionization detector. The gas chromatograph measurement was performed on water diluted dispersions (10 wt%).

About 2 ml of the diluted dispersion was centrifuged at 13 000 relative centrifugal force for 10 min and the supernatant was mixed 1:1 with 5 mM NaOH. This mixture was used to quantify the anion composition with a Dionex DX50 equipped with an ATC-1 ion trap, two Ionpac columns (AS11-2 mm and AG11-2 mm) and an electrochemical detector. The separation of the different anions was achieved with a gradient of sodium hydroxide. Particle size distributions (PSD) were obtained with a Sympatec laser diffraction equipped with a Quixel wet dispenser and a Helos laser diffraction sensor (Range: 0.13 - 32.5 μm). Fraunhofer theory based calculations were used and the obtained particle size distributions are ISO 13320 compliant. Glass transition temperatures (T_g) were derived from total heat flow and reversing heat flow curves determined with a modulated differential scanning calorimeter (mDSC) from TA Instruments (Q1000; 1 °C/min; amplitude: 0.5 °C; period: 60 s; large volume stainless steel pans; 20-50 mg dispersion as is).

**Results**

**Screening**

The procedures described in the experimental section were used to prepare extruded RP and WP starch with different levels of OSA derivatization. The selected DS_{max} were 0.01, 0.02, 0.03 and 0.04. The efficiency of the OSA reaction is ~70 % for RP and ~85 % for WP starch and the DS_{act} were calculated with these values. The OSA products based on RP starch are designated as RO1, RO2, RO3 and RO4 and the WP starch varieties as WO1, WO2, WO3 and WO4. The starches with the codes RO0 and WO0 represent the extruded RP and WP starches without an OSA derivatization. The ten obtained products were tested as protective colloid in the pVAc polymerization procedure described in the experimental section. The obtained latexes were characterized with the variables viscosity, dry matter, volume mean diameter (VMD) and span (Table 1A & 1B).

<table>
<thead>
<tr>
<th>Code</th>
<th>OSA derivatization (DS)</th>
<th>Viscosity (mPa·s)</th>
<th>Dry matter (%)</th>
<th>PSD (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Actual</td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td>RO0</td>
<td>0</td>
<td>0</td>
<td>1475</td>
<td>52.4</td>
</tr>
<tr>
<td>RO1</td>
<td>0.01</td>
<td>0.007</td>
<td>2460</td>
<td>53.0</td>
</tr>
<tr>
<td>RO2</td>
<td>0.02</td>
<td>0.014</td>
<td>3100</td>
<td>53.1</td>
</tr>
<tr>
<td>RO3</td>
<td>0.03</td>
<td>0.021</td>
<td>9560</td>
<td>52.4</td>
</tr>
<tr>
<td>RO4</td>
<td>0.04</td>
<td>0.028</td>
<td>8240</td>
<td>53.0</td>
</tr>
</tbody>
</table>

Remark: Calculated dry matter is based on the actual dosed amounts.
Table 1B: Latex (WP) related responses: Viscosity, dry matter and PSD variables VMD and span.

<table>
<thead>
<tr>
<th>Code</th>
<th>OSA derivatization (DS)</th>
<th>Viscosity (mPa·s)</th>
<th>Dry matter (%)</th>
<th>PSD (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Maximum</td>
<td>Actual</td>
<td>Calculated</td>
<td>Found</td>
</tr>
<tr>
<td>WO0</td>
<td>0</td>
<td>0</td>
<td>1490</td>
<td>52.8</td>
</tr>
<tr>
<td>WO1</td>
<td>0.01</td>
<td>0.008</td>
<td>3950</td>
<td>53.1</td>
</tr>
<tr>
<td>WO2</td>
<td>0.02</td>
<td>0.017</td>
<td>11700</td>
<td>53.2</td>
</tr>
<tr>
<td>WO3</td>
<td>0.03</td>
<td>0.026</td>
<td>16380</td>
<td>53.0</td>
</tr>
<tr>
<td>WO4</td>
<td>0.04</td>
<td>0.034</td>
<td>13520</td>
<td>52.9</td>
</tr>
</tbody>
</table>

Remark: Calculated dry matter is based on the actual dosed amounts.

The selected formulation (10 wt % starch derivative on pVAc) and polymerization procedure (80 °C; SPS initiation) resulted in a latex with a viscosity of approximately 1500 mPa·s if WP or RP starch was used for stabilization without an OSA derivatization. Application of WP and RP starches with an OSA derivatization resulted in distinct higher viscosities than their unsubstituted counterparts. Moreover, latexes based on WP starch displayed significantly higher viscosities than their counterparts based on RP starch. The level of reactor fouling after the polymerization procedure was also slightly lower for the varieties based on WP starch. This reactor fouling is inversely proportional to the recoveries found in dry matter. This is in line with expectation because the reactor fouling originates mainly from the solid part of the latex. Some small differences in dry matter content were present between WP and RP based products. A part of the observed differences might therefore originate from fluctuations in dry matter content. However, the actual impact of these differences is assumed to be negligible. The latexes stabilized with RO3 and RO4 were excluded from further evaluation due to their distinct lower level of recovery (i.e. < 96 %) since then a relevant proportion of the end product (either starch or the (grafted) polymer pVAc onto starch) would systematically be excluded from the analysis.

The use of OSA starch as protective colloid did not only result in higher viscosities but also in an increased VMD of the latex particles. A possible explanation is capture of the VAM by the clusters of hydrophobic moieties of the starch derivative in the initial stage of the polymerization. These VAM rich clusters are excellent nucleation sites for the actual polymerization and the polymer formed is stabilized during this process by the starch derivatives of these clusters as well. The VMD of the WP starch stabilized latexes tended to be lower than their counterparts based on RP starch and this appeared to be also the case for the span of the PSD obtained. The observed differences in viscosity between latexes based on WP and RP starch can therefore be partly deduced to differences in PSD. The DS_{max} did not correlate with VMD, which in turn did not correlate with the latex viscosity. However, DS_{max} seemed to correlate with viscosity; thus another factor (influenced by DS_{max}), besides VMD, must display a relevant influence on the measured viscosity. This is probably the amount of starch derivative dissolved in the water phase. The actual PSD of the varieties based on WP starch (the one for the RP starch based products was very similar and not shown for brevity) are given in Figure 4. The importance of DS_{max} on PSD as well as the absence of a directly clear correlation is both evident. There was also a pronounced impact of DS_{max} on the level of bi-modality of the PSD, but the observed behaviour requires additional research in order to obtain a deeper understanding.
During the emulsion polymerization process, the latex based on WO0 showed a gradual increase in torque of the stirrer once the VAM dosage was started. This tended to level off at the point when the initiator solution was dosed and the VAM dosage was reduced to a third (Figure 5).
The observed behaviour is not micelle related because the WO0 formulation did not contain any ingredients with an amphiphilic nature. However, an interaction between pVAc generated during polymerization and WP starch might be feasible since WP starch is known to form viscosity increasing aggregates with hydrophobic molecules [6,7]. Distinct changes in torque profile were observed between 1.5 and 4.5 hours if WO1, WO2, WO3 or WO4 was used for stabilization instead of WO0. Particle formation takes place in this period of time according to a visual observation of the same polymerizations executed in a transparent reactor made of borosilicate glass. The level of torque is expected to depend on the level of excess VAM because the size of a latex particle is proportional to its VAM content [19,20]. The observed increases in torque between 1.5 and 4.5 hrs of processing are therefore not only based on the PSD but on free VAM content as well. The decay in torque after the VAM dosage was stopped confirms the significance of this assumption. The monomer stored in particles is consumed from this point on and results in a considerable torque reduction in time. The stirrer torque profiles of the latexes stabilized with starch derivatives WO3 and WO4 display a higher level of erratic behaviour than the other three varieties. The fluctuations in stirrer torque probably originated from depositions of polymer on the stirrer blade during processing. This is plausible because the amount of depositions on the stirrer blade was proportional with the level of derivatization.

Figure 4 shows that the torque increase is proportional to the DS_max of the starch once the monomer dosage is finished. The maximum torque during the preparation of the latex stabilized with WO1 was higher than its WO0 counterpart. The observed behaviour is probably induced by a change in the particle formation process because the corresponding latex does not only contain larger particles but has an increased span as well (Table 1). This assumption is also in line with the observed changes in torque profile if WO2 is used for stabilization. A change from WO1 to WO2 results in a reduction in span and VMD of the PSD. Moreover, an increase in initial torque was observed if WO3 was used instead of WO2 and this replacement induced a change in PSD as well. The VMD showed a pronounced increase after this change and this is indicative that the PSD is not the only factor that controls the torque profile during processing. The fact that WO2 and WO3 have approximately the same span is also in agreement with this hypothesis. The PSD appeared to be linked to the level of torque in the early stage of processing because latexes based on WO3, WO4 had a similar PSD and the corresponding torque profiles were the same up to 3 hrs of processing. The observed differences in latex particles smaller than 3 μm and larger 20 μm limits the validity of this hypothesis, even if these deviations might also originated after 3 hrs of processing.

**Potential wood adhesives**

Latexes stabilized with WO2 and RO2 were selected for a more elaborate investigation because of their lower level of reactor fouling and the fact that the corresponding latex viscosities range from 3 000 to over 10 000 mPa·s (Table 1). This range coincides largely with the viscosity specification of roller applications, which is frequently used in the wood adhesive industry [21]. Latexes stabilized with RO2 and WO2 were prepared and compared to the WO0, whose behaviour was similar in all aspects to RO0 (which was then, for the sake of brevity, left out of the discussion). The polymerizations were executed in triplicate and the...
obtained results were averaged. The torque profiles of WO2 and WO0 were significantly different according the variation (2 times the standard deviation (σ)) of the triplicates executed (Figure 6). Both profiles showed a decrease in level of torque after the VAM dosage was finished. This was related to the amount of VAM in the swollen latex particles (vide supra).

![Figure 6: Torque as function of the polymerization time for WO2 and WO0. The lines are smoothed by a moving average and the error bars represent 2 times σ of a triplicate. The dotted line represents the dosage profile of VAM.](image)

The difference between WO2 and RO2 was pronounced and close to systematic but only up to 7-8 hours after the initiation of the procedure (Figure 7). From this point the torque of WO2 remained close to constant whilst the torque of RO2 continued to decrease. The difference between WO2 and RO2 became even more pronounced once the WTR dropped below 65°C. Dissolved WP starch is known to associate with hydrophobic groups and this interaction can considerably increase the viscosity of the corresponding mixtures [6,7]. WO2 had a pronounced higher torque level during processing than its RO2 counterpart and it is tempting to assign the increased torque level of WO2 totally to the interaction between WP starch and hydrophobic groups. However, there was also a distinct difference between the DS_{act} of WO2 (0.017) and RO2 (0.014) (Table 1). The actual impact of this difference in DS_{act} is not known and the observed behaviour is probably a combination of a difference in DS_{act} and the association between WP starch and the hydrophobic groups bound to WP starch.

The use of OSA potato starch did not only have a distinct impact on the torque profile during the polymerization reaction, but also viscosity level, thermal transitions and PSD of the final products were influenced (Figure 8 and Table 2).
Extruded octenyl succinylated starch stabilized polyvinyl acetate latexes

Figure 7: Torque as function of the polymerization time for WO2 and RO2. The lines are smoothed by a moving average and the error bars represent 2 times σ of a triplicate. The dotted line represents the applied WTR profile.

Table 2. Product characteristics: VMD, thermal transitions and viscosity.

<table>
<thead>
<tr>
<th>Code</th>
<th>Viscosity (mPa·s)</th>
<th>T\text{g, onset} (°C)</th>
<th>T\text{g, inflection} (°C)</th>
<th>T\text{g, endset} (°C)</th>
<th>ΔT\text{g} (°C)</th>
<th>VMD (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO2</td>
<td>10380</td>
<td>8.8</td>
<td>11.6</td>
<td>14.6</td>
<td>5.8</td>
<td>4.5</td>
</tr>
<tr>
<td>RO2</td>
<td>3020</td>
<td>8.8</td>
<td>11.0</td>
<td>13.3</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>WO0</td>
<td>1280</td>
<td>10.7</td>
<td>13.3</td>
<td>15.3</td>
<td>4.6</td>
<td>1.4</td>
</tr>
</tbody>
</table>

We start by noticing how the thermal properties (T\text{g,x} values in Table 2) of RO2 and WO2 are factually similar to each other with differences within the experimental detection limits (i.e. 0.5 °C). On the other hand relevant variations can be observed in the variables viscosity and VMD.
Differences in PSD can influence the level of viscosity and the differences between the PSD of WO0 and WO2 could therefore be a plausible explanation of the observed levels of viscosity [22]. However, the PSD’s of WO2 and RO2 were very similar whilst their viscosities differ considerably. The observed differences in viscosity between WO2 and RO2 are probably related to differences in rheology of the water phase (vide supra). The origin of this behaviour might be attributed to the fact that only WP starch can exhibit associative behaviour with hydrophobic domains [6,7]. Unfortunately, the viscosities at 20°C of the 10 wt % solutions of RO2 (920 mPa·s; turbid), WO2 (338 mPa·s; clear) and WO0 (178 mPa·s; clear) cannot be used to confirm this assumption because RO2 showed severe signs of retrogradated material which also resulted in an increase in viscosity.

The PSD’s of WO2 and RO2 showed a bimodal distribution and this might be explained by either the occurrence of coagulation of latex particles and/or of two separate nucleation stages during preparation. Both processes can be influenced by differences in the amount of octenyl succinate groups bound to the starch fragments. In the first case, insufficient starch is present at the surface of the the latex particle to prevent it from coalesce. In the other, not enough micelle like structures are present to store the amount of monomer to prevent other nucleation mechanisms (e.g homogeneous nucleation). The latter might also be the reason of the bimodal distribution of the latex stabilized with WO1 (Figure 4).

WO2 and RO2 had HST during processing which were sometimes considerable higher than equilibrium HST, especially the WO2-based polymerization (Figure 9). Previous research showed that RMT correlates with the HST [15]. A HST higher than the equilibrium HST is therefore indicative for a RMT higher than generated by the applied WTR. This phenomenon is possible due to the highly exothermic nature of the vinyl based polymerization [23]. The level of pVAc branching introduced during polymerization is proportional to the RMT [24,25]. The RMT of WO2 was systematically higher than RO2 during polymerization but the impact in the level of pVAc branching between both varieties was limited according the $T_g$’s measured (Table 2).

Figure 9: HST as function of the polymerization time for WO2 and RO2. The lines are smoothed by a moving average and based on a triplicate measurement. The dotted line shows the temperature profile and both straight lines represent the initial equilibrium HST of WO2 and RO2.
The difference in $T_{g,\text{infection}}$ between WO0 (13.3 °C) and WO2 (11.6 °) can be explained by either a change in composition or level of branching of the pVAc generated. Octenyl succinylated starch anchored on the surface of the latex particle affects the purity level of the pVAc prepared but the observed difference can probably mainly be explained by a considerable difference in HST during processing (Figure 10).

Figure 10: HST as function of the polymerization time for WO2 and WO0. The lines are smoothed by a moving average and the error bars represent 2 times $\sigma$ of a triplicate. The dotted line shows the dosage profile of monomer.

The HST during polymerization of WO0 was in the range of 65-68°C. This is close to the boiling point of the VAM-water azeotrope (66°C) and transport of considerable amounts of heat from the reaction mixture to the cooler are therefore feasible [15,26]. The higher water bath power consumption (WPC) of the processing procedure of WO0 with respect to the other two varieties is also in line with this assumption (Figure 11).

Figure 11: WPC as function of the polymerization time with WO2, RO2 and WO0. The lines are smoothed by a moving average and based on a triplicate experiment.
The HST was higher than the reflux temperature of the azetrope VAM - water (66 °C) most of the time. The optimal azetrope composition (VAM : water = 93 : 7) was probably never present during the polymerization of WO2, RO2 and WO0, maybe besides the two short periods of 66 °C during the preparation of WO0. The actual RMT was therefore probably much higher than 66 °C most of the time but there were no indications that RMT exceeded the WTR setting of 80 °C. The level of pVAc branching is proportional to RMT and this might be an explanation for the observed inverse correlation between HST and T_g,inflection (vide supra). Radicals were generated by thermal dissociation of SPS and changes in reaction temperature will have an impact on the radical formation process as well. Differences in concentrations of hydrogen ion, ethanol, VAM, acetate, sulfate and thiosulfate in the final product were present but on a limited scale only. Significant correlations between these radical formation related responses and the observed change in latex viscosity and PSD were therefore not expected.

Conclusions
Octenyl succinylation of starch has a considerable impact on the protective colloid properties of the product in a VAM based free radical polymerization. A product with a DS\text{max} 0.02 showed pronounced differences in polymerization process (e.g. torque) and product (viscosity, particle size etc...) characteristics compared to product without this derivatization. The derivatization reduced the energy demand during processing and the latexes showed a higher viscosity and larger particle sizes than counterparts without this type of modification. The latex viscosity appeared to be proportional to the DS\text{max} of the derivatization up to a level of 0.02 for both regular and waxy potato starch based products. The latexes based regular potato starch with a DS\text{max} 0.03 and 0.04 cannot be properly compared with the other products because of a higher loss of material due to coagulation and fouling of the reactor. A change in process conditions is needed to increase the material recovery of this type of latexes and make them more suitable for comparison with latexes based on starch derivatives with a lower degree of substitution. The higher latex viscosity of the waxy potato variety with respect to its regular counterpart can probably be explained by associative behaviour between waxy potato starch fragments and the hydrophobic domains present. This is a unique property of waxy potato starch and fragments of this type of starch apparently still exhibit this characteristic after the applied polymerization conditions.

Abbreviations
WP : Waxy potato starch.
RP : Regular potato starch.
OSA : Octenyl succinic anhydride.
DS\text{max} : Maximum degree of substitution based on the amount of reagent added.
pVAc : Polyvinyl acetate.
DS\text{act} : Actual degree of substitution calculated from DS\text{max} and efficiency.
RPM : Revolutions per minute.
VAM : Vinyl acetate monomer.
SPS : Sodium persulfate.
SBC : Sodium bicarbonate.
Extruded octenyl succinylated starch stabilized polyvinyl acetate latexes

STS : Sodium thiosulfate.
HST : Headspace temperature of the reactor.
WTR : Water bath temperature reactor.
RMT : Reaction mixture temperature.
PSD : Particle size distribution.
$T_g$ : Glass transition temperature.
mDSC : Modulated differential scanning calorimeter.
WO0-4 : Extruded WP starch with a DS$_{max}$ OSA of 0, 0.01, 0.02, 0.03 and 0.04.
RO0-4 : Extruded RP starch with a DS$_{max}$ OSA of 0, 0.01, 0.02, 0.03 and 0.04.
VMD : Volume Mean Diameter.
$\sigma$ : Standard deviation.
$T_{g, \text{onset}}$ : Onset point based glass transition temperature.
$T_{g, \text{inflection}}$ : Inflection point based glass transition temperature.
$T_{g, \text{endset}}$ : Endset point based glass transition temperature.
$\Delta T_g$ : $T_{g, \text{endset}} - T_{g, \text{onset}}$.
WPC : Water bath power consumption.
References