Potato starch stabilized synthetic latexes
Terpstra, Karsjen

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CHAPTER 4

Modified waxy potato starch stabilized polyvinyl acetate latexes: Influence of polymerization temperature and initiator concentration on process and product characteristics
Abstract
Polyvinyl acetate latexes with only modified starch as stabilizing agent are interesting alternatives for counterparts based on synthetic additives (i.e. detergents, emulsifiers and/or protective colloids). These latexes do not only have a reduced amount of oil-based products but can be tuned towards relatively high solid contents, thus reducing the amount of water (solvent) needed. This work focused on the synthesis of latexes (57 wt % solid content) stabilized by maltodextrins. In particular it aimed at investigating the impact of changes in temperature (i.e. 75 – 85 °C) and the persulfate amount (i.e. 2 – 4 wt %) during the polymerization on the latex characteristics. The prepared materials displayed viscosities in the range of 700 – 2300 mPa·s and differences in processing conditions were observed as well. Product properties indicated distinct changes in the radical formation process. The viscosity of the latex was related, via a statistical model, to the processing factors mentioned above.

Introduction
Starch containing polyvinyl acetate (pVAc) latexes with dry solid contents higher than 50 wt % (i.e. dry material relative to the total dispersion) are interesting from a commercial and environmental point of view [1-5]. This is not only due to their renewable nature but also with respect to their preparation and application characteristics. Higher dry solid content increases the throughput of the reactor and makes transport of the final product more efficient and cheaper. The presence of less water also diminishes the time for drying and film formation and reduces the energy requirement when drying equipment is required (e.g. in the preparation of plywood). Dry solid contents up to 55 wt % are very common for commercial latexes and modifications in the particle size distribution allow for values up to 75 wt %. However, the viscosity of these latexes is known to increase rapidly once the dry solid content exceeds the 50 wt % level and the latexes become sensitive for shear stress, which might then introduce problems during preparation, handling and/or application [6-8].

Latexes with high dry solid content can be designed by calculation of the maximum obtainable value for monodisperse latex. Several models are available for this purpose and the Krieger-Dougherthy equation is shown below [6-8]:

$$\eta_r = \frac{\eta}{\eta_0} = \left[ 1 - \frac{\phi}{\phi_m} \right]^{-[\eta]} \phi_m$$

with $\eta_r$ being the relative viscosity, $\eta$ the viscosity of the suspension, $\eta_0$ the viscosity of the medium, $\phi$ the volume fraction of solids in the suspension, $\phi_m$ the maximum packing fraction and $[\eta]$ the intrinsic viscosity.

Dry solid contents up to 63 wt % are feasible for inert solid spheres arranged in a random close packing (e.g. silica or polyvinyl chloride) [8]. Even higher dry solid contents are accessible by mixing two monodisperse suspensions with a size difference ratio of approximately 4.5. However, the particles in polymer latexes are seldom inert and hard indeformable solids, which limit the applicability of these equations in a number of cases considerably [8]. For example, the effect of inter-particle repulsive forces increases with decreasing particle size and this
factually limits the size of the particles (to increase the dry solid content) down to a minimum of 100 nm [8]. High dry solid content latex based on mixing of two monodisperse latexes can also be prepared in one processing step by introducing a second particle nucleation stage during polymerization. This approach requires less processing steps than mixing different latexes and is therefore favoured from a green chemistry and engineering point of view. Secondary particle formation can be initiated by adding emulsifiers after the initial nucleation stage of the polymerization process. The second particle size distribution can be influenced by the time of addition and the particle size decreases with the dosage time. A drawback of this approach is that it increases the amount of material (i.e. emulsifiers) that can migrate out of the polymer layer after application and contaminate the local environment. This migratory risk needs to be minimized according the generally defined rules of producing in a more save and sustainable way. Several indications are already found that more stringent regulations will emerge in the near future [9,10].

Pyrodextrins can be used to generate pVAc latexes with high dry solid content up to 70% in a different way [11]. The starch derivative remains in the water phase of the latex and therefore does not increase the volume of the dispersed phase relative to the total volume of the dispersion. The particle size distribution of this type of solid latexes can be selected in a proper range with respect to sensitivity to shear stresses and the resulting viscosity increases. Unfortunately, commonly available latexes are often prepared with emulsifiers, which render them less interesting when making allowances for the migration of these additives during application (vide supra). Moreover, there are also indications that the colouration and chloride content of pyrodextrins affects the polymerization rate to an extent that makes the polymerization process more energy demanding [12]. Maltodextrins might be interesting alternatives because they are less coloured than pyrodextrins and they contain hardly any chloride. However, the exceptional behaviour of pyrodextrins finds its origin in their high degree of degradation (i.e. relatively low molecular weight) and increased density which cannot be matched by commercially available maltodextrins yet [13,14].

Heat during processing can be transferred from the reaction mixture to the reflux cooler by refluxing of the low boiling azeotrope vinyl acetate monomer (VAM) and water (92.7 / 7.3 wt %; 66°C). The addition of VAM to a water based mixture results in a boiling point in the range of 100 - 66°C depending on the composition and the presence of contaminants [14-16]. These considerations are of paramount importance since they clearly indicate that, depending on the chemical composition (in turn related to the conversion of the polymerization reaction) reflux of the liquid might occur resulting in relatively high (and undesirable) energy consumption. On the other hand, this also suggests that the head-space temperature (HST), being directly related to the VAM concentration (and thus the polymerization reaction extent), can be conveniently used to monitor the progress of the reaction in those cases (e.g. industrial settings) in which the use of a sensor is not possible or desirable.

In this work we systematically investigated the use of a modified waxy potato starch (maltodextrin) for the stabilization of a pVAc latex in the absence of synthetic emulsifiers [14]. The starch content of the formulation was 25 wt % with respect to pVAc and the total dry solid content was approximately 57 wt %. The selected modified starch has not been investigated before in the literature in the range of composition employed here. The increase in starch
content was expected to have a pronounced effect on product and process characteristics. Information about the impact of changes in these two factors on product and process characteristics is not available in the literature for the selected formulation and this justifies a thorough investigation in this direction. The experiments were designed according to the rules of a $2^2$ factorial augmented with a center point measured in fivefold [17].

**Experimental**

**Materials**
The modified waxy potato starch (maltodextrin) used is commercially available under the name of Eliane MD2 (AVEBE U.A.; The Netherlands). The vinyl acetate monomer (VAM) was obtained 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 pro analyse quality and from Merck Germany. STS was added as a 0.3 M solution. 2.0, 3.0 and 4.0 wt % SPS was dissolved in water together with SBC in the ratio 3:4 and. All ingredients were used without additional purification and the solvent was demineralised water in all cases.

**Equipment**
A double 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 10.5x7 cm (height x diameter)) was applied. The spiral ribbon stirrer was replaced by a rushton impeller (Teflon; 8 cm) in the pH, dissolved oxygen and temperature of the reaction mixture (RMT) experiment. A lid of borosilicate glass with several connection points was placed on top and the reactor was completely insulated with radiator foil. A reflux cooler was placed on top together with a pt-100 probe for measuring the temperature of the headspace in the reactor (HST). The dimensions and settings of the water baths used for temperature control of polymerization reactor and reflux cooler were the same and the temperature difference between inlets and outlets can therefore be used for a heat transport evaluation and energy consumption calculations of reactor and cooler. The feeding lines of VAM and SPS 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 1).

![Figure 1: Schematic representation of the polymerization reactor used.](image)
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. A syringe pump was used to add SPS and another syringe pump was used to add STS after the actual polymerization was finished. Differences in dosage amounts were achieved by changing the concentration of solutions used. This approach minimizes the variation in water content during the polymerization and this is important since the initial radical formation takes place in the water phase and is concentration dependent.

**Statistical design**
A randomized $2^2$ factorial design with five center points was selected to investigate the influence of two factors (i.e. SPS concentration and the temperature of water bath connected to the reactor (WTR)) on the polymerization reaction [17].

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<th>WTR (°C)</th>
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<tr>
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<td>LH1</td>
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</table>

**Procedure**
A 25 wt % starch/water mixture was prepared by adding the modified starch to a demi-water containing beaker whilst stirring (3-bladed impeller; 1000 RPM; 10 minutes). The polymerization reactor was filled with 322.8 g of this mixture. Automatic mixing (0-0.75 Hrs: 240 RPM; 0.75-9.0 hrs: 120 RPM) was started and the applied WTR profile and dosage protocols of VAM, SPS and STS are given in Figure 2. VAM was used without inhibitor removal in order to closely match the experimental conditions applicable at industrial level. A total of 0.27 kg VAM was added in all cases and a pre-dosage of 13.5 g VAM was chosen since this ensures a relevant reproducibility level as well as a limited level of reflux [14]. The actual dosage was monitored in time and the amount of VAM added was used for mass balance calculations. The three levels of SPS solution were prepared by weighing 1.00, 1.50 or 2.00 g of SPS in centrifuge tube together with SBC in the ratio 3:4. The weighed SPS and SBC were added to demineralised water and the grand total was 50 g in all cases. The actual addition of the SPS starts after 104 minutes with a pre-dosage of 4.5 ml (4.5 ml/min) 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 reaction temperature drops below 65 °C during the cooling down. Agitation was continued for at least one hour after the temperature of the water bath
reaches a temperature of 20 °C. The dispersion was transferred into a storage container without any additional treatments after this short period of equilibration.

![Figure 2: Applied WTR profiles and dosage protocols of SPS/SBC, VAM and STS.](image)

**Characterization**

Viscosity, pH and dry matter of the final latex were determined with the help of a Brookfield DV-II+ (20RPM), WTW pH320 and Mettler Toledo PM100/LP16 (80 °C) respectively. The hydrogen ion and oxygen content of the reaction mixture during processing were monitored, when applicable, with a P915 controller from LTH equipped with a pH-SterProbe and a DO-electrode 316SS. 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 mx0.32 mm) and a flame ionization detector. The gas chromatography measurement was performed on water diluted dispersions (10 wt %). About 2 ml of the diluted dispersion was centrifuged at 13000 relative centrifugal force for 10 minutes 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 were ISO 13320 compliant. Glass transition temperatures \(T_g\) were derived from reversing heat flow curves determined with a modulating 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 untreated latex).

**Results**

**Process characteristics**

The hydrogen ion and oxygen concentration of the reaction mixture during the first 3 hours of polymerization CC are given in Figure 3.
The amount of dissolved oxygen increased in the first stage of the dissolution process but gradually returned to 87% saturation before one hour was passed. The change in oxygen content is probably related to the air trapped in the maltodextrin, which is transferred to the water phase during dissolution process and then slowly removed through the headspace and reflux cooler of the reactor. The pre-dosage of VAM resulted in a sharp decrease in oxygen concentration. This is in line with the assumption that a pre-dosage of VAM is suitable to replace an inert gas purge as pre-polymerization step. The pre-dosage of SPS results in a pronounced increase in oxygen content and shows that it is difficult to execute this type of polymerization in the absence of oxygen. It took approximately one hour to reach a constant pH. The maltodextrin is at this point properly dissolved and the ion exchange between the maltodextrin and water phase is probably in equilibrium as well. After the VAM addition, the pH suddenly dropped. This is most likely caused by the formation of acetic acid originating from the dissociation of VAM.

Reaction scheme 1:

The pre-dosage of the SPS mixture, with a pH of approximately 8.5, results in a sharp increase in pH up to 6.5 (Figure 3). Base catalyzed saponification of VAM is assumed to be acceptable at the observed circumstances. Figure 4 shows HST and water bath power consumption (WPC) consumption profiles of polymerizations performed at a WTR of 75 (LL1) and 85 (HH1) °C.

A systematic difference was observed between the HST of LL1 and HH1 just before the VAM dosage was started (1.5 hours) and, at the same point, a systematic difference was observed for the WPC profiles of LL1 and HH1 as well. Both differences are linked to the selected WTR. The HST drops to approximately 65 °C after the dosage of VAM was started and showed a pronounced increase after the dosage was stopped. This phenomenon can be mainly related to the fact that VAM and water forms an azeotrope (VAM / water: 92.7 / 7.3 wt %) with a boiling point of 66 °C, at least if enough VAM is present in the mixture [16]. WPC showed a
small increase during the dosage of VAM. This can probably be linked to an increased level of refluxing. This is also in line with the assumption that the RMT is close to 66 °C during the VAM dosage. This close relationship between HST and RMT is shown in Figure 5. The manual addition of 35ml VAM was carried out in order to show the impact of a sudden change in VAM and water on HST and RMT.

Figure 4: HST during processing for experiment HH1 (85°C) and LL1 (75°C) together with the corresponding WPC profiles.

Figure 5: Correlation between HST and RMT as function of the time. The dotted line represents the VAM dosage profile during the polymerization experiment CC.

This confirms that the two temperatures (i.e. RMT and HST) are intimately related and that the latter can in principle be used to monitor the progress of the reaction in those cases in which a direct use of a sensor is practically unfeasible.

The temperature difference between inlet and outlet of the reactor and cooler are defined as ΔTR and ΔTC respectively. ΔTR and ΔTC of experiments HH1 and LL1 appeared to be similar (~0.7 °C) up to 4.5 hrs and suggests that reflux based heat transfer was the most important factor in heat loss process (Figure 6).
This boiling did not only transfer heat from the reaction mixture to the cooler but can also induce significant changes in distribution and concentration of the reaction mixture [18]. A small change in ΔTC for HH1 was observed after approximately 4.5 hours, which might be linked to a reduction in free VAM of the water phase due to its migration to the pVAc particles. This is in agreement with the fact that polymer particles can, when they reach a certain size, store significant amounts of monomer [19-21]. A logical consequence of this observation is that the size of the particle is related to the amount of free monomer that migrates into the polymeric phase. Therefore, changes in free monomer content can significantly affect the viscosity level of the reaction mixture, which constitutes an undesired effect if such thickening effect results in a poor level of mixing. The level of torque (proportional to the viscosity of the reaction mixture) was around 55 Ncm at the initial stage of the polymerization and showed a small gradual increase during polymerization (Figure 7). The torque profiles of all latexes fall within a range equal to twice the σ of the CC settings, thus indicating that no extreme changes in viscosities took place during processing.
**Latex composition and properties**

The latex characteristics and chemical composition (including dry matter, ethanal, acetate, thiosulfate and sulfate contents) were determined and evaluated using Pareto calculations (Table 2 and 3).

All dry matter recoveries exceeded 97% and the small differences cannot be deduced to the applied reaction conditions according to the calculations performed. Some changes in final pH were significantly linked to the factors investigated but the observed variation was only modest and did not exceed the region 4.8 - 5.0. An increase in SPS intake leads to a decrease in residual VAM (negative sign of the corresponding effect in Table 3). This can be explained by the fact that more radicals during processing lead to less unreacted VAM in the final latex. On the other hand, the amount of residual VAM was positively influenced by WTR. This is not expected since SPS is used in thermal dissociation mode and the radical generation during processing increases with the RMT. One might then speculate that WTR is therefore not linked to the RMT, which is in corroborated by the observation that the interaction between SPS and WTR is not statistically significant. The observed behaviour is in line with the hypothesis that all polymerizations are executed at the boiling temperature of the azeotrope water and VAM mainly (*vide supra*).

<table>
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<th>Run</th>
<th>Code</th>
<th>Latex Dry matter Recovered (%)</th>
<th>pH</th>
<th>Ethanal (mg/g)</th>
<th>VAM (mg/g)</th>
<th>Acetate (mmol)</th>
<th>Sulfate (mmol)</th>
<th>Thiosulfate (mmol)</th>
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<td>1</td>
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<td>98.8</td>
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Table 3. Pareto calculations: Dry matter, pH, ethanal, VAM, acetate, sulfate and thiosulfate content (x = not significant).

<table>
<thead>
<tr>
<th>Factors</th>
<th>Dry matter recovered</th>
<th>pH</th>
<th>Ethanal</th>
<th>VAM</th>
<th>Acetate</th>
<th>Sulfate</th>
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<td>x</td>
<td>0.04</td>
<td>x</td>
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Residual ethanal and acetate were not influenced in the same way by the changes in SPS and WTR. This cannot be explained only by the hydrolysis of VAM, which would result in equal amounts of acetate and ethanal (*vide supra*). The boiling point of ethanal is 21°C and
evaporates therefore easily during preparation, storage or sample treatment. The value found for ethanal might therefore be considerably lower than the actual amount formed during processing. The observed increase in acetate concentration with initiator intake is plausible due to the fact that the ratio between amounts of SPS and SBC is fixed. An increase in SPS was therefore coupled with an increase in the amount of added SBC. This influences the reaction pH and, as a consequence, the VAM hydrolysis. Part of the acetate might also originate from the hydrolysis of pVAc, which remained in the water phase after the centrifugation step. Thiosulfate was added in the final stage of the polymerization in order to convert remnant SPS. The stoichiometry of the redox equation of thiosulfate and SPS is 2 to 1 [22].

Reaction scheme 1: \( S_2O_8^{2-} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2SO_4^{2-} \)

About 0.02 mmol thiosulfate, of the 0.81 mmol added, was still present in the latexes and this justified the assumption that all SPS was converted. All latexes had similar thiosulfate concentrations and this is indicative for a similar SPS concentration at the point of thiosulfate dosage (10 hrs after initiation of the experiment). The sulfate concentration was influenced by both investigated factors and their interaction. The observed differences probably originate from a combination of amounts of SPS were added and changes in radical formation process. The thermal dissociation of SPS was not only influenced by temperature but by changes in composition of the reaction mixture as well [23-29]. However, the experimental setup does not allow solid conclusions in this area and additional research is required to address this aspect of the polymerization properly. The volume mean diameter (VMD), thermal transitions (\( T_\text{g, onset} \), \( T_\text{g, inflection} \) and \( T_\text{g, endset} \)) and viscosity of the latexes were also determined (Table 4). Latex prepared with the setting HL1 and its counterpart HH1 appeared to differ considerably from the average PSD but coincide with the PSD’s CC1 and CC4 respectively. The observed differences in PSD can therefore be considered as noise of the experiment.

No significant differences were observed between the determined \( T_g \)’s and this was indicative for a similar composition and structure of the pVAc formed in all cases. The level of pVAc branching (theoretically a crucial factor influencing the \( T_g \) values) is known to be proportional with RMT and the assumption that all polymerization are executed at similar RMT’s is therefore plausible [20,30].

Table 4: Product characteristics VMD, thermal transitions and viscosity.

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<th>( T_\text{g, onset} ) (°C)</th>
<th>( T_\text{g, inflection} ) (°C)</th>
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<th>( \Delta T_g ) (°C)</th>
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<td>1.8</td>
<td>1685</td>
<td>8.0</td>
<td>10.1</td>
<td>12.6</td>
<td>4.6</td>
</tr>
<tr>
<td>9</td>
<td>LH1</td>
<td>1.7</td>
<td>2330</td>
<td>8.4</td>
<td>10.6</td>
<td>12.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>
The VMD of the latexes were not significantly affected by the applied settings according to the Pareto calculations and the corresponding PSD’s did not show significant differences either (Figure 8).

![Figure 8: PSD’s of the experiments HH1, HL1 and the average of the CC experiment (error bars representing 2 times σ of the CC experiment).](image)

The impact of WTR on the latex viscosity (as represented by the sign and magnitude of the corresponding statistical coefficients, not shown for brevity) was positive on its own and negative in combination with SPS. The effect of WTR on the actual RMT was probably small, or maybe even absent, due to reflux based heat transport from the RMT to the cooler and can therefore not be a direct cause for the proportional relationship between WTR and viscosity (section 3.1 & 3.2). WTR, and its interaction with SPS, had no influence on the measured PSD of the latex also and the observed changes in viscosity might therefore originated from alterations in the water phase composition. Indeed, a change in degree of degradation of the starch derivative present in the water phase might be a proper explanation for the observed behaviour even if additional research is needed to validate this assumption properly.

Factorial calculations (Minitab 16) allow quantification of the effect of process conditions on latex viscosity (Equation 2). A difference of 4.2% between $R^2$ (95.9 %) and $R^2_{adj}$ (91.7 %) was observed, thus indicating that the corresponding model is acceptable even if it does not fit all information totally.

Equation 2:

$$\text{Latex viscosity} = -21335 + 4820*\text{SPS} + 287*\text{WTR} - 61*\text{SPS} *\text{WTR} + 150.$$

The observed deviation between $R^2$ and $R^2_{adj}$ might originate from the absence of a relevant factor in the statistical analysis, namely the amount of residual VAM. This response was significantly influenced by the applied changes in WTR and initiator concentration (Table
The viscosity of the latex was correlated with its residual VAM content because viscosity was strongly related with the particle size, which in turn increased with the residual VAM content. Increases in particle size up to a factor of 7 are reported [31]. This is nicely in agreement (vide supra) with the hypothesis of monomer migration from the water to the polymeric phase (particles) as deduced from the reflux profile during the polymerization process. Moreover, there were also indications that the latex viscosity was linked to the residual VAM content. However, this correlation was poor and the presence of outliers cannot be excluded yet (Figure 9). More detailed investigations on the mechanism (at molecular level) are needed to further clarify this point; it is worth noticing how both process and product characteristics seem in this case to consistently indicate such a mechanism.

Figure 9: Latex viscosity as function of its residual VAM content.

**Conclusions**

The viscosity of waxy potato maltodextrin protected polyvinyl acetate latex (57 wt % dry matter) can be influenced by changes in water bath temperature and initiator concentration during processing. The applied reaction conditions resulted in latex viscosities ranging from 700 to 2300 mPa·s. The maltodextrin used is investigated before but not in this particular ratio modified starch to polyvinyl acetate (i.e. 25 wt % on polyvinyl acetate). The differences in latex compositions were indicative for changes in the radical formation process while both process and product characteristics indicate the presence of vinyl acetate monomer in the polymeric particles (during the polymerization). The processing conditions also resulted in differences in vinyl acetate monomer content and this variable has an influence on the latex viscosity. Observed variations in viscosity can be deduced to either differences in residual vinyl acetate monomer, degree of maltodextrin degradation during processing or combinations thereof. Additional research is required if the actual contribution of each parameter needs to be known exactly. On the other hand, the observed data demonstrates the feasibility of the original idea (i.e. use of maltodextrin as protective colloid in relatively high solid-content latexes) and also the robustness of the applied polymerization settings in terms of process (e.g. viscosity) and product (e.g. thermal) properties.
**Abbreviations**

pVAc : Polyvinyl acetate.
VAM : Vinyl acetate monomer.
HST : Headspace temperature.
SPS : Sodium persulfate.
SBC : Sodium bicarbonate.
STS : Sodium thiosulfate.
WTR : Water bath temperature reactor.
L : Low level.
H : High level.
C : Centre level.
RPM : Revolutions per minute.
PSD : Particle size distribution.
\( T_g \) : Glass transition temperature.
mDSC : Modulating differential scanning calorimeter.
WPC : Water bath power consumption.
RMT : Reaction mixture temperature.
\( \Delta T_R \) : Temperature “inlet reactor” – “outlet reactor”.
\( \Delta T_C \) : Temperature “inlet cooler” – “outlet cooler”.
\( \sigma \) : Standard deviation.
VMD : Volume Mean Diameter.
\( T_{g_{\text{onset}}} \) : Onset point based glass transition temperature.
\( T_{g_{\text{infection}}} \) : Inflection point based glass transition temperature.
\( T_{g_{\text{endset}}} \) : Endset point based glass transition temperature.
\( \Delta T_g \) : \( T_{g_{\text{endset}}} - T_{g_{\text{onset}}} \)
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