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):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
**Starch as protective colloid**

The use of native starch as protective colloid is not only interesting from a cost-price perspective but also according the principles of green chemistry – these principles favour ingredients with minimal pre-treatments. Native starch can be used to stabilize synthetic latexes as long as it is (partly) dissolved before the actual free radical polymerization is initiated [1]. Unfortunately, this approach has not only benefits. Firstly, the dissolution of starch granules takes time and this reduces the manufacturing throughput if this pre-treatment is executed in the polymerization reactor. In the second place, native starch dissolves with a considerable peak in viscosity and additional measures, with respect to proper mixing, might be needed to avoid unacceptable heterogeneities during processing. Thirdly, the starch molecules need to be degraded, either mechanical or (bio)chemical, before the polymerization can be started. And finally, native starch is hydrophilic and starch with a slight hydrophobic nature might be required for some important latex characteristics (e.g. rheology and particle size distribution) [2-4].

Polymerization procedures can be tuned to ensure proper dissolution and degradation of native starch, but there are also starch pre-treatments which can incorporate the desired starch characteristics a priori. Extrusion is an example of an energy efficient starch modification which results in products without the presence of granules and a peak viscosity during dissolution. When compared to other modification strategies, several advantages can be outlined. For instance, the amount of water needed during this kind of starch modification is less than its enzymatic counterpart. As a consequence, enzymatic treatments require more energy during dissolution of starch granules and drying of the final product. For this reason, extrusion is an interesting starch pre-treatment from a sustainability point of view [5-8].

Hydrophobic (e.g. octenyl succinylated) starch has emulsifying properties and can therefore be used to change the particle formation process during polymerization and/or the rheology of the final latex [2-4,9-12]. The octenyl succinylation step of the in thesis investigated extruded starches was performed in suspension (~39 wt % in water) and the obtained product needed to be (partly) dried before extrusion. As a result, it is interesting to investigate if it is possible to execute this derivatization in line at semi-dry conditions (< 30 wt % water) just before the extrusion step [13]. This preparation process is considerably less energy demanding than its suspension counterpart for less water needs to be removed during drying. Moreover, there are other ways to prepare hydrophobic starches in an efficient way. The superheated steam driven acylation of starch is an interesting one because fatty acids, which are more environmental benign than octenyl succinic acid for example, can be used [14].

**Free radical reactor configuration and polymerization procedure**

It is common practice in the latex industry to execute vinyl acetate polymerizations above the boiling point of the azeotrope water and vinyl acetate monomer (66 °C). This precondition renders the desire to start with a formulation with modified starch as only additive quite a challenging one. Indeed, the absence of emulsifiers does not only affect the particle formation process, but increases the concentration of vinyl acetate monomer in the water phase as well [10,12]. The latter increases the risk of excessive refluxing and this need to be avoided
because it is a waste of energy and it lowers the temperature of the reaction mixture. Moreover, the polymerization process might become suboptimal at reflux conditions or even terminate in case the free radicals are (also) generated by thermal dissociation. A reflux induced drop in reaction temperature frequently occurred during attempts to convert available polymerization procedures into a reference procedure based on the thermal dissociation of persulfate [1,3,4,15-20]. As a consequence, the desired polymerization procedure in this study had to be designed from scratch [21]. The defined method is suitable for generating latexes with viscosities ranging from water thin to a paste (Figure 1).

![Figure 1: The consistency of the latexes prepared during the investigation of this thesis. From left to right: latexes with a low, moderate and high level of viscosity.](image)

The reactor configuration and polymerization procedures used in this study were not yet fully optimized. It is recommended to use fundamental mathematical models in case a thorough optimization is desired [22]. These kinds of models are not only very powerful tools for optimization but are also suitable for scale-up, process control, monitoring, operator training and often allow for a better understanding of underlying mechanisms.

**Final product**

Commercially available homopolymers of polyvinyl acetate are usually blended with other materials for an optimal price/performance ratio. In this respect, the high wood bonding strength (EN204:D2) of Mowilith DHS S1 (33 MPa) offers more possibilities for blending with (cheap) materials than the evaluated potato starch stabilized latexes (17 - 24 MPa) [23]. However, the bonding strength of the latter might be improved considerably by making a switch from a homopolymer to a polyvinyl acetate based copolymer. Monomers with a hydrophobic character (e.g. butyl acrylate) or cross-linking abilities (e.g. low formaldehyde releasing N-methylol acrylamide) might be interesting options to investigate if the bonding strength of latex needs to be changed [12].

A switch from a vinyl acetate homopolymer to a copolymer will not only influence the bonding strength of the latex but the glass transition temperature \(T_g\) will be changed as well. Monomer types that lower the \(T_g\) of the latex are preferred because that might reduce the need of plasticizers in the final product. Plasticizers are frequently added to vinyl acetate
homopolymers for optimal performance but they tend to migrate out of the adhesive layer after application. The need of plasticizer in the final product might become even superfluous if ethylene, or di-alkyl maleate, based copolymers are used [12].

The rheology of synthetic latex is complex because it is a liquid multiphase system with incompatible components. As a result, the microstructure of these systems can consist of droplets in a matrix, elongated fibrils or a co-continuous structure [24]. The level of viscosity that latex generates is therefore not a very good variable to describe the differences and similarities between different varieties prepared. Moreover, waxy potato starch tends to associate with hydrophobic chains and this interaction will influence the level of viscosity of the corresponding latex as well [2,25]. Large Amplitude Oscillatory Shear (LAOS) characterization, often referred in the literature as Fourier Transform Rheology (FTR), might be helpful in comparing the different available latexes to each other [24]. LAOS possesses a high sensitivity in the characterization of the morphology, thus allowing evaluation of properties that might otherwise be missed with traditional linear methodologies.

Starch can also be used as rheology modifier in those cases that the latex is prepared with starch as main stabilizing agent. Modifiers are usually added to the product in a separate blending silo after the polymerization is finished. No relevant studies were found during a quick screening of open literature, dealing with such two-step envisaged procedure and their actual need in practice. In addition, partial replacement of polyvinyl acetate in the polymerization recipe by a cheap rheology modifier might result in latexes similar to those prepared by the traditional two step approach. The accompanying loss in value of the latex prepared might be (partly) compensated by a shorter polymerization procedure, an easier preparation process and less handling losses. However, a polymerization reactor is more difficult to handle than a blending silo and more expensive in use as well.

A molar replacement of vinyl acetate monomer by other water soluble monomers should not be very problematic in the described preparation procedures of this study. Latexes based on hydrophobic monomers can also be prepared as long as there is sufficient affinity between the monomer and waxy potato starch fragments (or a hydrophobic starch derivative is used). This approach might unlock other application areas (e.g. paint, coating or ink) were (waxy) potato starch can be used as main stabilizing agent in free radical based polymerizations as well. Furthermore, the technology to prepare vinyl acetate and ethylene monomers from a renewable feedstock is available and the corresponding copolymer is already presented as the ideal binder for environmental friendly paints. It would be interesting to investigate the actual added value of these green polymers with respect to their conventional counterparts and make an estimate of the turning point at which these green polymers become commercial viable if they are stabilized with starch [26,27].

It is an improvement, from the point of view of sustainability, if oil-based and migration-sensitive ingredients are replaced by counterparts made of starch with only a slight chemical derivatization. However, getting a product safety legislation approval of a starch derivative is more difficult than starch without any chemical derivatization. Grafting of monomer onto
starch during the initial stage of the polymerization process might be a viable route if the desired properties of the latex require the presence of a hydrophobic starch derivative during processing. The mechanism how to achieve this type of grafting on polysaccharides is frequently described in literature but not yet in a way that can be easily translated to an industrial setting. For example, the industry needs guidance in controlling the level of grafting in a large semi-batch (or small continuous) reactor whilst most investigations provide information about grafting on a small scale in batch mode. As a result, the latex industry is waiting for research especially designed to make the available fundamental knowledge about grafting more accessible to them.
References


