Bio-based stabilizers for hydrophobic nanoparticle dispersions

Isabella Laurén

Master´s Thesis

Laboratory of Natural Materials Technology

Faculty of Science and Engineering

Åbo Akademi University 2020

Supervisors:

Docent Anna Sundberg
Laboratory of Natural Materials Technology
Åbo Akademi University
Turku, Finland

MSc Anneli Lepo
Kemira Oyj R&D and Technology Center
Espoo, Finland

ABSTRACT

The demand for bio-based and bio-degradable products is expanding at fast rate, increasing the need of bio-based stabilizers. In this work, the use of bio-based stabilizers in hydrophobic nanoparticle dispersions was investigated. These dispersions are applied in surface sizing of paperboard, making the properties of the dispersion important. The aim of reaching certain properties concerning solids content, viscosity and particle size, along with no residual monomers in the dispersion, was challenging. Factors, such as, pH, temperature and amount of stabilizer and initiator, were investigated in the dispersion polymerization process.

The polymerization reaction was faster at pH 5.0 and 6.0 compared to lower pH, making the target solids content of 25% reached in a shorter time. Furthermore, the particle size distribution (PSD) was narrower, but the amount of residual monomers in the dispersion was lower at lower pH values. A second feed of initiator was added to most polymerizations, to finalize the polymerization of the monomers and to reach the theoretical solids content. The goal of solids content was reached in shorter time at higher temperature, but these dispersions had clear phase separations, indicating the dispersions were unstable, and the dispersions contained large amounts of monomers.

Many dispersions had a very broad PSD and contained small amounts of very large particles, along with unpolymerized monomers. However, the particles in the dispersions were in average almost five times larger compared to particles in a reference dispersion, stabilized with a known polysaccharide-based stabilizer. By increasing the amount of stabilizer with almost 40% in addition to the original amount, the PSD became narrower and the dispersion did not contain any larger aggregates. The colloidal stability of the dispersions was good and even better than the reference dispersion. The particles did not degrade over a period of 16 weeks, nor sediment, making the stability of the dispersions promising.

Keywords: Stabilizer, stability, dispersion, nanoparticle, polymerization, particle size distribution, surface sizing

PREFACE

This thesis was carried out at Kemira R&D and Technology, as part of a larger project, and therefore many parts were involved in this thesis. First, I would like to thank my supervisors, MSc Anneli Lepo from Kemira Oyj and Docent Anna Sundberg from Åbo Akademi University, for all your guidance, help and trust through this fascinating, and sometimes challenging, work. Moreover, I am grateful to MSc Heli Vuorenpalo and MSc Elsi Turunen for trusting me with this project.

I would like to express my gratitude to all my colleagues in the Polymer Chemistries team, for all your help and expertise during my work. In particular, I would like to thank Mr. Jussi Arola for all his valuable help and thoughts concerning my laboratory work, and for teaching me most of the processes and methods. In addition, special thanks to the Analytics team, for all your contribution to my thesis work.

Furthermore, I would like to acknowledge my brother Mr. William Laurén, for his insightful thoughts on academic writing, and moral support.

Isabella Laurén

Helsinki, April 2020

ABBREVIATIONS

Abbreviation	*Definition*
DA	Degree of acetylation
DLVO	Theory describing the forces between colloidal particles approaching each other
DMF	Dimethylformamide (eluent)
HPC	Hydroxypropyl cellulose
HPLC	High-performance liquid chromatography
PCL	Polycaprolactone
PE	Polyethylene
PLA	Polylactic acid
PP	Polypropylene
PS	Polystyrene
PSD	Particle size distribution
SEC	Size-exclusion chromatography
SNC	Starch nanocrystals
UV	Ultraviolet
WVP	Water vapor permeability

UNITS

Unit	*Explanation*
µm	Micrometer, 10^{-6} m
nm	Nanometer, 10^{-9} m
wt.%	Weight percent

CHEMICAL SUBSTANCES

Substance	*Abbreviation*
Lithium chloride	LiCl
Nitrogen	N_2
Sodium hydroxide	NaOH
Sulfuric acid	H_2SO_4
Water	H_2O

SYMBOLS

Symbol	*Explanation*	*Unit*
c	Concentration	mg/kg
η	(Brookfield) Viscosity	mPas
D50	Particle size where 50% of the particles are smaller than the given value	nm
D90	Particle size where 90% of the particles are smaller than the given value	nm
n/d	Not defined	-
S_1	Sample taken after 120 min of polymerization	-
SC	Solids content	%
T	Temperature	°C
V	Volume	m^3 or l
ζ	Zeta-potential	mV

CONTENT

1 INTRODUCTION

The need of bio-based and bio-degradable materials, along with low carbon footprint, are increasing in the society of today. Better and more eco-friendly materials are constantly investigated and developed. To change a previously synthetic non-renewable material towards a more bio-friendly product, variables need to be replaced one at a time.

Bio-based stabilizers need to have similar or better properties to be able to replace synthetic or inorganic stabilizers. Natural stabilizers are found in large quantities in nature, and polymers, such as, cellulose, lignin, chitosan and hemicellulose, to mention a few, are widely used in the industry and in different applications (Doelker, 2005). The focus in this thesis is on the colloidal stability of a dispersion, *i.e.*, how bio-based materials prevent aggregation of particles in the dispersion.

In this thesis, the dispersions made will be utilized in surface sizing of paper board. In the surface sizing process, the fibers on the surface of the paper are sealed by the addition of specific compounds, such as starch. This increases the paper strength and improve the surface properties for further modification of the paper (Dai, *et al.*, 2011).

1.1 Definitions and desired properties

Nanoparticles are defined as particles with at least one dimension of 100 nm or less. The chemical and physical properties of the nanoparticles should differ from those of the bulk compounds (Kumar, *et al.*, 2009). Because of high surface-to-volume ratio and exceptional characteristics, such as electric and optical properties, nanoparticles can be utilized in many applications, *e.g.*, in medicine and pharmaceutical industries (Guerrini, *et al.*, 2018).

A dispersion is a blend of a material dispersed in another material. The dispersed compound can be in the same or in different state as the continuous phase, where the continuous phase is defined as the phase in which fluid or solid particles are dispersed. A suspension is a subsection of a dispersion, where solid particles are dissolved in a liquid media (Mewis & Vermant, 2000). Furthermore, colloidal dispersions usually contain smaller particles and will not settle over time. Nanoparticle dispersions are considered colloidal systems, where the particles will either flocculate or remain dispersed, but not sediment, depending on the desired stability. The stabilizer can protect the polymers inside the particles from external influence, but the stabilizer alone cannot determine the lifetime of the polymer, *i.e.*, how fast or slow the polymer degrades (Katainen, *et al.*, 2006; Mewis & Vermant, 2000).

The dispersions polymerized in this thesis work will be applied in surface sizing of paper board, hence target properties concerning solids content and viscosity along with particle size and particle size distribution (PSD) are of importance. Polymer particles at nanoscale have a large surface area, and therefore, greater adhesive forces than larger particles. Larger particles have more interaction with the paper and have a major impact on the adhesion between the two surfaces (Katainen, *et al.*, 2006). Hydrophobic particles have lower surface energy compared to hydrophilic materials, and this generates a water-repellant surface. The hydrophobicity of a material can be determined by calculating the contact angle between the surface and a droplet, where the surface is hydrophobic if the contact angle is ≥ 90° (Güleç, *et al.*, 2005).

1.1.1 Target properties

To be utilized in surface sizing, the dispersion must have certain properties. The desired properties of the dispersion for the target application, are described in *Table 1.1.* The target was to reach a dispersion with particles at nanoscale and with a low viscosity, to facilitate the surface sizing process.

Table 1.1 *Target properties of the dispersion*

Property	Target
Solids content (SC)	20 – 30%
pH	4.0 – 6.0
Brookfield viscosity spd 18 (η)	< 200 mPas
Particle size D90[1]	< 200 nm
Particle size D50[2]	< 100 nm

[1] Particle size D90 refers to the particle size where 90% of the particles are smaller than the measured value, based on volume.

[2] Particle size D50 refers to the particle size where 50% of the particles are smaller than the measured value, based on volume.

1.2 Electrostatic and steric stabilization

The electrostatic potential is one of many important factors concerning the stability of a dispersion (Rescignano, *et al.*, 2014). In the DLVO theory (established and named after Derjaguin, Landau, Verwey and Overbeek), the zeta potential (ζ-potential) explains how forces are developed between two particles approaching each other. The theory describes two main forces between a pair of colloidal particles: van der Waals forces (attractive) and electrostatic forces (repulsive). The overall interaction is either attractive or repulsive, depending on the balance between these two forces. Hydrogen bonds are also considered attractive forces in dispersions with high solids content. If the ζ-potential is close to zero, the attractive forces might outpace the repulsion forces and the polymeric dispersion will flocculate. Colloids with a higher positive or lower negative ζ-potential are therefore electrostatically stabilized, since the charge of the particles repel each other (Ishikawa, *et al.*, 2005).

By adding electrolytes to the dispersion, more ions are concentrated around the particles, shielding the charge of the particle, see *Figure 1.1*. If two or more particles are close to each other, the concentration of ions generates an osmotic pressure and the particles will repel each other. If the distance between the two particles is short enough, attractive forces overcome the osmotic pressure, and when these forces increase, the colloidal stability decreases, resulting in coagulation (Bowen & Williams, 1996).

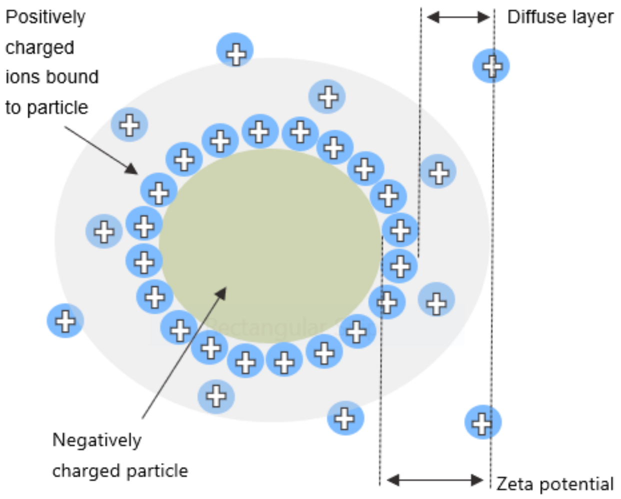


Figure 1.1 *Sketch of a charged particle and its potential difference and ionic concentration. The ions close to the particle are strongly bound to the particle, whereas in the diffuse layer, the ions are loosely attached to the negatively charged particle. Picture adapted from (NanoComposix, 2019).*

Particle dispersions can also be stabilized by steric stabilization, where additives inhibit the coagulation. These non-ionic macromolecules, such as hydrophilic surfactants and polymers, are absorbed onto the surface of the particles with side chains into the medium. High surface coverage is of importance. Sterically stabilized systems tend to persist being well dispersed even at zero ζ-potential and at increasing concentrations of electrolytes (Parfitt & Barnes, 1997).

To maintain the stability of a nanoparticle dispersion, steric and electrostatic stabilization can be combined. In this case, polyelectrolytes can be used as polymeric surfactants. Such substances have polar head-group that generate the electric double layer, while its side chains provide steric repulsion (Ivanov & Ivanov, 2012). Steric stabilization is not sensitive to fluctuations in ionic strength or pH, however, the temperature might affect the stability (Mewis & Vermant, 2000). Many steric stabilizers are surface active, and some stabilizers adsorb onto the surface of the particles (Paine, 1990).

1.2.1 Stability of a dispersion

By modifying the surface of the nanoparticles, the repulsive forces between the particles are improved and the dispersion can be more stable. One of the easiest techniques to modify the surface is by adsorption of polymeric compounds onto the surface, furthermore, the roughness and surface energy can as well be altered, among other things. Parameters such as pH, molar and molecular mass, size, structure and charge of the surfactant are of importance. To disperse hydrophobic nanoparticles in an aqueous media, polymers with both hydrophobic and hydrophilic groups are used: the hydrophobic parts are involved in the adsorption of surfactants onto the hydrophobic nanoparticle, while the hydrophilic segments improve the compatibility between the particle and the aqueous media. In hydrophobic systems, the interface between the solvent and the particle affect the behavior of the system (Iijima & Kamiya, 2009).

Another method to ensure colloidal stability is by grafting polymeric macromolecules onto the surfaces of the particles, to form a protective layer, and the dispersion is therefore sterically stabilized. Due to van der Waals attractions, the layer prevents the particles to aggregate (Zhulina, *et al.*, 1990).

Considering economic reasons and the aspiration to minimize potential toxic leakages, the amount of stabilizer or other additives to increase the stability of a dispersion should be as low as possible. To decrease the degradation of a polymer dispersion, the stabilizer needs to, *e.g.*, react with free radicals or with chain ends. Generally, a variety and different combinations of stabilizers are used for the dispersion to operate under different conditions (Villain, *et al.*, 1995).

1.3 Heterophase radical polymerization

Heterophase polymerization is commonly described as the process producing polymer dispersions, or latexes, where polymers are dispersed in a continuous phase, usually water (Asua & Schoonbrood, 1999). Emulsion polymerization is the most common polymerization process, where the monomers are fed to the reactor with constant rate and the polymer is created by nucleation processes (Antonietti & Tauer, 2003). The first step of the polymerization process is the initiation, where an initiator and catalyst form radicals, and then transferred to the monomer present. Further, more and more monomer units are added to the chain, in a propagation process that creates the most stable radical (Reusch, 2015). A radical polymerization of styrene is illustrated in *Figure 1.2*, explaining a polymerization reaction. Free radicals are formed in the redox initiation process from *e.g.* peroxides as initiator and with ferrous ions as catalysts (Braun, 2009).

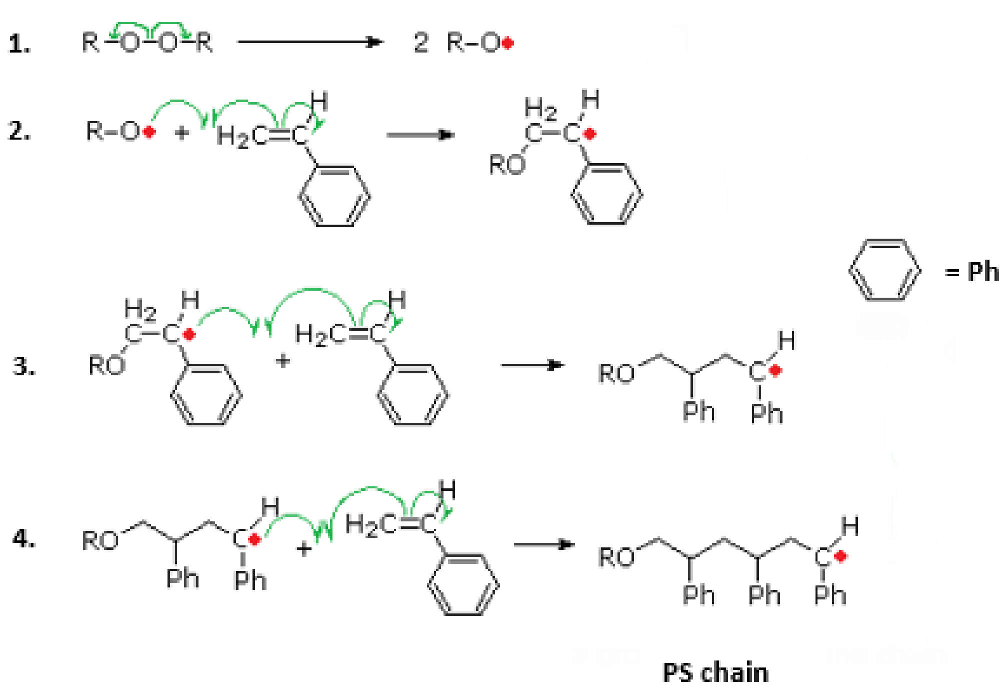


Figure 1.2 *Illustration of a radical polymerization of styrene. Equation 1 and 2 are explaining the redox initiation process, and equation 3 and 4 are illustrating the chain propagation, creating a polystyrene (PS) chain. Picture adapted from (Reusch, 2015).*

In this thesis work, the dispersions were polymerized with a radical emulsion polymerization process. To interrupt the polymer chain growth, a chain-transfer agent is added. This compound has at least one weak bond and can therefore react with the radical position of the polymer chain. In this reaction, the radical is momentarily transferred to the chain-transfer agent and further transferred to a monomer or another polymer to initiate the growth (Monteiro & de Barbeyrac, 2001).

2 LITERATURE STUDY

A review of potential bio-based stabilizers and their properties in the stabilization of nanoparticle dispersions was undertaken. Only non-ionic and anionic compounds were taken into consideration, according to the research plan. Stabilizers work according to different mechanisms, depending on if they stabilize the interface of the dispersion or if the stabilizer protects the material against external influences, such as oxygen or UV-radiation. Considering the scope of this thesis, bio-based stabilizers which protect the polymer from external influences, such as antioxidants, are not included in the literature study.

Stabilizers in dispersions inhibit or delay the degradation of the polymer, preventing the particles to aggregate or the material to lose its properties. The stability depends on the concentration and type of stabilizer. Using bio-based stabilizers in hydrophobic dispersions can be divided into two approaches: doing the polymerization with the stabilizer present (*in-situ*) or blending the stabilizer with the polymer after the polymerization (*ex-situ*). The in-situ approach reduces the processing steps and potential errors and manipulations (Bel Haaj, *et al.*, 2014).

2.1 Soluble stabilizers

The focus in this thesis was on water-soluble stabilizers. This chapter is divided into structures with lower molar mass (*Chapter 2.1.1 - 2.1.3*) and components with higher molar mass (*Chapter 2.1.4 - 2.1.7*).

2.1.1 Biosurfactants

Surfactants are surface-active molecules, since they consist of both hydrophobic and hydrophilic groups, with a diverse field of applications, *e.g.*, in the oil, food and mining industries (Vijayakumar & Saravanan, 2015; Rosenberg & Ron, 1999). Biosurfactants are produced by micro-organisms, and can be used as stabilizers, emulsifiers, foaming agents *etc.* The broad area of application is due to their ability to increase the solubility and the surface area of hydrophobic water-insoluble substances, and to reduce the surface tension (Vijayakumar & Saravanan, 2015). Biosurfactants with lower molar mass, such as glycolipids, lower the surface tension, whereas substances with higher molar mass are more efficient in stabilizing emulsions (Rosenberg & Ron, 1999).

2.1.2 Phenolic polymers

Natural phenols consist of an aromatic hydrocarbon group bonded to a hydroxyl group, and are widely found in nature, where lignin is the most eminent compound (Panzella & Napolitano, 2017).

Lignin

Lignin is a phenolic polymer found in higher plants, mostly in wood, and is generally obtained as a by-product from the pulp production. The properties vary depending on the plant origin and isolation method, for the moment is most of the lignin obtained used as energy. To be used as a stabilizer for polymer emulsions, the compound should have quite low molecular mass and limited molecular polydispersity (Gregorová, *et al.*, 2005). Lignin is classified as a non-enzymatic natural antioxidant and can lower the formation of free radicals and reactive oxygen during processing and application. Lignin reacts with, *e.g.*, peroxy radicals and transition metals. Due to its phenolic hydroxyl groups and polyphenol structure, lignin has a stabilizing and radical scavenging effect in polymers (Kirschweng, *et al.*, 2017). According to experiments mentioned in the article "*Natural antioxidants as stabilizers for polymers*" by Kirschweng *et al.* (2017), the stabilizing effects of lignin has been mostly studied in PP, PE, PLA and PCL. In the polymer industry, lignin is mainly used as fillers.

In research done by Schmidt *et al.* (2017), lignin fragments were successfully used as a stabilizer of styrene in an emulsion polymerization process. Depending on the concentration of the stabilizer, a polystyrene latex with a solids content of 21% was obtained. Furthermore, the stabilizer showed comparable properties and efficiencies with those of stabilizers based on non-renewable compounds, such as nonylphenol or methylparaben. However, the dispersions coagulated unexpectedly to some extent, indicating on a complicated phase behavior.

Lignosulfonates

Lignosulfonates are produced during the delignification step in the sulfite pulping process. They have an incredibly broad range of molar mass and can be separated from the black liquor by, *e.g.*, ultrafiltration. As of today, the main applications of lignosulfonates are as plasticizer and binder in concrete, making the concrete stronger by reducing the amount of added water. The lignosulfonate molecule has both lipophilic and hydrophilic parts, and, according to Gundersen & Sjöblom (1999), the molecule does not have high surface activity although it is divided into lipophilic and hydrophilic components. Discoloring is considered a disadvantage concerning the use of lignin and lignosulfonates (Gundersen & Sjöblom, 1999).

2.1.3 Alginates

Alginates are the main structural element in, *i.a.*, *Phaeophyceae* (marine brown algae) and a polysaccharide in soil bacteria. They consist of varying sequences of α-L-guluronic acid and β-D-mannuronic acid residues, see *Figure 2.1*. According to K.I. Draget (2009), alginates do not have regular repeating units and the sequences depend on the species in question, *e.g.* bacteria can consist of up to 100% mannuronic acid. Alginates as a resource is regarded as an unlimited source, even for a growing industry, since the production of algae by fermentation is possible but limited today, due to economic aspects.

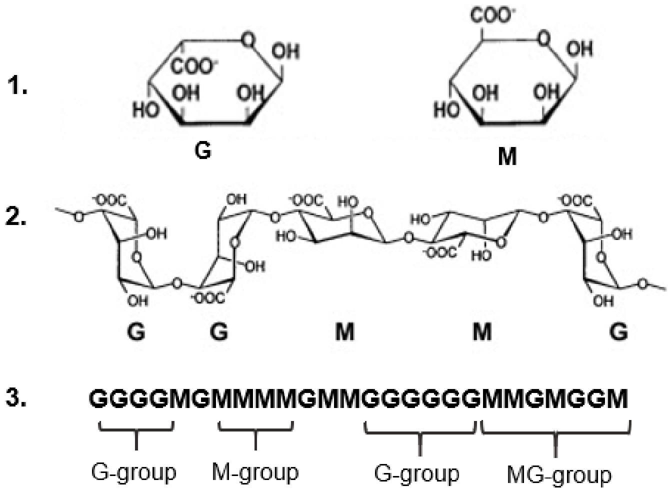


Figure 2.1 *Chemical structure of alginates: 1) α-L-guluronate (G) and β-D-mannuronate (M) as monomers, 2) chain conformation and 3) block distribution of alginates. Picture adapted from (Draget & Taylor, 2009).*

In brown algae, this polysaccharide occurs as a gel that also contains, *e.g.*, calcium, sodium and magnesium ions (Draget, 2009). Thanks to the ability to retain water, along with their viscosifying, stabilizing and gelling properties, alginates are extensively used in different industrial applications (Nan, *et al.*, 2014). The gelling abilities of alginates are based on their ion-binding properties and are independent of temperature. On the other hand, parameters such as chemical composition, sequence, alginate concentration and the ratio gelling/non-gelling ions are important and need to be optimized. Alginates might interact with other charged compounds, *e.g.* proteins, since they are polyelectrolytes, resulting in phase transitions or changes in viscosity. These interactions are of importance in stabilization of a dispersion (Draget, 2009).

According to research done by Daemi *et al.* (2013), when a solution of sodium alginates and aqueous polyurethane was prepared, the alginates were distributed as agglomerations in the polymer matrix. Also, the hydrophilicity of the blend increased with increasing content of sodium alginate. In another similar research, done by Yun *et al.* (2007), the properties of a blend between aqueous sodium alginates and polyurethane-urea as a coating material with high water vapor permeability (WVP), were investigated. The aim was to create a stable formation of a micropore structure. According to the study, the dispersion was stable when the content of sodium alginates was approximately 30 wt.%. Films containing sodium alginates had larger and more micropores, compared to films done with only polyurethane-urea. Also, the WVP was significantly increased in dispersions containing more sodium alginate. This study was utilized in creating better breathable fabrics.

2.1.4 Cellulose

Cellulose is the most important polymeric component in plants. It is composed of repeated *D*-glucose blocks and is a linear semi-crystalline polysaccharide with fascinating properties. Cellulose is described by, *e.g.*, its chirality, hydrophilicity, chemical modifying capacity and biodegradability. It has both crystalline and non-crystalline regions and is insoluble in most organic solvents and in water, due to its supramolecular structure (Klemm, *et al.*, 2005). Cellulose derivatives can be grafted with synthetic polymers to create amphiphilic materials. Grafted polymers are co-polymers where the main-chain and the branches are different compounds. This gives the polymer new characteristics, such as adhesion, hydrophilicity or biocompatibility (Paine, 1990). These derivatives are used in many applications, such as, cosmetics, food, packaging and pharmaceutics, thanks to their non-toxic nature (Rescignano, *et al.*, 2014; Doelker, 2005).

Hydroxypropyl cellulose, HPC

Hydroxypropyl cellulose, HPC, is one of many derivatives from cellulose, this polymer is soluble in both water and in organic solvents (Chattopadhyay, *et al.*, 2001). HPC is a branched, anionic polysaccharide and widely used as a thickening agent due to its surface-active properties (Mezdour, *et al.*, 2008).

According to experiments described in the article "*Dispersion polymerization of styrene in polar solvents. IV. Influence of reaction parameters on particle size and molar mass on Poly(N-vinylpyrrolidone)-stabilized reactions*", by Paine *et al.* (1990), by using HPC as a stabilizer in the polymerization of styrene, the HPC become grafted and end up as 10 – 20 nm thick layers on the surface of the styrene particles. The initial styrene concentration determines the particle dispersity, lower concentrations result in monodisperse particles while polydispersity is a result of higher styrene concentrations. However, the average molecular mass remained practically constant. Depending on the solvent used in dispersion polymerization of styrene with HPC as a stabilizer, the particle size varies (Paine, *et al.*, 1990; Paine, 1990).

2.1.5 Chitosan

One of the most important natural polymers is chitin, a polysaccharide found in many crustaceans and in some insects and microorganisms. The main sources of commercial chitin are shrimp and crab shells and is extracted by acid treatment followed by an alkaline treatment. Chitosan is a derivative of chitin; when the deacetylation of chitin under alkaline conditions reaches 50%, the polymer becomes soluble in aqueous acidic solution. Due to the semi-crystalline structure of chitin, chitosan has acetyl groups distributed along its chains (Rinaudo, 2006). The properties of chitosan depend on its degree of acetylation (DA) and the distribution of the acetyl groups along the polymer chain (Phan, *et al.*, 2019). Chitin is harder to process compared to chitosan, however, chitosan has a lower stability due to a more hydrophilic nature and pH sensitivity. Chitosan is a non-toxic cationic polymer and is utilized to prepare films, hydrogels fibers *etc.*, mostly in the biomedical field (Rescignano, *et al.*, 2014; Rinaudo, 2014).

According to research done by Marie *et al.* (2002), mere chitosan as a stabilizing agent for nanoparticle emulsions is insufficient. As stated in the experiment in the article "*Synthesis of chitosan-stabilized polymer dispersions, capsules, and chitosan grafting products via mini-emulsions*", chitosan cannot prevent the polymer particles from coagulation. However, by adding small quantities of some other surfactant with low molar mass or a flexible polymer as a co-stabilizer, the structure on the surface of the particles improves significantly and the overall stability is enhanced.

2.1.6 Hemicelluloses

Hemicelluloses are polysaccharides found in cell walls of plants and they are the third most abundant polymer found in plants, after cellulose and lignin. The structure and the amount of hemicelluloses vary depending on the plant type. They are soluble in alkaline environments, arabinogalactan (AG) from larch is also extractable in hot water. Some parts of the hemicellulose are entrapped in cellulose or lignin or is bond to them by hydrogen bonds. The lower the molar mass, the easier solubilized in the solution. Also, the degree of branching and content of uronic acid and acetyl groups influence the solubility. Hemicelluloses are destroyed during the kraft pulping process, but can be extracted from wood by hot-water extraction (Whistler, 1993).

In a research done by Zhang *et al.* (2015), an emulsion polymerization of acrylamide and butyl acrylate was done using hemicellulose as a stabilizer, generating a monomer conversion of almost 98%. Apart from stabilizing the dispersion, the hemicellulose also lowered the particle size significantly. This latex was used in water clarification processes, as an absorbent towards methylene blue dyes.

2.1.7 Other polysaccharides

Pectin

Pectins are a mixture of polysaccharides found in the primary cell walls of almost every plant grown on land. Commercially, pectin is used as a gelling agent and stabilizer in food and are mainly extracted from citrus fruits and sugar beet pulps. The structure is quite complex and depends on the extraction process and the original source. Best emulsifying properties were found in pectins with a low content of acetyl groups and depending on the extraction method, low molar mass (60 – 70 kg mol^{-1} according to Leroux *et al.* (2002)), and had also a high degree of methoxylation (Leroux, *et al.*, 2002; Akhtar, *et al.*, 2002). Pectin derived from citrus fruits have emulsifying properties and the pectin itself is a very surface-active molecule that can create emulsions with droplets on a smaller scale in oil-in-water emulsions (Verkempinck, *et al.*, 2018).

2.2 Insoluble stabilizers

Stabilizers insoluble in water are described in the following chapter, with focus on particle stabilized emulsions.

2.2.1 Pickering emulsions

Pickering emulsions are stabilized by either organic or inorganic colloidal particles, which form a steric barrier against coalescence around the droplet, whereas surfactants stabilize classical emulsions, see *Figure 2.2* (Chevalier & Bolzinger, 2013; Horozov & Binks, 2006). Pickering emulsions can be a replacement for classical emulsions in many applications, since they preserve the main properties of classical emulsions (Chevalier & Bolzinger, 2013).

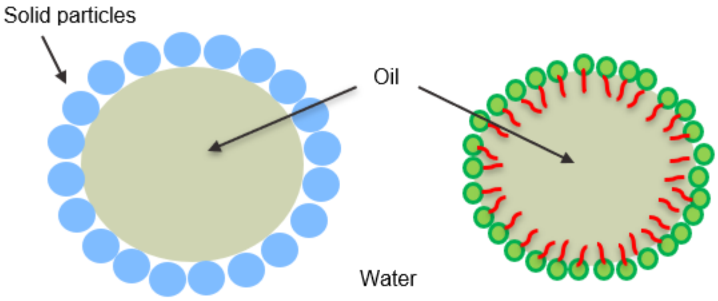


Figure 2.2 *Illustration of Pickering oil-in-water emulsions (left) and classical emulsions (right). Picture adapted from (Chevalier & Bolzinger, 2013).*

By modification of the particle surface, they can be less or more hydrophobic, depending on the desired outcome of the stabilization (Horozov & Binks, 2006). According to the article "*Ferritin as a bionano-particulate emulsifier"* written by Fujii *et al.* (2009), numerous organic particles, such as, microgel and core-shell particles or sterically- or charge-stabilized polymer particles can work as potential particulate stabilizers, *i.e.*, organic polymers turn the surface of the particle more hydrophobic. Also, inorganic particle, *e.g.*, silica, ceramics, metals or semiconductors have possibilities in this area.

In the example illustrated in *Figure 2.2*, the adsorption of the particles at the interface between oil and water requires partial wetting of the particles by both oil and water. If the surface of the solid is very hydrophilic, the particle will be entirely wet by water. Additionally, a hydrophobic surface will be completely wet by the oil. The stability of the emulsion is at maximum when the adsorption is as strong as possible, *i.e.*, when the contact angle between the solid particle and the liquid is 90° (Chevalier & Bolzinger, 2013).

In experiments explained in the article "*Pickering polymerization of styrene stabilized by starch-based nanospheres*", by Pei *et al.* (2016), starch is one of the most promising natural polymers to function as a stabilizer of styrene. Inorganic particles, such as zinc oxide or silica, have generally been used as stabilizing agents in Pickering emulsions. Nevertheless, these compounds need modification to obtain stabilizing abilities, contrary to natural polymers such as starch. In addition, chitosan nanoparticles, cellulose nanofibrils and modified starch nanoparticles have been utilized in stabilization of Pickering emulsions.

Starch

Starch is a polysaccharide consisting of glucose units linked by α-glycosidic bonds, compared to β-glycosidic bonds in cellulose. Starch is providing energy to green plants and is a common compound in the human diets, as it is found in, *e.g.*, potatoes, corn, rice and wheat. Furthermore, starch is widely used in the food industry due to its stabilizing and emulsifying properties. Starch is mainly used as a stabilizer in Pickering emulsions (Pei, *et al., 2016)*.

In a research done by Bel Haaj *et al.* (2014), latex using starch nanocrystals (SNC) as stabilizing agent in Pickering emulsions was successfully attained. SNC hydrolyzed by HCl showed improved stabilization effect and a reduced average particle size, compared to nanocrystals from H_2SO_4 hydrolysis. However, the SNC were not sufficient in stabilizing the monomers by themselves, due to this, a cationic surfactant was added to improve the stabilization. In another research, done by Pei *et al.* (2016), starch-based nanospheres were successfully used as a Pickering stabilizer in the polymerization of styrene.

In the article "*Optimization of synthesis and characterization of oxidized starch-graft-poly(styrene-butyl acrylate) latex for paper coating*" by Cheng *et al.* (2015), different variables such as, temperature, monomers, initiator *etc.*, were investigated to improve the properties of the latex used as a binder in paper coating. The best results were achieved at 70°C with a concentration of 40% monomers, 4.4% stabilizer and 0.3% initiator. According to the results, these latexes can be used as coating alternatives since they improved the gloss and picking resistance in coated papers.

3 EXPERIMENTAL PART

The aim of this work was to evaluate performance of different bio-based stabilizers in nanoparticle dispersions and achieve satisfying dispersion properties. The dispersions will be utilized in surface sizing of paper board. This means good properties, especially regarding viscosity and particle size distribution, are desired. The aim to achieve particles at nanoscale was due to the dispersion's application in surface sizing, since smaller particles have greater adhesive forces. Furthermore, the viscosity needed to be below a certain limit, to facilitate the sizing process.

The reference polymerization was performed using a polysaccharide-based stabilizer, and the same recipe was used as base recipe in the polymerizations stabilized by other stabilizers.

3.1 Materials

3.1.1 Stabilizers

The reference polymerization was done by using Stabilizer 1, a polysaccharide dissolved in water. In most polymerizations, Stabilizer 2 was used, which was a water-soluble compound consisting of certain polysaccharides combined with lignin-based polyelectrolyte polymers, and has an average molar mass of approximately 4 500 g/mol. Furthermore, several polymerizations using Stabilizer 3 were tested, which was a stabilizer consisting of the lignin-based polyelectrolyte in Stabilizer 2, to compare its properties to Stabilizer 2. Stabilizer 1 and 3 were powders, and Stabilizer 2 was in liquid form.

3.1.2 Initiators

Initiator 1 was used in most of the polymerizations, diluted in water into a 3.5 wt.% solution. In two polymerizations Initiator 2 was utilized, diluted into a 9 wt.% solution. In several polymerizations, Initiator 3 was added to promote the polymerization and decrease the amount of residual monomers. An iron catalyst was part of the redox initiation in the polymerization process.

3.1.3 Monomers

The monomer mixture contained three different monomers, named Monomer 1, 2 and 3. All polymerizations had the same amount of monomers, with a mass ratio of 50% of Monomer 1 and 25% each of Monomer 2 and 3.

3.1.4 Other compounds

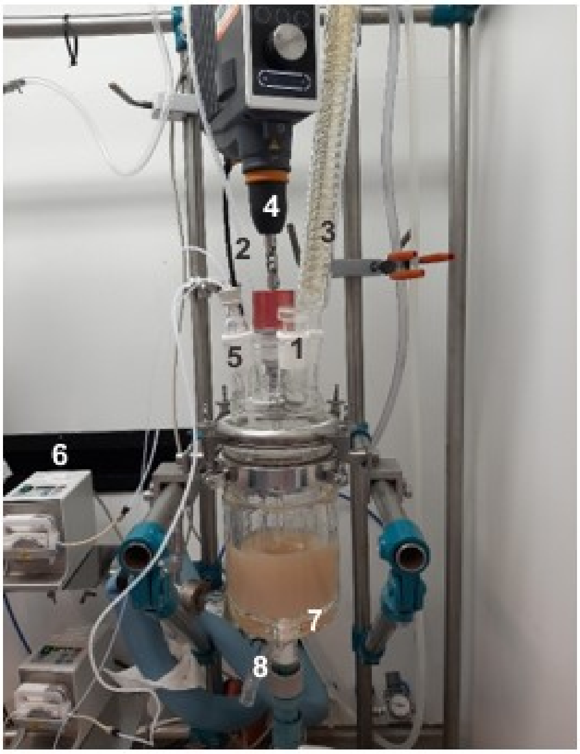
The reaction medium was distilled water, and the polymerization was executed in a continuous flow of nitrogen (N_2). Either sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4), both 30%, were used for pH adjustment. In a few polymerizations, a chain-transfer agent was added to modify the polymer chain, referred to as Substance A.

3.2 Methods

The standard recipe mentioned in this thesis is referring to the recipe used in the reference polymerization by Stabilizer 1. Variations in the recipe were made to achieve better results concerning the polymerization process. The recipe using Stabilizer 1 was used in the first polymerization using Stabilizer 2, and only adjustments according to the stabilizer's solids content were made. The polymerization process is explained in the following section.

3.2.1 The polymerization process

This polymerization is referred to as the standard recipe. The first step in the polymerization process was to add the stabilizer dissolved in water to the reactor, followed by the addition of a catalyst as part of the redox initiation. A schematic picture of the reactor is shown in *Figure 3.1*, where all these compounds are added through the valve (1). A flow of N_2 was continuously fed through the system, (2).



1. Input of stabilizer, catalyst and H_2O
2. Continuous N_2 feed through the system
3. Condenser with cooling water
4. Stirrer
5. Monomer and initiator at constant rate
6. Pump
7. Heating jacket
8. Discharge valve

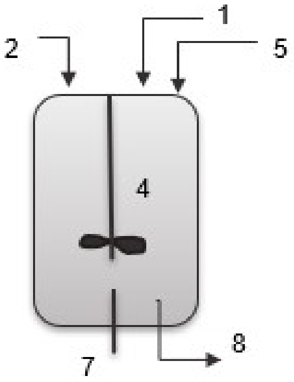


Figure 3.1 *Scheme of the polymerization reactor and its functions, step 1 to 8. Photo: Private.*

The compounds were mixed during 60 minutes at a given temperature (75°C; 85°C or 93°C in this thesis). After 60 min, the pH was adjusted to a given value and a sample was taken to assure the pH was stable at 25°C.

This was followed by the radical polymerization with monomers and an initiator to initiate the polymerization, here Initiator 1, explained in *Figure 3.1* as (**5**) and (**6**), where the pump was feeding the monomers and initiator to the reactor at constant rate. The feeding time was 120 min and stirring rate was 200 rpm (**4**).

A sample was taken after 120 min (referred to as S_1) through the valve at the bottom of the reactor, (**8**). The same properties as the target properties, mentioned in *Table 1.1* in *Chapter 1.1*, were analyzed. If the solids content was below the theoretical solids content of the recipe, approximately 25%, a second feed of initiator was added, at the same rate and concentration as before. The second feed of initiator was on until the solids content met the criteria of 25%, but not longer than 120 min. When the targeted solids content was achieved, in other words, the polymerization was presumably completed, a further mixing of 45 min at constant temperature was done to finalize the polymerization and to minimize the extent of residual monomers.

The reactor and dispersion cooled down to room temperature. The pH was adjusted to approximately 4.5, whereupon the dispersion was filtered through a 100 µm filter and, if necessary, diluted if the solids content was too high. The dispersions were stored at room temperature in glass bottles. The polymerization process steps are also found in *Appendix A*.

The polymerization time was in total a maximum of 225 min + max.120 min + cooling time, where the 120 min feed was depending on the solids content of S_1. If Initiator 3 was added to the polymerization, another 60 min of stirring was added.

3.2.2 Variations in the recipe

Variations in the recipe and the polymerization process were done, to achieve better results and to investigate impacting factors.

pH

Different factors were investigated, such as, pH. The pH during polymerization was adjusted between 1.8 and 7.0, to investigate the impact of the pH on the polymerization rate and the properties of the dispersion. All polymerizations were made with the standard recipe, described in *Chapter 3.2.1*, and with Stabilizer 2 and Initiator 1, at 85°C. The polymerizations are listed in *Table 3.1*. The pH mentioned was maintained during polymerization, the final dispersion was always adjusted to approximately 4.5. The polymerization at pH 5.0 was repeated.

Table 3.1 *Variations in pH at 85°C, polymerized with Stabilizer 2 and Initiator 1*

Test No.	pH	T [°C]	Recipe
5	1.8	85	Standard
2	2.3	85	Standard
6	2.8	85	Standard
7	3.2	85	Standard
8	3.8	85	Standard
14 & 19	5.0	85	Standard
9	6.0	85	Standard
20	7.0	85	Standard

Temperature

The polymerizations were mainly done at 85°C but a few were done at 93°C and one at 75°C, keeping the pH constant, see *Table 3.2*. Polymerizations were done using Stabilizer 2 and Initiator 1.

Table 3.2 *Variations in temperature at pH 5.0, polymerized with Stabilizer 2 and Initiator 1*

Test No.	pH	T [°C]	Recipe
12	5.0	93	Standard
15	5.0	93	40% more initiator
17	5.0	93	20% more stabilizer
14 & 19	5.0	85	Standard
13	5.0	75	Standard

Variations at pH 5.0

At pH 5.0 and 85°C, polymerizations using additional amounts of Stabilizer 2 and different feeding rates of monomers and initiators were investigated, see *Table 3.3*. The polymerizations were done using Stabilizer 2 and Initiator 1.

Table 3.3 *Variations at pH 5.0 and 85°C, polymerized with Stabilizer 2 and Initiator 1*

Test No.	pH	T [°C]	Recipe
14 & 19	5.0	85	Standard
16	5.0	85	20% more stabilizer
26	5.0	85	40% more stabilizer
21	5.0	85	Different feeding rates

Variations at pH 6.0

As clarified in *Table 3.4,* Substance A and Initiator 3 were added to the polymerization process at pH 6.0. If Initiator 3 was added, an additional mixing of 60 min was necessary. A dispersion containing 20% more stabilizer was executed for comparison to the similar dispersion polymerized at pH 5.0. The polymerizations were done using Stabilizer 2 and Initiator 1.

Table 3.4 *Variations at pH 6.0 and 85°C, polymerized with Stabilizer 2 and Initiator 1*

Test No.	pH	T [°C]	Recipe
9	6.0	85	Standard
18	6.3 [a]	85	20% more stabilizer
22	6.0	85	Substance A added
23	6.0	85	Initiator 3 added
24	6.0	85	Substance A & Initiator 3 added

[a] *pH adjusted to 6.3 due to misleading pH measurements.*

Initiator

In all polymerizations, Initiator 1 was used as initiator, apart from two polymerizations, see *Table 3.5*, where initiator 2 was used. These polymerizations were not pursued any further due to shortage of time. The polymerization was stabilized by Stabilizer 2 and Initiator 2, at 85°C.

Table 3.5 *Polymerizations at 85°C with Stabilizer 2 and Initiator 2*

Test No.	pH	T [°C]	Recipe
10	5.5	85	Standard, Initiator 2
11	2.3	85	Standard, Initiator 2

Stabilizer 3

Four polymerizations using Stabilizer 3 were done, to compare the properties to polymerizations stabilized with Stabilizer 2. Since Stabilizer 3 was a powder, a different ratio stabilizer-to-water was necessary to meet the solids content criteria. All polymerizations were executed with Initiator 1 at 85°C, at pH 2.3 and 5.0, see *Table 3.6*.

Table 3.6 *Polymerizations at 85°C with Stabilizer 3 and Initiator 1*

Test No.	pH	T [°C]	Recipe
27	2.3	85	Standard
28	5.0	85	Standard
29	5.0	85	Substance A and Initiator 3 added
30	5.0	85	40% more stabilizer

Zeta potential measurements

The ζ-potential was measured for some dispersions, to predict their colloidal stability. The dispersions are stated in *Table 3.7*.

Table 3.7 *Zeta potential measurements of dispersions polymerized with Stabilizer 1; 2 and 3, all initiated by Initiator 1 at 85°C*

Test No.	pH	Stabilizer
Ref.	2.3	1
8	3.8	2
19	5.0	2
28	5.0	5

3.3 Determinations and analyses

3.3.1 pH and viscosity

The pH was measured with *Knick Portamess 911 pH Meter*, and the viscosity (η) with *Brookfield Ametek Dv1 Digital Viscometer.* Brookfield viscosity was measured with spindle 18 and at 60 rpm if nothing else is stated.

3.3.2 Solids content

The solids content (*SC*) was analyzed by *Mettler Toledo – Halogen moisture analyzer HR73*. Approximately 3 g of the dispersion was needed for one measurement.

3.3.3 Particle size distribution

The particle size distribution (PSD) and average particle size (D50 and D90) were measured by *Malvern Zetasizer Nano*, where light scattering is used to measure the distribution. One drop of the dispersion was diluted in 1 ml H_2O, in some cases the ratio was increased to either two drops in 1 ml H_2O or one drop diluted in 2 ml H_2O, depending on the mean count rate that should be between 200 and 500 kcps, according to the instructions. The device can measure particles between approximately 1 nm to 6 µm.

3.3.4 Molar mass and molar mass distribution

The molar mass and the molar mass distribution were determined by *SEC Agilent 1100 series with RI detector*, a method separating molecules according to their size and molar mass, or more correctly, their hydrodynamic volume (Stevens Creek, 2015). The samples were freeze-dried and dissolved in an eluent (DMF + 5 g/l LiCl) before the analysis.

3.3.5 Residual monomers

Residual monomers were analyzed by *HPLC Agilent 1200 Series Infinity II LC Systems*. HPLC, high-performance liquid chromatography, is an analysis method used to identify and quantify individual molecules in a mixture (Stevens Creek, 2014). A few dispersions were analyzed by HPLC to identify and quantify residual monomers, to adjust the following polymerizations by enhancing the polymerization rate to minimize the amount of residual monomers.

3.3.6 Zeta potential

One important property of the dispersion was its stability, and the ability to remain stable over time. The determination of ζ-potential was measured by *Malvern Zetasizer Nano*. The pH of the suspension was adjusted between 2.0 and 8.0, to investigate at what pH the dispersion was stable. The explanations of the generated values of the ζ-potential are found in *Table 3.8*.

Table 3.8 *Explanations of ζ-potential values (Ishikawa, et al., 2005)*

ζ-potential [mV]	Stability behavior of the colloid
From 0 to ± 5	Rapid coagulation or flocculation
From ± 10 to ± 30	Incipient instability
From ± 30 to ± 40	Moderate stability
From ± 40 to ± 60	Good stability
More than ± 61	Excellent stability

4 RESULTS AND DISCUSSION

The target of this thesis was to identify and adjust impacting factors of the polymerization and to reach approximately the same results concerning properties as the dispersions stabilized with an already known polysaccharide. One important aspect was to identify the correlation between various factors that affected the polymerization and optimize the factors to improve the polymerization reaction. Different recipes and polymerization conditions were tested to obtain optimal properties of the dispersions.

Properties such as solids content and pH were adjusted to reach the target, whereas particle size was depending on the conditions during polymerization. The target properties are found in *Table 4.1*, and are described in *Chapter 1.1*.

Table 4.1 *Target properties of the dispersion*

Property	Target
SC [%]	20 – 30
pH	4.0 – 6.0
η spd 18 [mPas]	< 200
D90 [nm]	< 200
D50 [nm]	< 100

Polymerizations were generally not repeated due to shortage of time, but to receive more reliable data, polymerizations should be done at least three times. Considering this, the achieved data might be to some extent deceptive. Some polymerizations were repeated due to deviant essential results. All polymerizations were initiated by Initiator 1 unless something else is stated.

4.1 Polymerization with Stabilizer 1

As a reference, a polymerization using Stabilizer 1 was performed. The use of Stabilizer 1 has been investigated earlier and the dispersion showed good properties, hence the use as a reference dispersion in this thesis work. This stabilizer was commonly used in nanoparticle dispersions, since the stabilizer was grafted to the monomers and created small particles

(Pei, *et al.*, 2016). The achieved properties of the dispersion are found in *Table 4.2*, and all properties were within the target (*Table 4.1*).

Table 4.2 *Properties of the dispersion stabilized with Stabilizer 1 and Initiator 1, at 85°C and pH 2.3*

Property	**Result**
SC [%]	28
pH	4.5
η [mPas]	4.0
D90 [nm]	115
D50 [nm]	57

The polymerization was executed according to the recipe described in *Chapter 3.2.1*, apart from an addition of a pretreatment with a solution of 8 wt.% of Initiator 1, that was added to the reactor before the monomer feed.

4.2 Polymerizations with Stabilizer 2 at different pH

All polymerizations were accomplished using the same standard recipe, using Stabilizer 2 and Initiator 1, with only variations in pH. In *Figure 4.1*, the solids content of the dispersion after 120 min of polymerization, S_1, and the final dispersion are shown at different pH, compared to the amount of additional initiator.

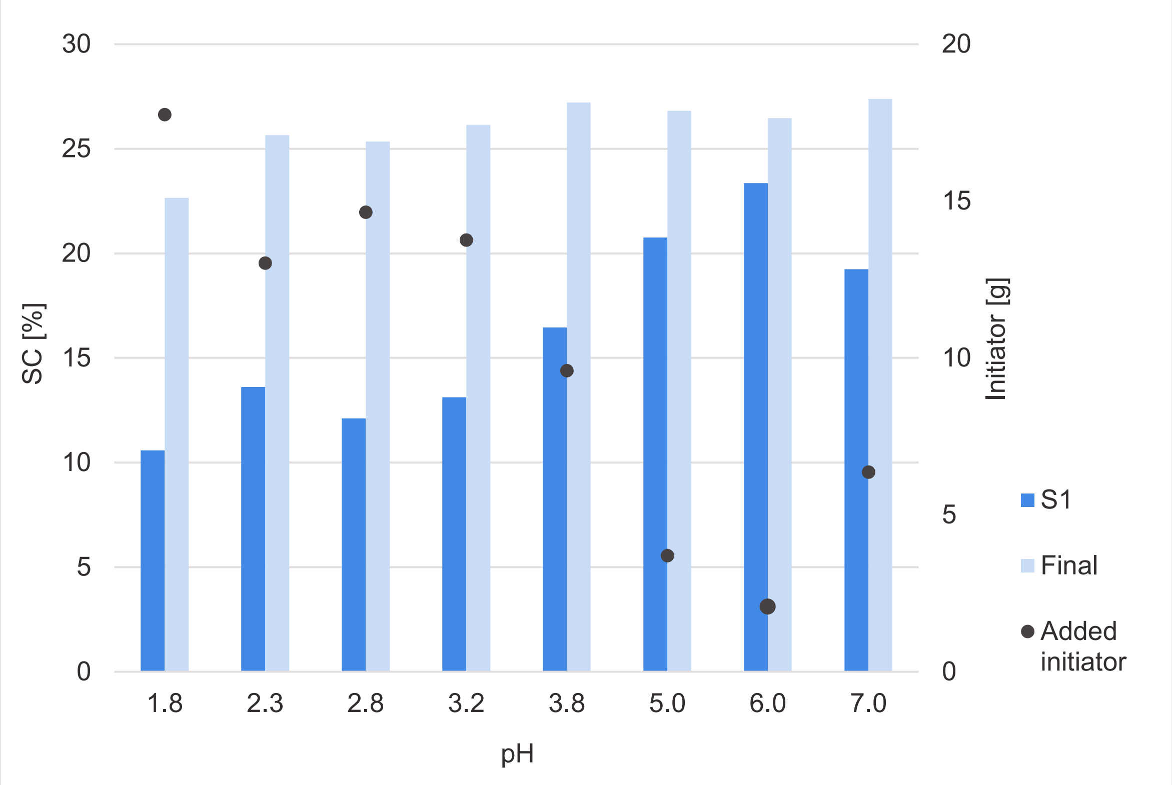


Figure 4.1 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and different pH.*

Increasing the pH above 1.8, increased the solids content of S_1, meaning that the monomers did not polymerize completely at lower pH (*Figure 4.1*). Due to this, the initiator feed was continued at the same rate to increase the solids content, after the monomer feed was completed. The highest solids content after 120 min of polymerization, about 24%, was achieved at pH 6.0, as S_1 in *Figure 4.1*. This indicates the polymerization process was presumably successful, since, in these polymerizations, lower solids content indicates an unfinalized polymerization (Reed & Alb, 2014). Polymerizations were not executed at higher pH than 7.0 since the monomers were starting to hydrolyze at higher pH. If the solids content was high, above approximately 29%, water was added to dilute the final dispersion.

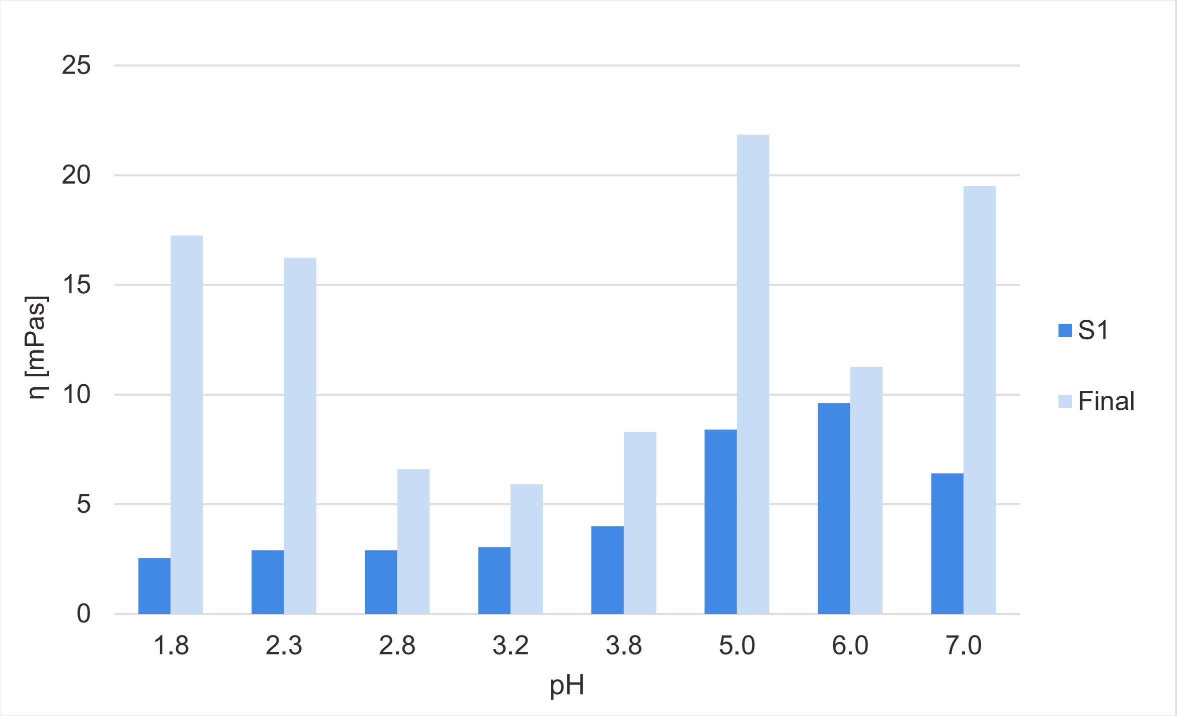


Figure 4.2 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and different pH. The Brookfield viscosity was measured with spindle 18 at 60 rpm.*

As observed in S_1 in *Figure 4.2*, the viscosity increased as the solids content increased in *Figure 4.1*. The target was to obtain dispersions with a viscosity below 200 mPas, which making the highest obtained viscosity at approximately 22 mPas at pH 5.0 considerably under the limit (*Figure 4.2*). Only small differences in viscosity were seen for dispersions from different polymerizations; the maximum scale was 25 mPas.

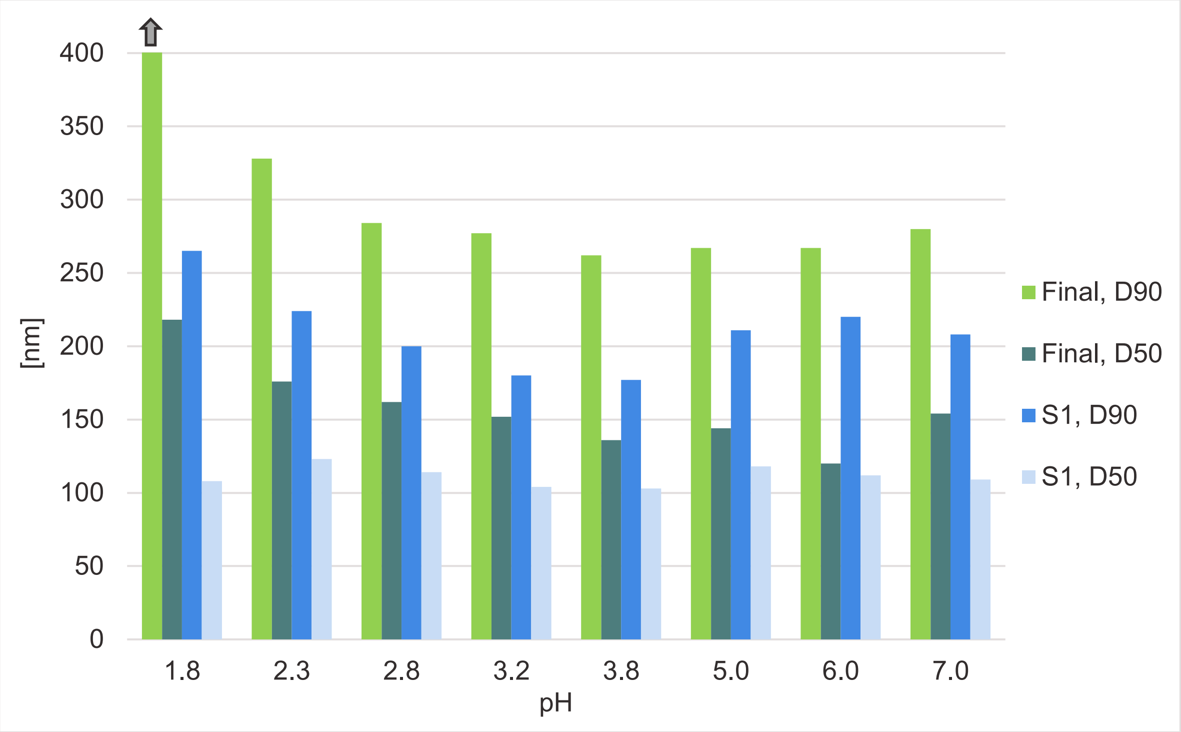
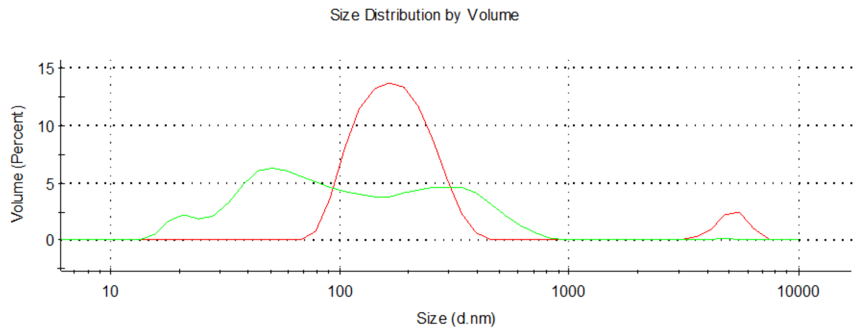


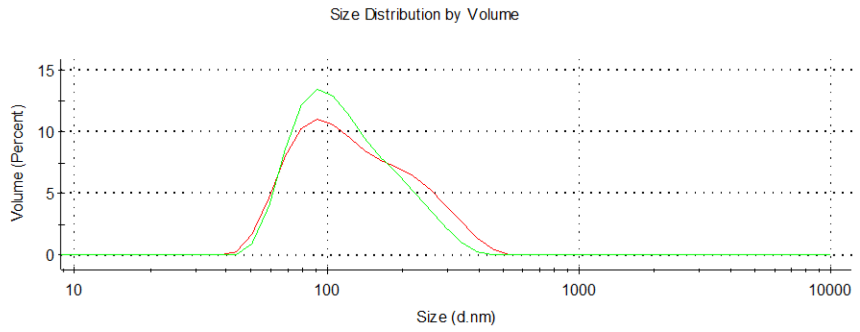
Figure 4.3 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and different pH. The final D90 value at pH 1.8 was 4 380 nm.*

The average particle size did not change remarkably when comparing polymerizations at pH 2.8 to 7.0. However, as seen in *Figure 4.3*, the average particle size was very large at pH 1.8. The particle size D50 of the final dispersion was at its smallest at pH 6.0, about 220 nm, along with practically no variations in particle size D90 between pH 3.8 and 6.0. The particle sizes (D50 and D90) were larger than the target values (*Table 4.1*). Considering this, further polymerizations were attained at pH 5.0 and 6.0 while changing other factors, to obtain a smaller particle size.

As seen in *Figure 4.4*, the PSD was significantly broader for S_1 in dispersions made at pH 2.3, compared to those made at pH 6.0. In the final dispersion, there was a second peak in the dispersion polymerized at pH 2.3, indicating that the dispersion did contain a small number of very large particles. Since the PSD was weighted by volume, even a small amount of larger particles would skew the distribution graph. PSD graphs from all polymerizations are found in *Appendix F*.



pH 2.3: S1 and Final



pH 6.0: S1 and Final

Figure 4.4 *Particle size distribution by volume, in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 2.3 (above) and pH 6.0 (below). The red curve shows the PSD of the final dispersion and the green curve shows the PSD of the S_1 sample.*

All dispersions contained residual monomers (*Figure 4.5*), which means the polymerization was not completed even though the solids content was between 25 and 30%. The sample marked as “pH 6.0^a” was taken immediately after the solids content of the dispersion was higher than 25% (after 195 min), whereas the dispersion labeled as “pH 6.0^b” was the final dispersion after a full polymerization time (300 min). The reference dispersion polymerized with Stabilizer 1 contained 0 mg monomers/kg (results not shown).

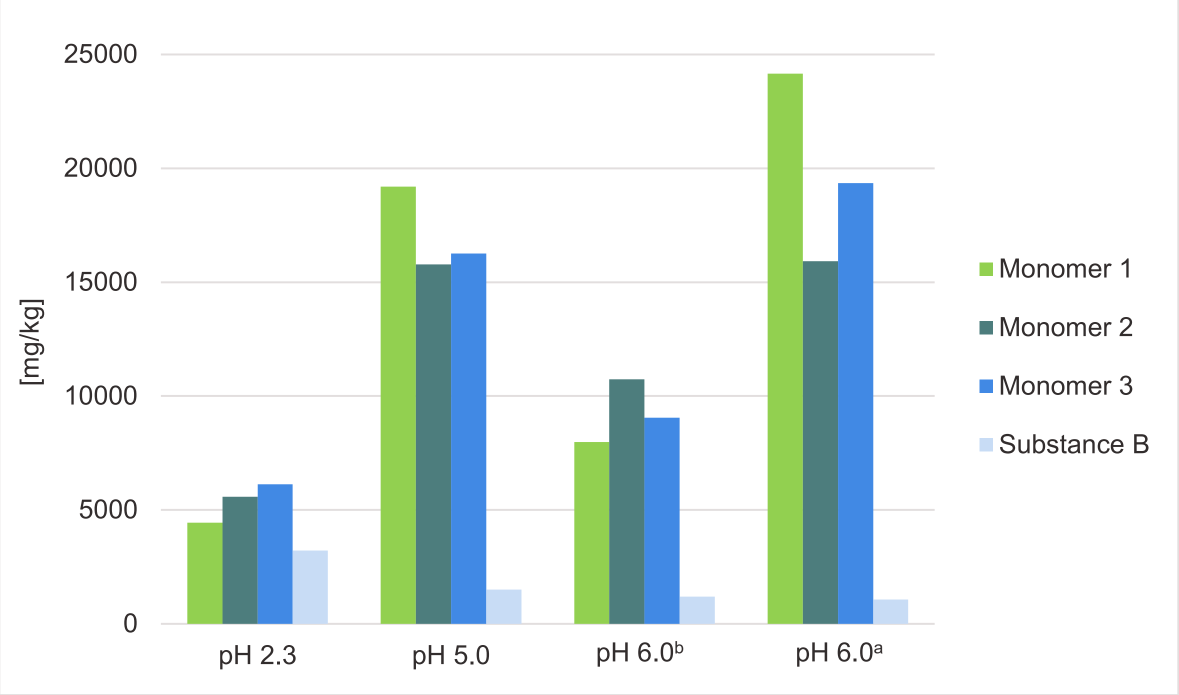


Figure 4.5 *Residual monomers in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 2.3: 5.0 and two dispersions at pH 6.0. The analysis sample "pH 6.0^a" was taken after the solids content was higher than 25% and a mixing time of 45 min (a total time of 195 min), while the sample "pH 6.0^b" was taken after a fulltime polymerization (a total time of ca. 300 min). Substance B was a by-product from Monomers 2 and 3.*

The dispersion polymerized at pH 2.3 contained the smallest amount of residual monomers, since the polymerization had the longest additional feeding time of the initiator, to reach the solids content of 25%. Furthermore, the dispersion that had a fulltime polymerization at pH 6.0 (pH 6.0^b) contained less monomers compared to the sample taken earlier in the same polymerization process (pH 6.0^a). All presumably successful dispersions, *i.e.* had a solids content of approximately 25%, had a dark color and did not show evidence of phase separation, see *Figure 4.6*.

Figure 4.6 *Dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and at pH 5.0 (left) and pH 7.0 (right). No phase separation was observed, a small amount of dispersion was dried on the inside of the left bottle creating the illusion of a false phase separation. Photo: Private.*

Considering the results in this chapter, the dispersions polymerized at pH 5.0 and 6.0 generated the best average results when comparing the results from polymerizations done at different pH to the target properties listed in *Table* in *Chapter 4*. Furthermore, the PSD was narrower in polymerizations executed at pH 5.0 and 6.0, compared to polymerizations at lower pH values. The polymerization was possibly hindered by impurities in the stabilizer since it is a bio-based compound. Also, phenolic groups or inorganic salts can slow down the polymerization reaction, making the additional feed of initiator necessary to reach the final solids content and complete the polymerization of the monomers. Phenolic groups have radical scavenging effects and, since the polymerization was a radical polymerization process, the phenolic compounds might interact with the radicals formed by the initiator and the catalyst, and disturb the reaction between monomers and radicals (Braun, 2009; Kirschweng, *et al.*, 2017).

4.3 Polymerizations at pH 5.0 with Stabilizer 2 and with modified recipe

Polymerizations executed at pH 5.0 with varying temperature, amount of stabilizer and initiator, and feeding rate of initiator are investigated in this chapter. All dispersions were stabilized by Stabilizer 2 and initiated by Initiator 1.

4.3.1 Polymerizations at 85°C and pH 5.0 with added stabilizer and different monomer feed

Four polymerizations at pH 5.0 and 85°C were executed with Stabilizer 2, as polymerization at this pH gave one of the most promising results declared in *Chapter 4.2*. Apart from the dispersion polymerized at pH 5.0, two dispersions containing approximately 20% and 40% more stabilizer and one dispersion with different feeding rates of initiator and monomers, were executed. The modified feeding rate was executed as following: during the first 15 minutes of the polymerization, 1/3 of the initiator and monomers were added to the reactor at a constant rate. For the following 120 min, the other 2/3 of the amount were added to the reactor at constant rate. This gave a total time of 135 min. All other polymerizations had a feeding time of 120 min, with constant rate.

As observed in *Figure 4.7*, the dispersion polymerized at different feeding rates generated the highest solids content for the S_1 sample. The polymerization rate was faster if there was a larger amount of initiator in the reactor when the monomers started to polymerize, considering the radical polymerization process (Braun, 2009).

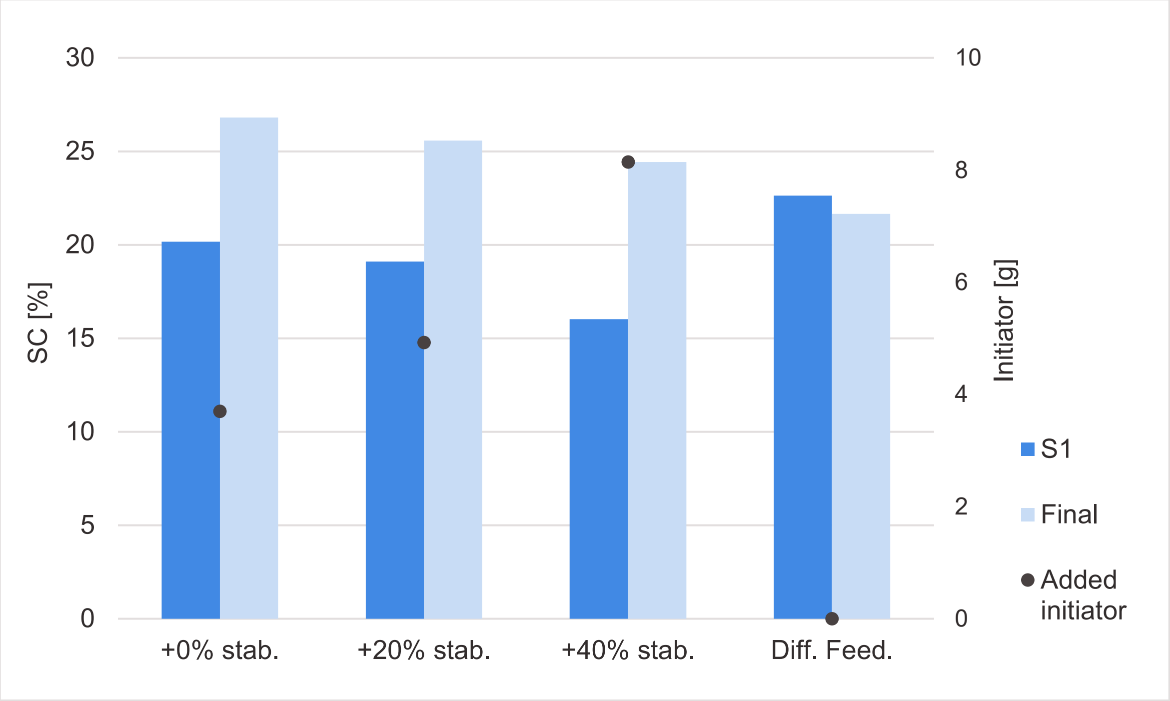


Figure 4.7 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 5.0 containing 0%, 20% and 40% more stabilizer, and with different feeding rates of the initiator.*

When more stabilizer was added to the reaction, the theoretical solids content was calculated to approximately 22%. The dispersion containing 40% more stabilizer contained also 35% more water, resulting in a more diluted dispersion and lower solids content. There was no second feed of initiator added to the dispersion polymerized with different feeding rates. In afterthought, a second feed of initiator could have been added to achieve higher solids content than 21.5%.

Concerning the viscosity, no considerable variations were detected (*Figure 4.8*). The narrow variations can be equally well explained by differences in repeating experiments since the difference was only approximately 13 mPas. With increasing amount of stabilizer, the amount of water increased proportionally. This lowered the calculated solids content of the dispersion to 22% and made it slightly more diluted, which lowered the viscosity.

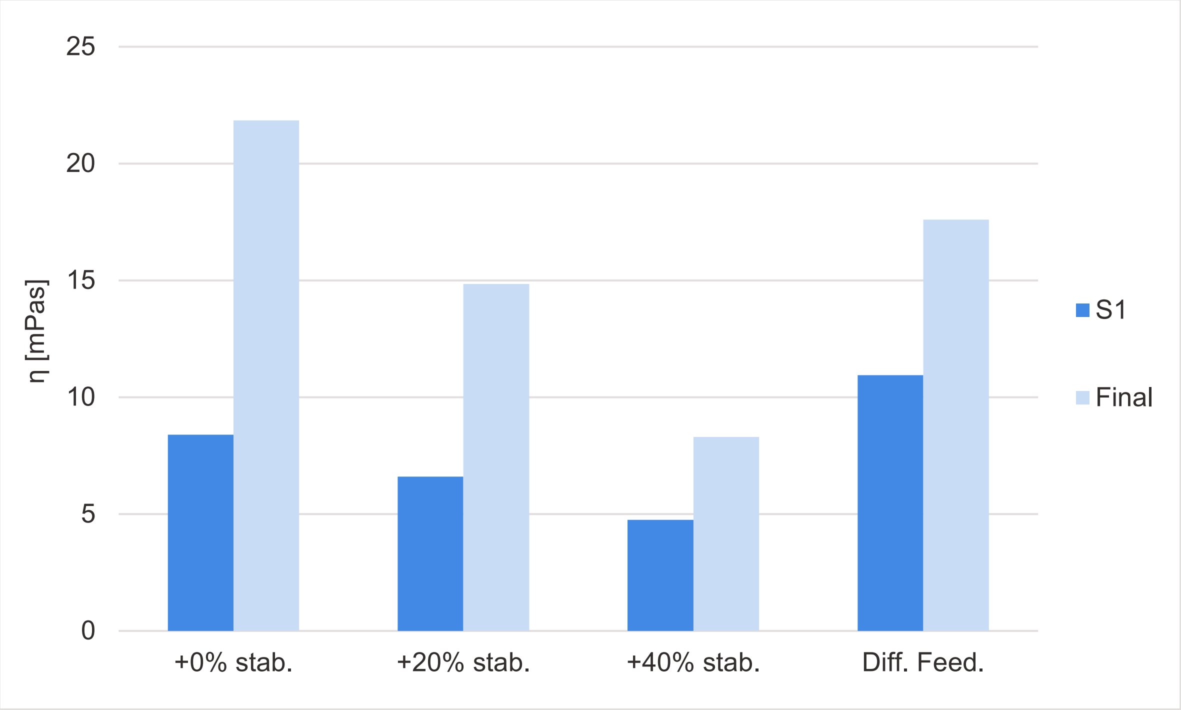


Figure 4.8 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 5.0, containing 0%, 20% and 40% more stabilizer, and with different feeding rates of the initiator. The Brookfield viscosity was measured with spindle 18 at 60 rpm.*

The particle size decreased when the amount of stabilizer increased, seen in *Figure 4.9*. Presumably, more stabilizer inhibited the molecules from agglomeration to some extent. Feeding the initiator and monomers to the reactor at different rates did not have any conspicuous impact on the particle size compared to normal feeding rates. However, the nucleation mechanism should presumably be different at various concentrations of initiator, making the average particle size of the dispersions different (Monteiro & de Barbeyrac, 2001).

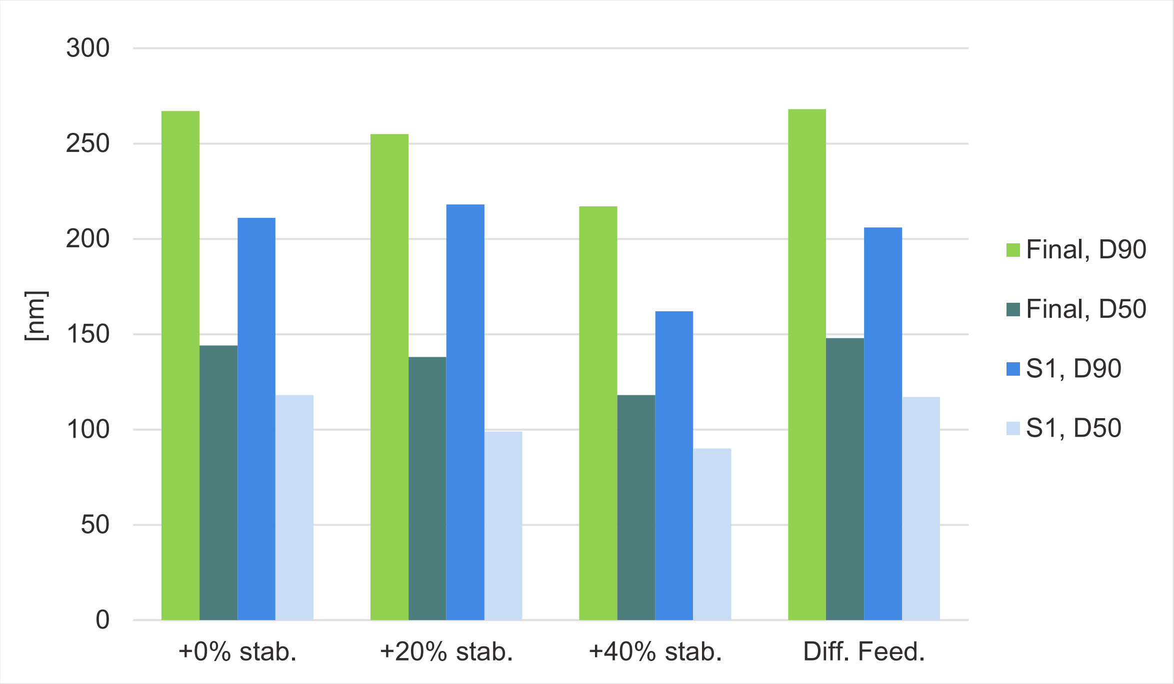


Figure 4.9 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 5.0 containing 0%, 20% and 40% more stabilizer, and with different feeding rates of the initiator.*

The dispersion containing 40% more stabilizer had lower content of residual monomers in the dispersion, as seen in *Figure 4.10*, presumably since the polymerization time was longer to reach the theoretical solids content of the dispersion, compared to the polymerization executed with the original amount of stabilizer.

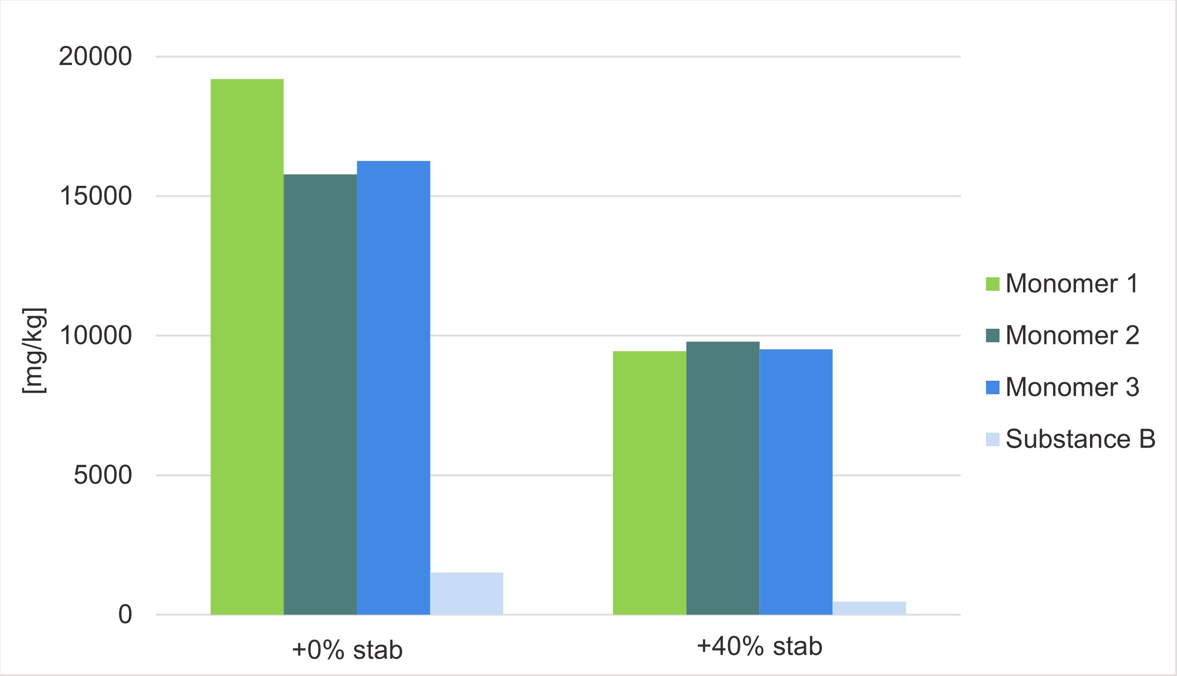


Figure 4.10 *Residual monomers in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 5.0 where one dispersion contained 40 % more stabilizer. Substance B was a by-product from Monomers 2 and 3.*

However, the dispersion containing 40% more stabilizer was more diluted than the other dispersion, making the ratio of monomers compared to the other components lower.

4.3.2 Polymerizations at pH 5.0 and different temperatures

Polymerizations were also performed at 75°C, 85°C and 93°C, all at pH 5.0 with Stabilizer 2 and Initiator 1. The polymerization at 75°C was not expanded any further due to shortage of time. However, three polymerizations were accomplished at 93°C. The first one with no extra modifications, along with one dispersion containing 40% more initiator and one polymerization having 20% more stabilizer.

The solids content was higher at 93°C (*Figure 4.11*), compared to polymerizations done at 85°C. Due to this, a second feed of initiator was not necessary, since the solids content was high enough, almost 25%, immediately after 120 min of polymerization (S_1).

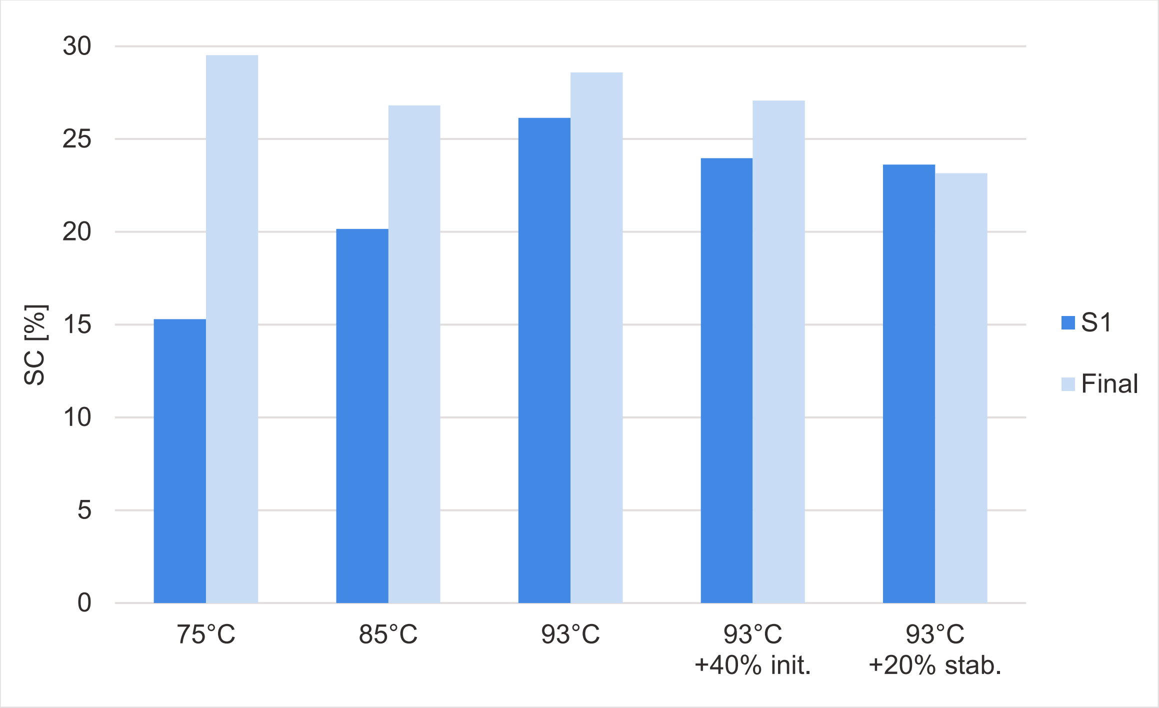


Figure 4.11 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 1, at 75°C, 85°C and 93°C, along with two dispersions done at 93°C with 40% more initiator and 20% more stabilizer. All dispersions were polymerized at pH 5.0.*

The polymerization executed at 75°C, however, had a lower solids content after 120 min (S_1) and a second feed of initiator was necessary to meet the targeted solids content of 25% (*Figure 4.11*). This showed that the polymerization rate was faster at higher temperatures, and at lower temperature a second feed of initiator was needed to complete the polymerization, compared to polymerizations at 85°C (Reed & Alb, 2014).

Major differences were found in the viscosity, see *Figure 4.12*. Due to a considerable increase in the viscosity, the polymerizations done at 93°C with no extra additives and the polymerization with 40% more initiator were not measurable at 60 rpm. All five dispersions were measured at 1.5 rpm to retrieve more comparable data, seen in *Table 4.3*.

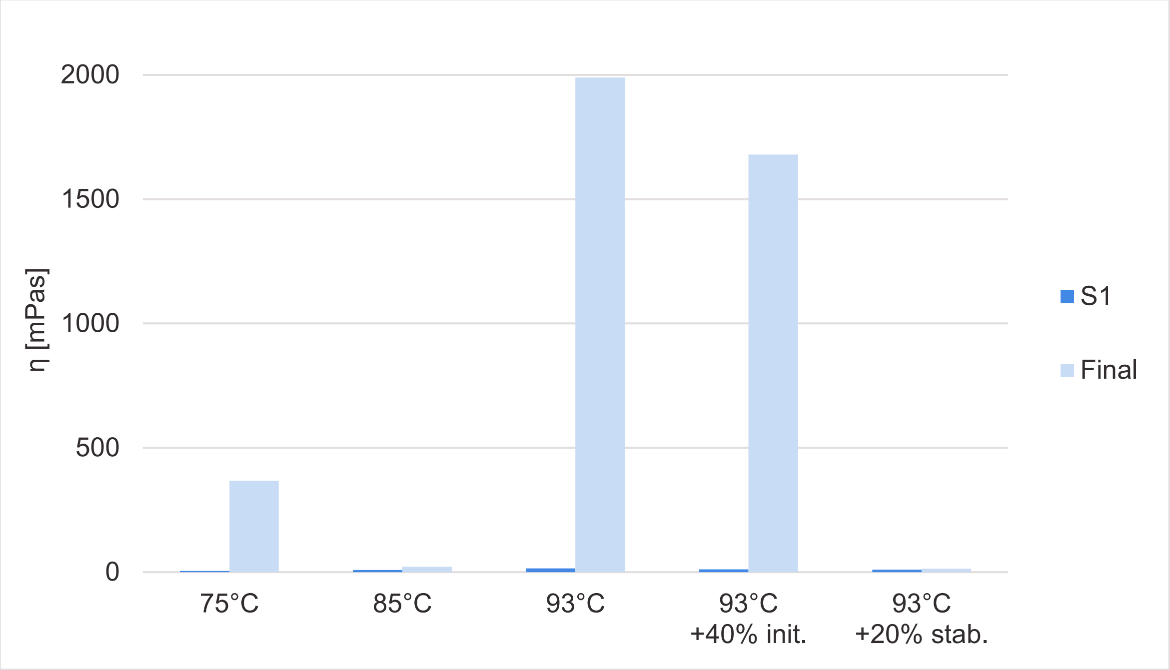


Figure 4.12 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 75°C, 85°C and 93°C, along with two dispersions polymerized at 93°C with 40% more initiator and 20% more stabilizer. All dispersions were polymerized at pH 5.0. The Brookfield viscosity was measured with spindle 18 at 1.5 rpm. For clarification, the data is also found in Table 4.3.*

Table 4.3 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 75°C, 85°C and 93°C, along with two dispersions polymerized at 93°C with 40% more initiator and 20% more stabilizer. All dispersions polymerized at pH 5.0. The Brookfield viscosity was measured with spindle 18 at 1.5 rpm*

Test	η, S_1 [mPas]	η, final [mPas]
75°C	5	368
85°C	8	22
93°C	15	1 990
+40% init.	11	1 680
+20% stab.	10	14

Considering these results, a higher temperature increased the viscosity. However, an increase in the amount of stabilizer, and therefore also a significant addition of water to the dispersion, lowered the viscosity. Furthermore, the increase in viscosity in the dispersion polymerized at 75°C (*Figure 4.12*), was presumably due to a significantly longer time of polymerization compared to the other polymerizations, approximately 100 min longer. The dispersion containing 40% more initiator was later diluted from a solids content to 27% to 23.5%, according to

$$c_1V_1 = c_2V_2 \tag{1}$$

where *c* = concentration and *V* = volume. The dilution noticeable decreased the viscosity, to approximately 200 mPas at 60 rpm.

Likewise, differences in the average particle size were detected, see *Figure 4.13*. Presumably, the dispersion achieved at 75°C did not polymerize properly since the S_1 D50 value was only 44 nm.

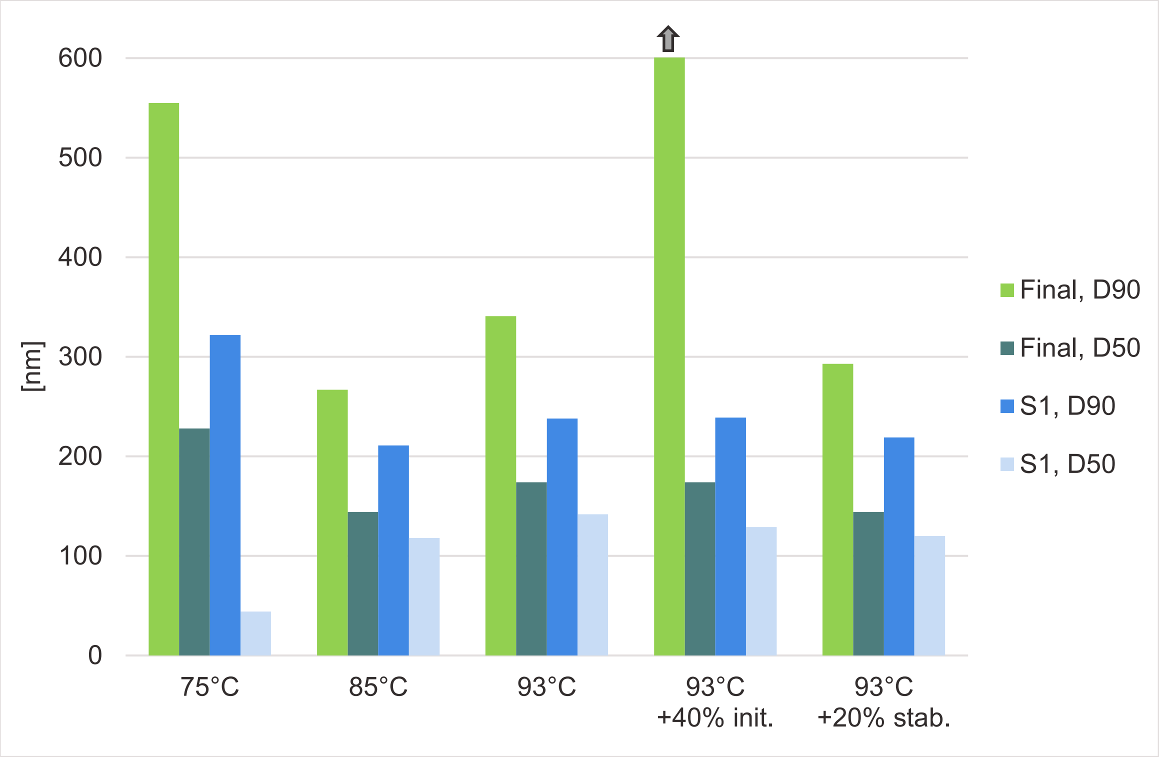
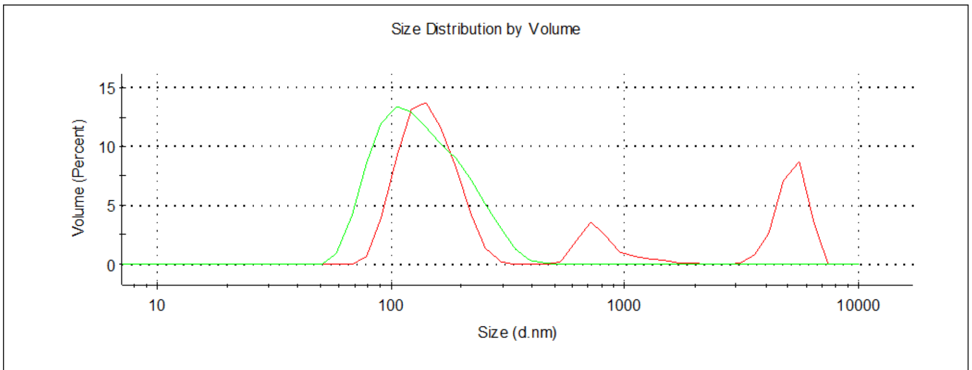


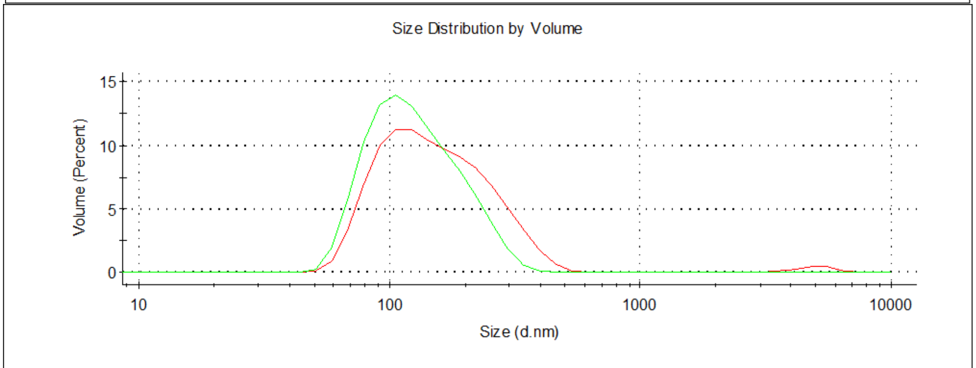
Figure 4.13 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 1, at 75°C, 85°C and 93°C, along with two dispersions done at 93°C with 40% more initiator and 20% more stabilizer. All dispersions were polymerized at pH 5.0. The final D90 value of the dispersion containing 40% more initiator was 5 360 nm. The dispersions polymerized at 93°C showed a very disperse nature and the measurements were somewhat unreliable due to a too polydisperse solution for the Zetasizer, according to the instrument instructions.*

The dispersion polymerized at 75°C did also contain several larger particles, increasing the average particle size, see PSD in *Appendix F*. The dispersion containing 40% more initiator generated a final D90 value of 5 360 nm, only partly observed in *Figure 4.13* to make the graph more comprehensible, indicating the dispersion contained very large particles.

As seen in *Figure 4.14*, the dispersion containing 40% more initiator and polymerized with Stabilizer 2 and Initiator 1 at 93°C had three peaks instead of one, indicating the dispersions contained aggregated particles, making the PSD broad. Especially in the distribution of the dispersion containing 40% more initiator, the peaks were sharp, which indicates a small number of very large particles.



40% more initiator: S1 and Final



20% more stabilizer: S1 and Final

Figure 4.14 *Particle size distribution by volume, in dispersions polymerized with Stabilizer 2 and Initiator 1 at 93°C and pH 5.0, with 40% more initiator (above) and 20% more stabilizer (below). The dispersions showed a very disperse nature and the measurements were slightly unreliable due to a too polydisperse solution for the Zetasizer, according to the instrument instructions. The red curve shows the PSD of the final dispersion and the green curve shows the PSD of the* S_1 *sample.*

Furthermore, three distinct populations indicates the average size was hard to calculate, demonstrating that the dispersion polymerized at 93°C with 40% more initiator has somewhat unreliable average particle size, found in *Figure 4.13*. The PSD measurements of these two dispersions declared in *Figure 4.14* did not meet the desired criteria of dispersity to correctly analyze the distribution according to the instrument instructions, meaning the data might be slightly unreliable.

The dispersions polymerized at 75°C and 93°C were more brown in color, compared to the dispersion polymerized at 85°C (*Figure 4.15*). At higher temperature, the dispersions were more unstable and showed clear phase separation, presumably due to ineffectiveness of the stabilizer at higher temperatures and formation of agglomerated particles.

Figure 4.15 *Dispersions polymerized at 75°C (left), 85°C (middle) and 93°C (right), with Stabilizer 2 and Initiator 1 at pH 5.0. A noticeable three-phase separation was observed in the dispersion polymerized at 93°C, i.e., the dispersion was unstable. Photo: Private.*

In conclusion, the monomers polymerized faster at higher temperature, and minimized the demand of a second feed of initiator. However, at higher temperature, the dispersions were seemingly more unstable, due to the visible phase separations and broader PSD, and the stabilizer was not working properly. By increasing the amount of initiator, the reaction rate increased significantly and the particles started to agglomerate and the PSD became very broad (Monteiro & de Barbeyrac, 2001).

However, at lower temperature, the polymerization was slower, and more time and initiator were needed to complete the polymerization. Presumably, the particles started to agglomerate in the end of the reaction process, generating large particles. To get more accurate statistics and to explain the major differences between the dispersions, the polymerizations should be repeated considering the measured data can be somewhat unreliable.

4.4 Polymerizations with different additives

Dispersions containing an addition of Initiator 3, Substance A, and 20% more stabilizer, are investigated in this chapter. All dispersions were polymerized at pH 6.0 and 85°C with Stabilizer 2 and Initiator 1.

4.4.1 Polymerizations at pH 6.0

The dispersion with the properties closest to the target properties using Stabilizer 2 and Initiator 1 was obtained at pH 6, as described in *Chapter 4.2*. Therefore, four more dispersions were polymerized at this pH. A polymerization containing 20% more stabilizer was executed but due to a misleading pH meter, the pH during polymerization was adjusted to 6.3 instead of 6.0. The differences are presumably negligible and not taken into consideration. To increase the rate of polymerization and minimize the amount of excessive residual monomers, Initiator 3 was added to one dispersion, after the polymerization reaction. To another dispersion a chain-transfer agent, Substance A, was added to the monomer feed. Finally, a dispersion containing both Initiator 3 and Substance A was polymerized. The addition of Initiator 3 was 0.1 g/ 100 g dispersion and Substance A was 0.3 g/ 100 g dispersion.

As shown in *Figure 4.16*, only small varieties in the solids content were detected. The dispersion containing no extra compounds had the highest solids content after 120 min (S_1), making the amount of additional initiator needed the smallest. The other dispersions were somewhat similar concerning the solids content in S_1, with minor differences in the amount of added initiator.

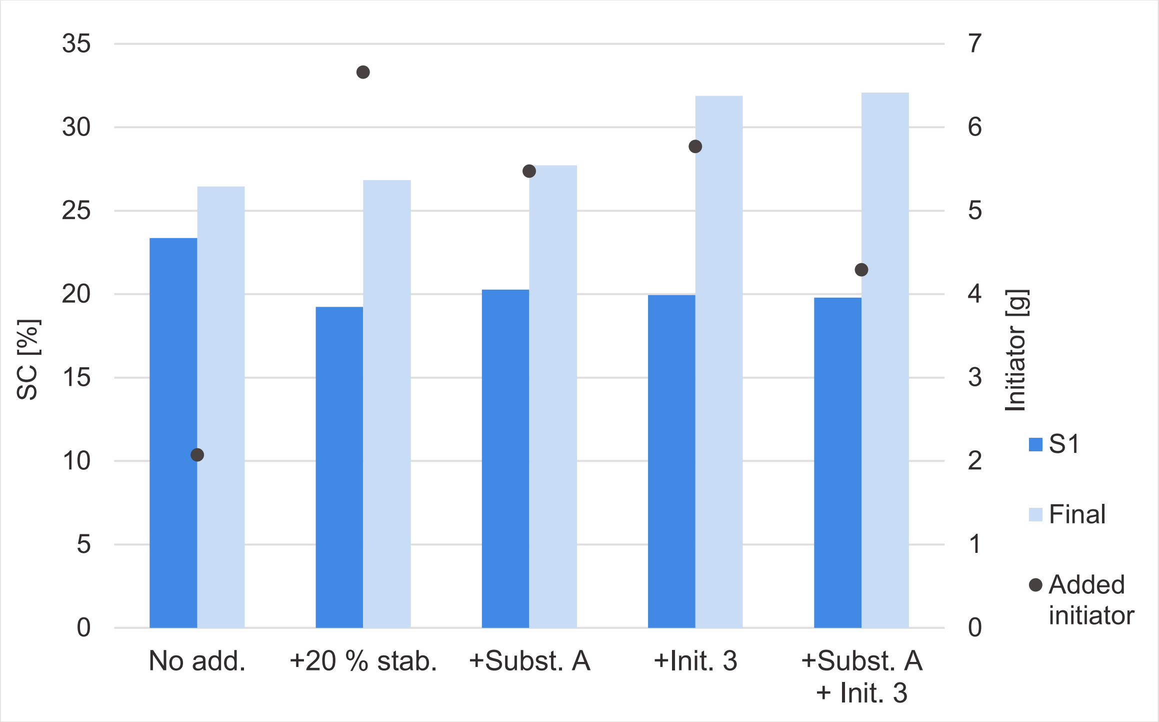


Figure 4.16 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 6.0, with different additives: no extra additions; 20% more stabilizer; addition of Substance A; addition of Initiator 3; and a dispersion containing both Substance A and Initiator 3.*

Initiator 3 was added after S_1 was taken. However, the two dispersions containing Initiator 3 did significantly increase in the solids content of the final dispersion. This indicates that residual monomers were found in S_1 and the polymerization continued to some extent after the addition of Initiator 3. Taken into consideration, the dispersions containing Initiator 3 had an additional mixing at 85°C during 60 min for the monomers to polymerize further. The solids content of the dispersions containing Initiator 3 were later diluted according to *Equation (1)* to approximately 25%.

The viscosities were low, differences were detected in the dispersions containing Substance A, where the viscosity was slightly higher, see *Figure 4.17*. Presumably, the addition of Substance A changed the structure of the polymer chain, and increased the viscosity due to, *e.g.*, branches and entanglements (Valles & Macosko, 1979). Nevertheless, the differences were small and all values were within the target of < 200 mPas.

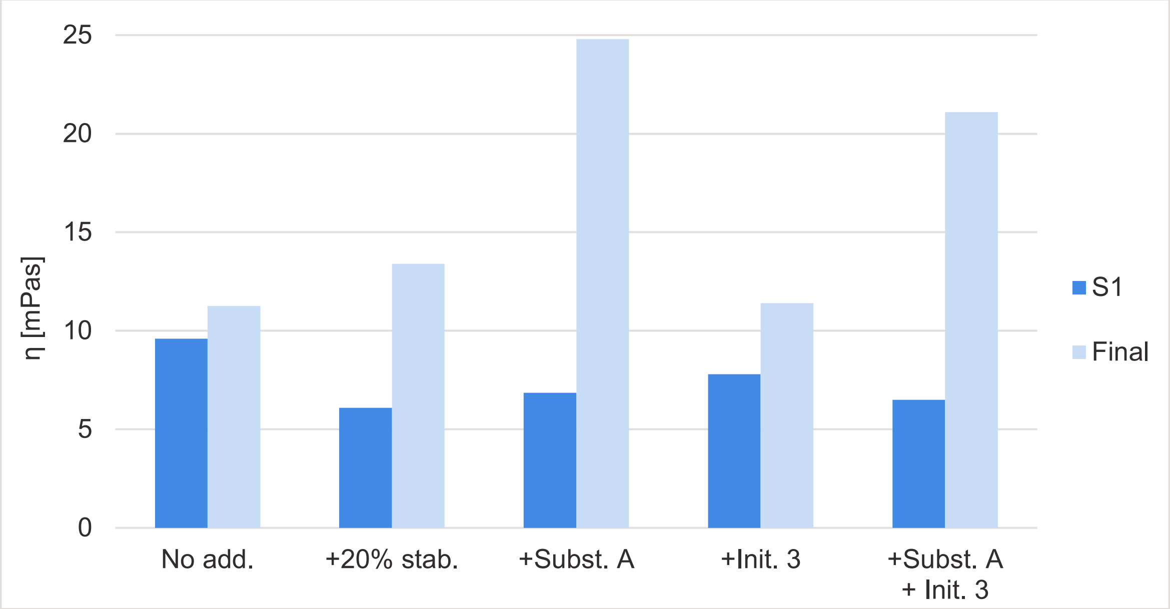


Figure 4.17 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 6.0 with different additives: no extra additions; 20% more stabilizer; addition of Substance A; addition of Initiator 3; and a dispersion containing both Substance A and Initiator 3. The Brookfield viscosity was measured with spindle 18 at 60 rpm.*

The average particle size of the dispersion containing no extra additions and the dispersion containing 20% more stabilizer had similar results, see *Figure 4.18*. Furthermore, the addition of Substance A increased the final D90 of the dispersion, especially when combined with Initiator 3. This was the opposite found in research done by Monteiro & de Barbeyrac (2001), were the particle size decreased with increasing concentration of a chain-transfer agent and initiator.

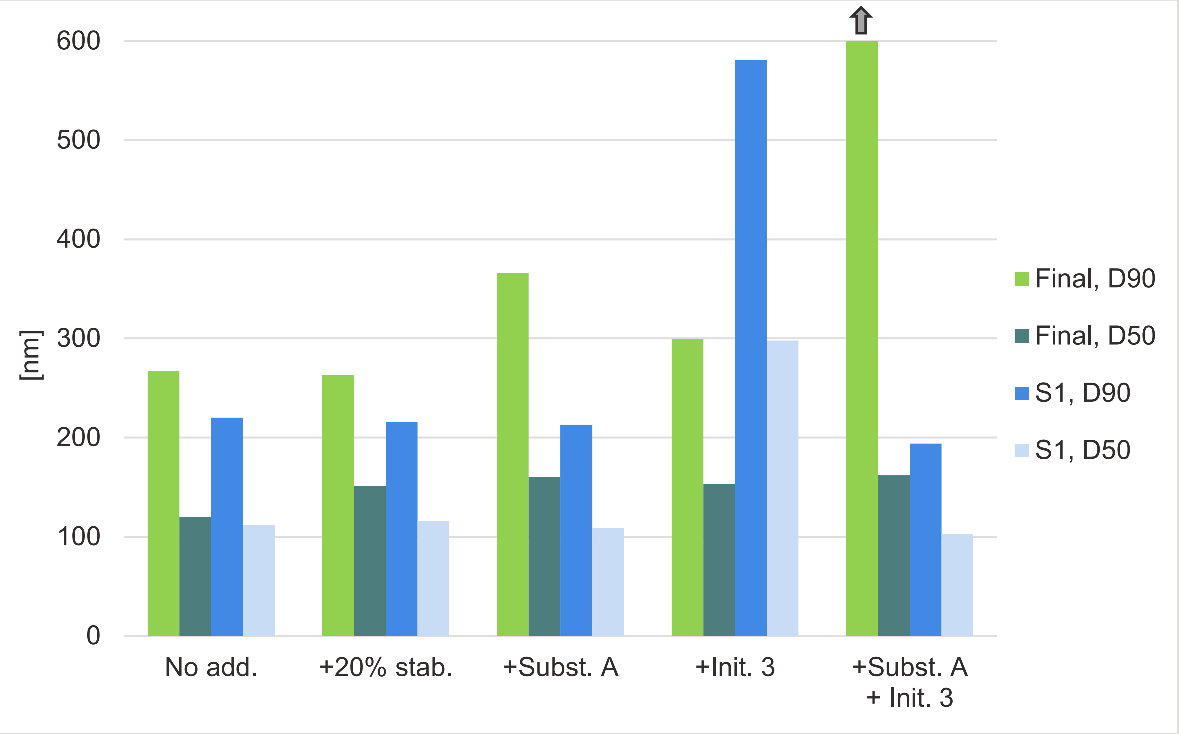


Figure 4.18 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 6.0 with different additives: no extra additions; 20% more stabilizer; addition of Substance A; addition of Initiator 3; and a dispersion containing both Substance A and Initiator 3. The final D90 value of the dispersion containing both Substance A and Initiator 3 was 4 600 nm.*

As displayed in *Figure 4.18*, the average particle size of S_1 in the dispersion containing Initiator 3 was larger than the average particle size of the final dispersion, since Initiator 3 was added to the polymerization after S_1 was taken. With this taken into consideration, the S_1 sample of the dispersion polymerized without any extra additives should be similar to the S_1 of the dispersion containing Initiator 3, since they have the exact same polymerization conditions, but significant differences were noticed. To receive more reliable data, these polymerizations should be repeated, considering the results should be comparable.

As mentioned, the addition of Substance A seemed to increase the value of D90, and in the dispersion containing both Substance A and Initiator 3, the final D90 value was approximately 4 600 nm. The difference can be explained by the results from the PSD in *Figure 4.19*, where two populations in the final dispersion can be seen, the second population was above 1 000 nm.

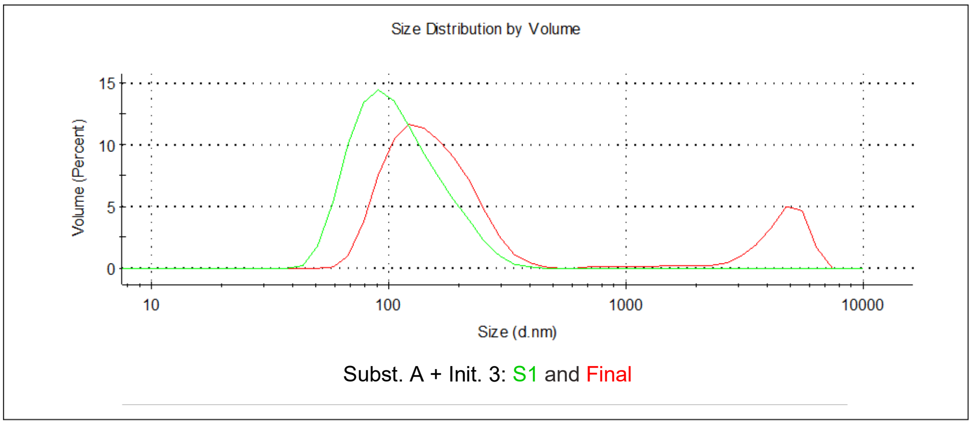


Figure 4.19 *Particle size distribution by volume, in a dispersion polymerized with Stabilizer 2 and Initiator 1, at 85° and pH 6.0 and containing both Substance A and Initiator 3. The dispersion showed a very disperse nature and the measurement was somewhat unreliable due to a too polydisperse solution for the Zetasizer, according to the instrument instructions. The red curve shows the PSD of the final dispersion and the green curve shows the PSD of the* S_1 *sample.*

The PSD results of the dispersion containing both Substance A and Initiator 3 contained larger aggregates or particles, and was too polydisperse to retrieve correct data, therefore these results might be slightly unreliable (*Figure 4.18 and 4.19*). According to similar radical polymerizations with the addition of a chain-transfer agent, the dispersity of the PSD increased when the agent was added to the reaction process (Ahmad & Tauer, 2003). The addition of a chain-transfer agent effects the rate of particle nucleation, leading to fewer nucleated particles. This would result in a broader PSD and larger particles (Smeets, *et al.*, 2010).

Furthermore, the molar mass was larger in dispersions with no addition of Initiator 3 and Substance A, as seen in *Figure 4.20*. According to Schmidt *et al.* (2017), these molar mass values are typical for these kinds of emulsion polymerizations and lead to an average particle size of 300 – 400 nm.

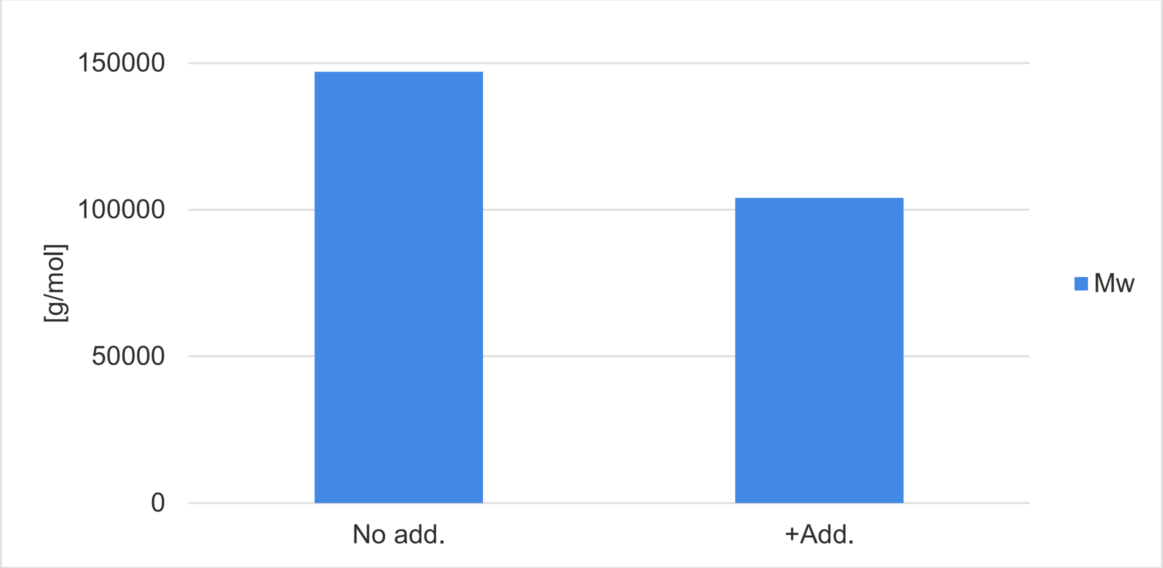


Figure 4.20 *Molar mass of particles in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 6.0 with no additions and with the addition of Substance A and Initiator 3.*

4.4.2 Polymerizations at pH 3.8 and 6.0 with additives

Considering the results in the previous chapter, the addition of Substance A did not work particularly well at pH 6.0. Hence, a similar polymerization at pH 3.8 were executed, to compare the addition of Substance A and Initiator 3 at pH 3.8 and 6.0, polymerized with Stabilizer 2 and Initiator 1 at 85°C. The solids content of S_1 and the final dispersion are seen for dispersions polymerized at pH 3.8 and 6.0 in *Figure 4.21*, along with the additional amount of initiator.

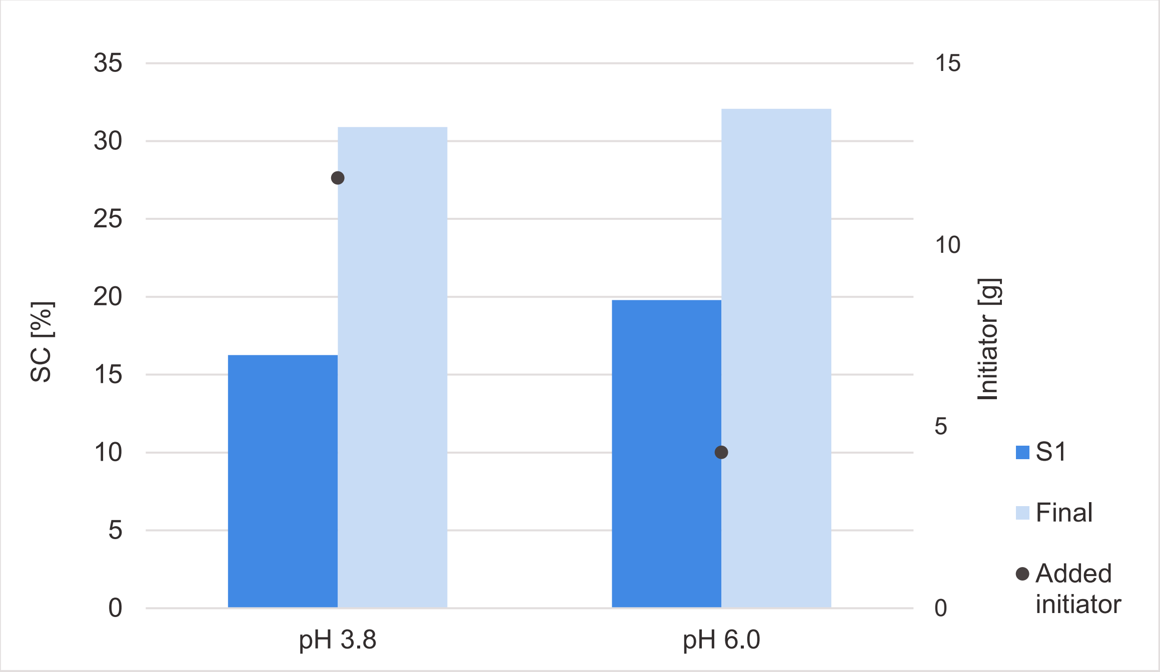


Figure 4.21 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 3.8 and 6.0. Both dispersions have an addition of Substance A and Initiator 3.*

As observed in *Figure 4.21*, the solids content was slightly lower at pH 3.8, according to same principles explained in *Chapter 4.2*. Both dispersions were later diluted to approximately 25%, according to *Equation (1).* Also, the viscosity was lower at pH 3.8 (*Figure 4.22*). In other words, the polymerization rate was slower at lower pH, but the final dispersion had roughly the same results concerning solids content and viscosity, as stated in *Chapter 4.2*. However, the viscosity of both dispersions was low and under the limit of the target viscosity, 200 mPas.

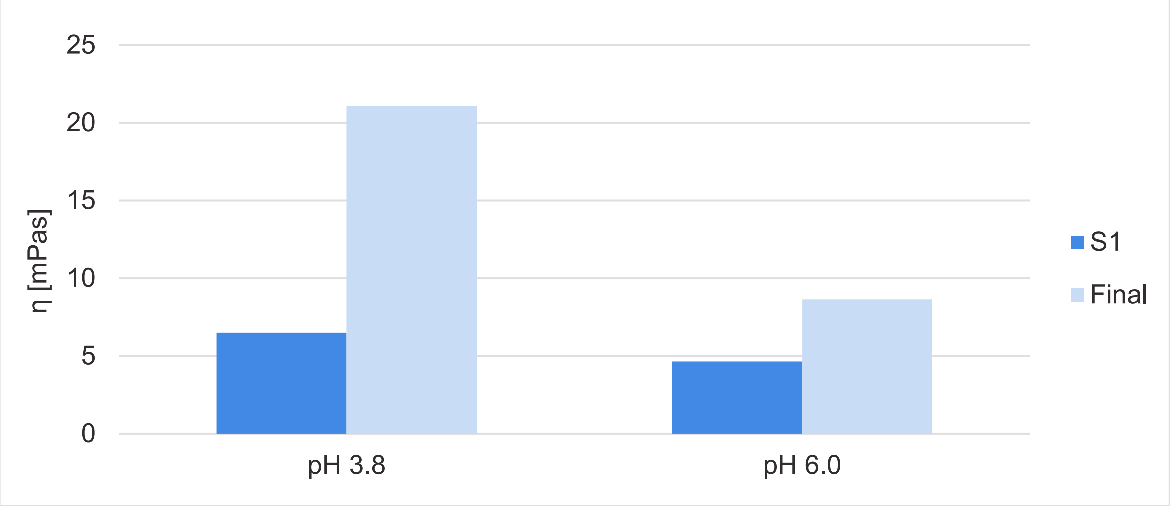


Figure 4.22 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 3.8 and 6.0. Both dispersions have an addition of Substance A and Initiator 3. The Brookfield viscosity was measured with spindle 18 at 60 rpm.*

As previously mentioned and observed in *Figure 4.18* in *Chapter 4.4.1*, the addition of Substance A did increase the average values of D90. Accordingly, at pH 3.8, the final D90 was noticeable higher, as seen in *Figure 4.23*, but not as high as the same value of the dispersion polymerized at pH 6.0, which was 4 600 nm.

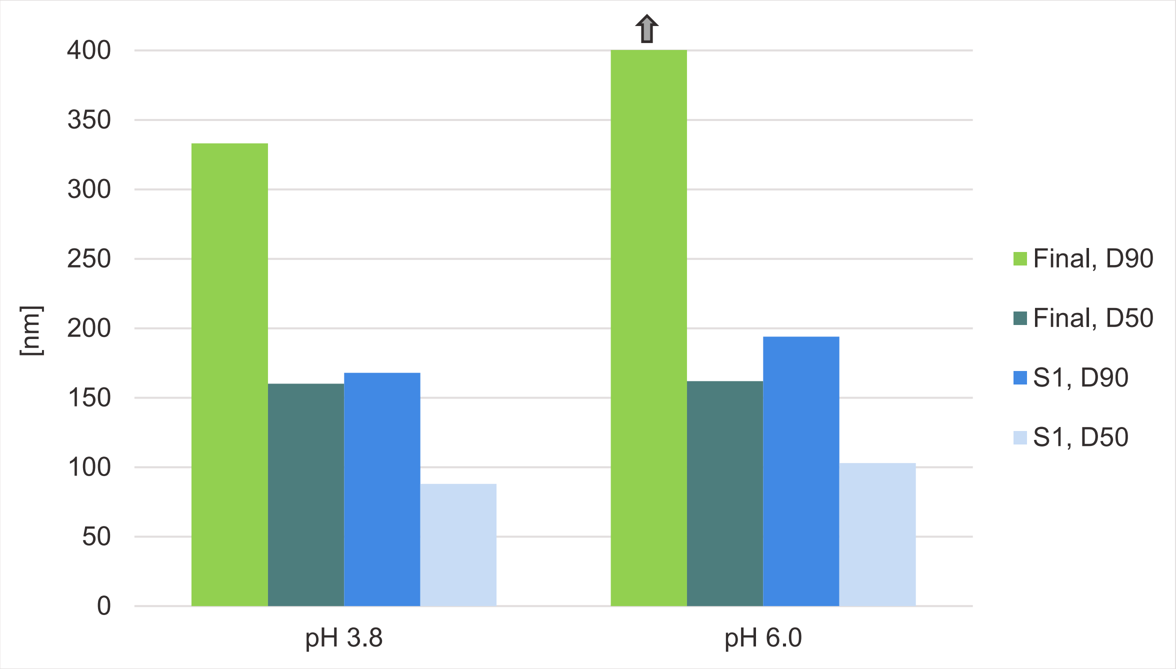


Figure 4.23 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 3.8 and 6.0. Both dispersions have an addition of Substance A and Initiator 3. The final D90 value at pH 6.0 was 4 600 nm.*

The average particle size of dispersions containing Substance A and Initiator 3 was high and the dispersions contained larger particles (see PSD graphs in *Appendix F*). As mentioned in the end of *Chapter 4.4.1*, variations in the nucleation process due to the chain-transfer agent can generate larger particles, especially over time (Smeets, *et al.*, 2010). This fact correlates to the data seen in *Figure 4.23*, where S_1 has significantly lower particle size D90, compared to the values of the final dispersion.

The addition of the chain-transfer agent, Substance A, made the dispersion more dispersed and it contained some larger particles. Considering the particle size and PSD, the additives worked better at pH 3.8 compared to pH 6.0. Hence, the dispersion polymerized at pH 3.8 was analyzed for residual monomers (*Figure 4.24*).

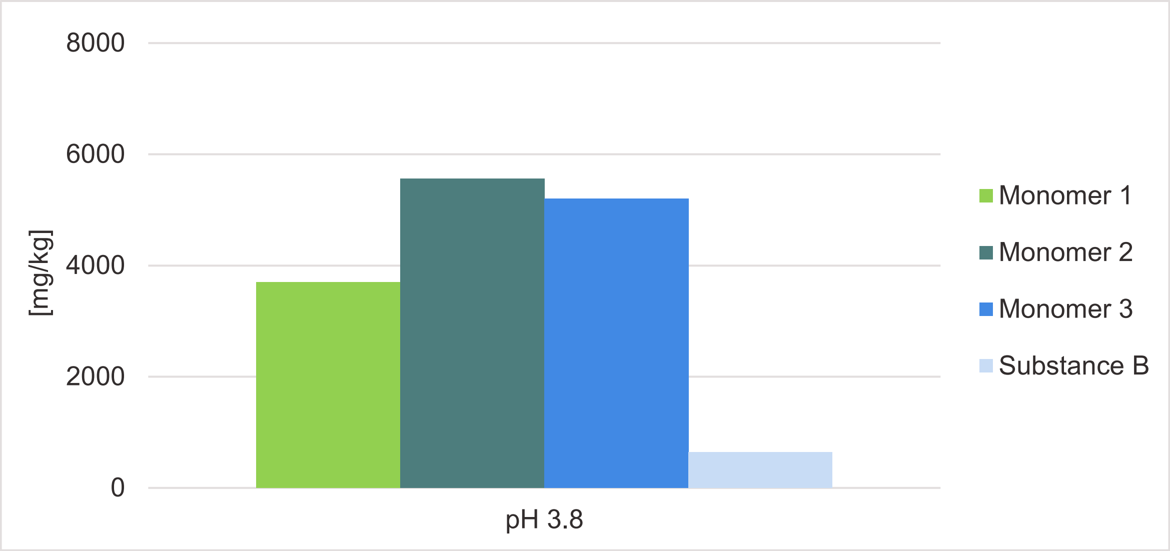


Figure 4.24 *Residual monomers in a dispersion polymerized with Stabilizer 2 and Initiator 1, at 85°C and pH 3.8 with the addition of Substance A and Initiator 3. Substance B was a by-product from Monomers 2 and 3.*

The dispersion contained lower amounts of unpolymerized monomers, compared to analyses declared in *Figure 4.5* in *Chapter 4.2* and in *Figure 4.10* in *Chapter 4.3.1*, where the dispersions polymerized at pH 5.0 and 6.0 with Stabilizer 2 and Initiator 1 at 85 °C contained amounts as large as 24 000 mg/kg. However, as predicted, the dispersion containing Substance A and Initiator 3 had significantly lower amounts of residual monomers. Initiator 3 continued the polymerization after the solids content was reached, lowering the amount of unpolymerized monomers.

4.5 Other polymerizations

Dispersions polymerized with Stabilizer 2 and another initiator, Initiator 2, are clarified and discussed. Further, polymerizations stabilized by Stabilizer 3 and Initiator 1 are discussed.

4.5.1 Polymerizations with Stabilizer 2 and Initiator 2

Two dispersions polymerized with Stabilizer 2 and Initiator 2 were executed. These dispersions were accomplished at 85°C and at pH 2.3 and 5.5, according to the standard recipe. The pH was adjusted to 5.5 instead of 5.0 due to a misleading pH meter. Due to shortage of time, these polymerizations were not further investigated. The additional feed of initiator was also Initiator 2.

As seen in *Figure 4.25*, the solids content at pH 2.3 and 5.5 were similar, both in S_1 and in the final dispersion. The additional feed of Initiator 2 was on for approximately 120 min in both polymerizations, with no increase in the solids content. The theoretical solids content was 23%, however, the experimental value was approximately 15%.

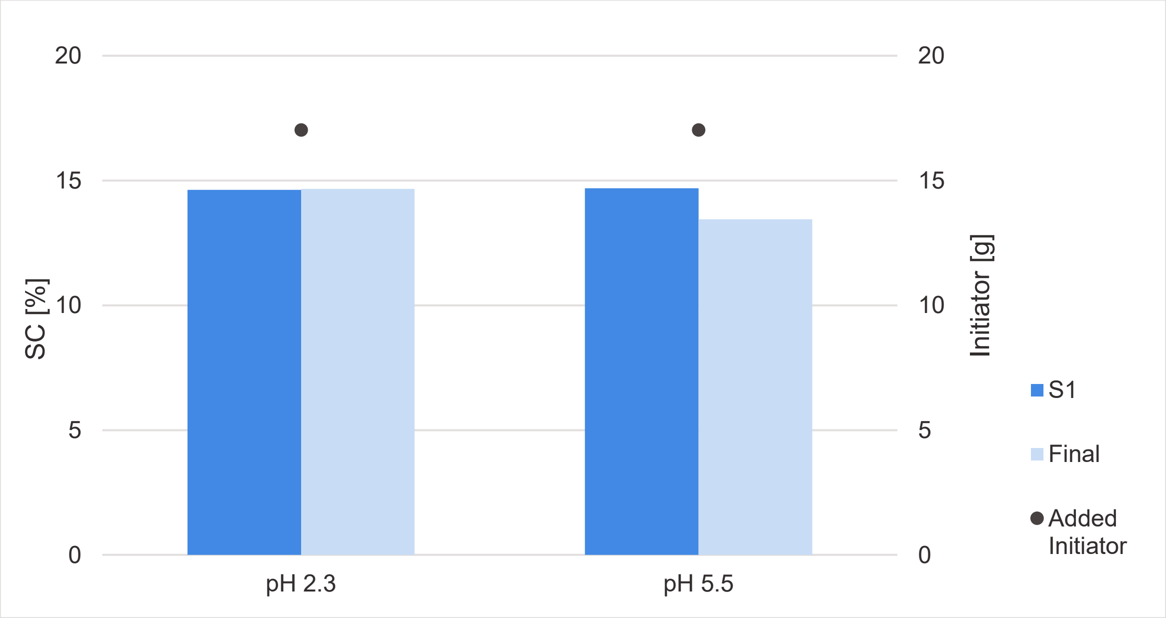


Figure 4.25 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 2 and Initiator 2, at 85°C and pH 2.3 and 5.5.*

The recipe contained approximately 10% more water than the dispersions initiated by initiator 1, due to the dilution of Initiator 1 to a 3.5 wt.% solution and Initiator 2 to a 9 wt.% solution. Since the initiator contained larger amounts of water, the additional feed of initiator diluted the dispersions approximately the same percentage the polymerization increased the solids content. Hence, the solids content did not increase by the addition of a second feed of initiator. According to these results, Initiator 2 did not initiate the polymerization process as efficient as Initiator 1, since the solids content did not increase (compared to *Figure 4.1* in *Chapter 4.2*).

Same tendencies can be seen in the viscosity, the more diluted dispersion caused by a more diluted Initiator 2 resulted in a lower viscosity. As observed in *Figure 4.26*, the viscosity of both S_1 and final dispersion was exceptionally low, all under 4 mPas. Presumably, since the product contained approximately 10% more water compared to the dispersions initiated by Initiator 1, the viscosity was significantly lower for the dispersions polymerized with Initiator 2.

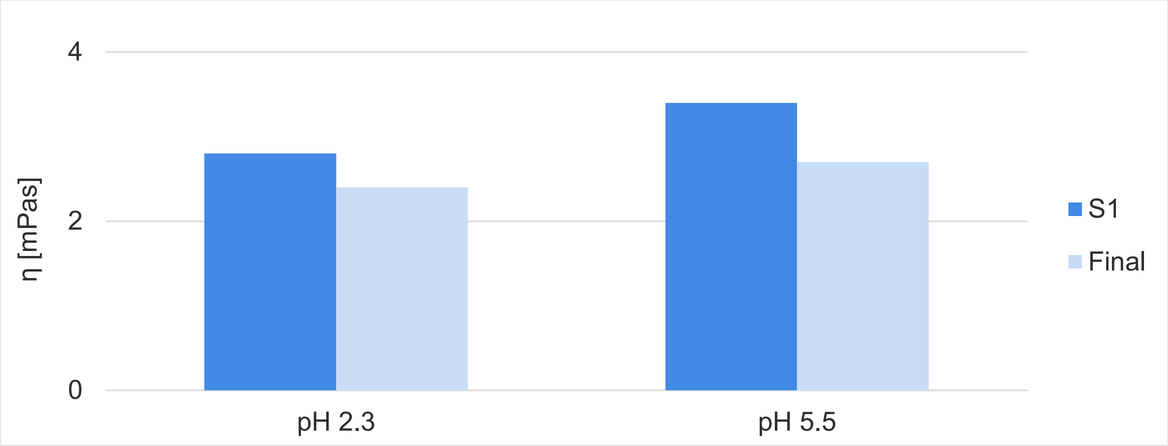


Figure 4.26 *Viscosity for dispersions polymerized with Stabilizer 2 and Initiator 2, at 85°C and pH 2.3 and 5.5. Brookfield viscosity was measured with spindle 18 at 60 rpm.*

Observing the average particle size (*Figure 4.27*), neither polymerizations were successful during the first 120 min, since the values of S_1 were under 10 nm. Furthermore, the PSD was very broad (*Figure 4.28*). S_1 varied from under 10 nm to almost 1 000 nm, whereas the final dispersion had smaller indications at 50 nm and 7 000 nm.

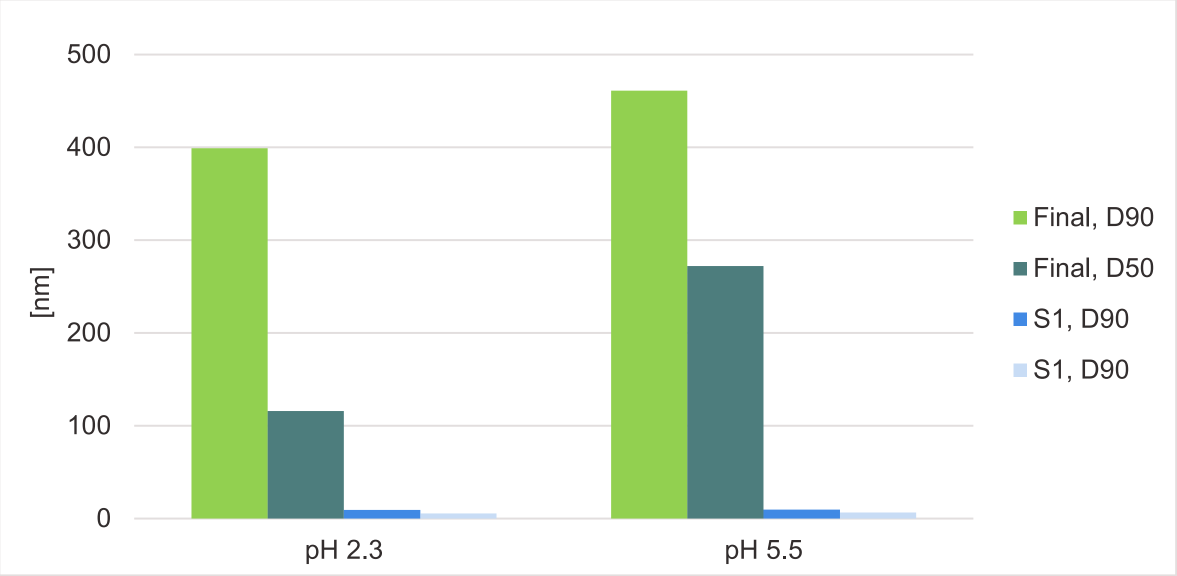


Figure 4.27 *D90 and D50 particle size in dispersions polymerized with Stabilizer 2 and Initiator 2, at 85°C and pH 2.3 and 5.5. Both dispersions have an S_1 D90 and D50 under 10 nm.*

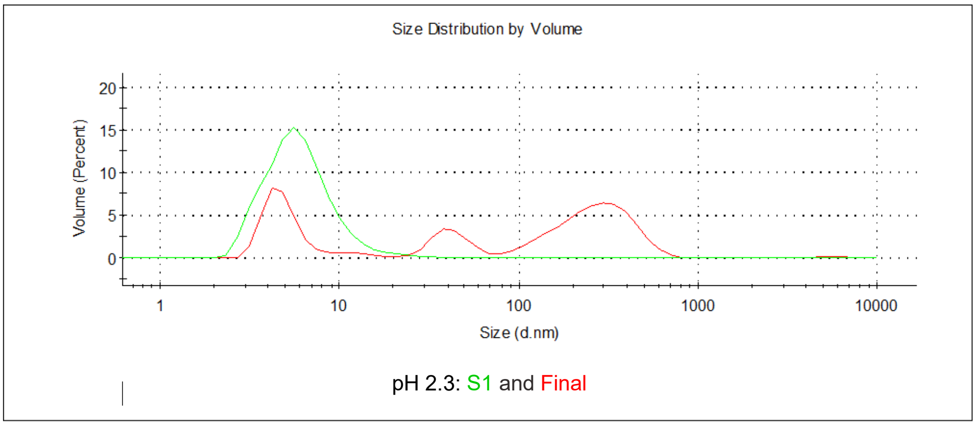


Figure 4.28 *Particle size distribution by volume, in a dispersion polymerized with Stabilizer 2 and Initiator 2, at 85°C and pH 2.3. The dispersion showed a very disperse nature and the measurement was slightly unreliable due to a too polydisperse solution for the Zetasizer, according to the instrument instructions. The red curve shows the PSD of the final dispersion and the green curve shows the PSD of the S_1 sample.*

However, the particle size was too polydisperse to achieve reliable information, therefore, the data explained in *Figure 4.27* are questionable. The final dispersions showed clear phase separations, as seen in *Figure 4.29*, indicating in an presumably unfinalized polymerization containing agglomerated particles.

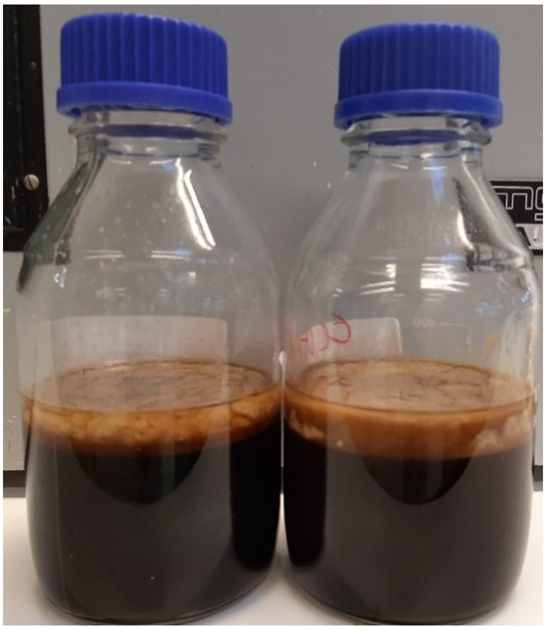


Figure 4.29 *Dispersions polymerized with Stabilizer 2 and Initiator 2, at 85°C and pH 2.3 (left) and 5.5 (right). Clear phase separations were observed, indicating in unstable particles. Photo: Private.*

Since these two dispersions did not polymerize successfully, further experiments using Initiator 2 were not done in this thesis work, due to shortage of time and to limit the impacting factors in the polymerization process.

4.5.2 Polymerizations with Stabilizer 3

Stabilizer 3 consisted of one of the two main components in Stabilizer 2, the lignin-based polyelectrolyte, so four polymerizations using Stabilizer 3 and Initiator 1 were executed. One polymerization was executed at pH 2.3 and three polymerizations at pH 5.0: one without any additions, along with one polymerization with the addition of Substance A and Initiator 3, and one with 40% more stabilizer. All dispersions were polymerized by Stabilizer 3 and Initiator 1 at 85°C. Stabilizer 3 was a powder, compared to Stabilizer 2 that was in liquid form. This acquired different ratio stabilizer-to-water to meet the theoretical solids content of approximately 25%.

Similar to Stabilizer 2, polymerizations with Stabilizer 3 reached higher solids content for the final dispersion at neutral pH (*Figure 4.30*). The pH of Stabilizer 3 dissolved in water was 8.3, when the similar pH value of Stabilizer 2 was approximately 5.0. As shown in *Figure 4.30*, the polymerization was not successful at lower pH, as the solids content of the final dispersion was below 10%. The additional feed of initiator did not increase the solids content in S_1 at pH 2.3, indicating the stabilizer inhibits or slow down the polymerization at low pH.

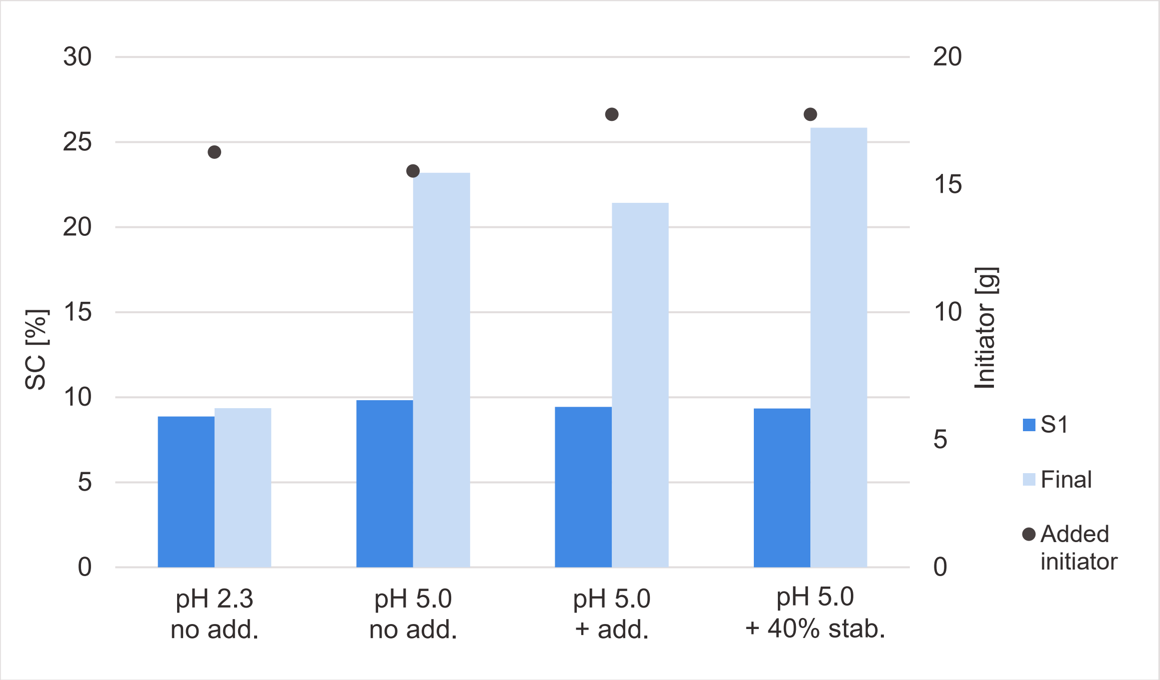


Figure 4.30 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 3 and Initiator 1, at 85°C and pH 2.3 with no additions, along with dispersions polymerized at pH 5.0 with no additions; the addition of Substance A and Initiator 3; and 40% more stabilizer.*

As seen in *Figure 4.30*, at pH 5.0, the solids content increased after a 240 min polymerization time (a full polymerization time + 120 min of additional feed of initiator). Furthermore, the addition of Substance A and Initiator 3 did not increase the solids content in dispersion polymerized with Stabilizer 3 as much as in dispersions stabilized by Stabilizer 2 (*Figure 4.16* in *Chapter 4.4.1*), the solids content was almost 10% lower. An increase in the amount of stabilizer did only increase the solids content slightly. Considering this, Stabilizer 3 needed significantly longer polymerization time, compared to polymerizations done with Stabilizer 2.

As noticed in *Figure 4.31*, the viscosity was very low at lower pH, presumably due to the low solids content. At pH 5.0, the viscosity increased when the chain-transfer agent (Substance A) was added to the reaction. Similar results have been showed earlier (Valles & Macosko, 1979). Furthermore, the viscosity increased significantly after an addition of 40% more stabilizer. However, this data was contradictory to the viscosifying properties of the stabilizer (Yang, *et al.*, 2007).

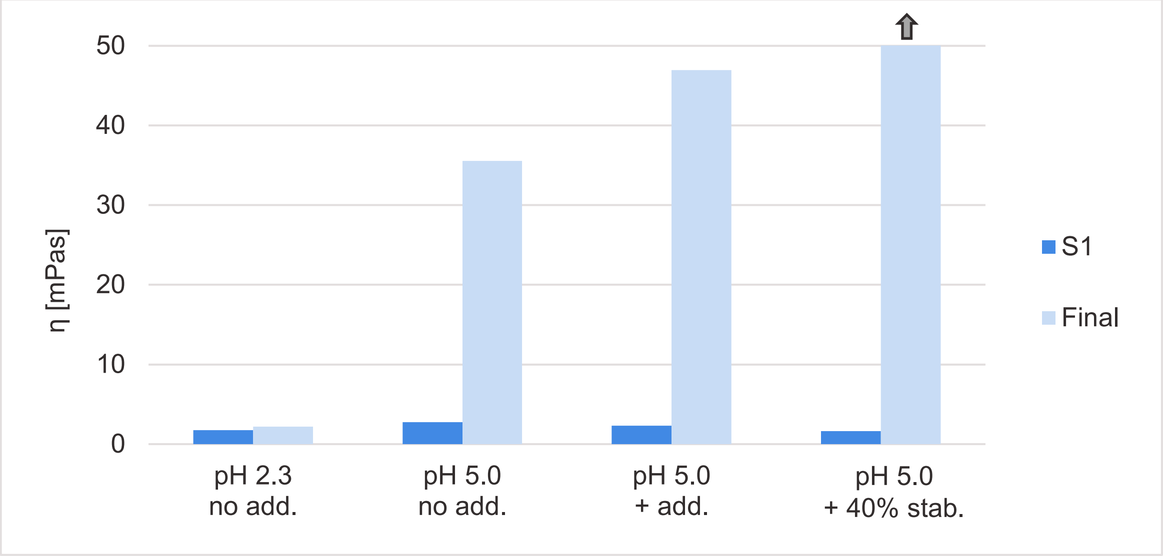


Figure 4.31 *Viscosity for dispersions polymerized with Stabilizer 3 and Initiator 1, at 85°C and pH 2.3 with no additions, along with dispersions polymerized at pH 5.0 with no additions; the addition of Substance A and Initiator 3; and 40% more stabilizer. The dispersion containing 40% more stabilizer had a final value of 193 mPas.*

In contrast to the particle sizes in dispersions polymerizations with Stabilizer 2, the average size was substantially larger in the dispersion stabilized by Stabilizer 3 (*Figure 4.32*), indicating the stabilizer did not hinder the particles from agglomeration.

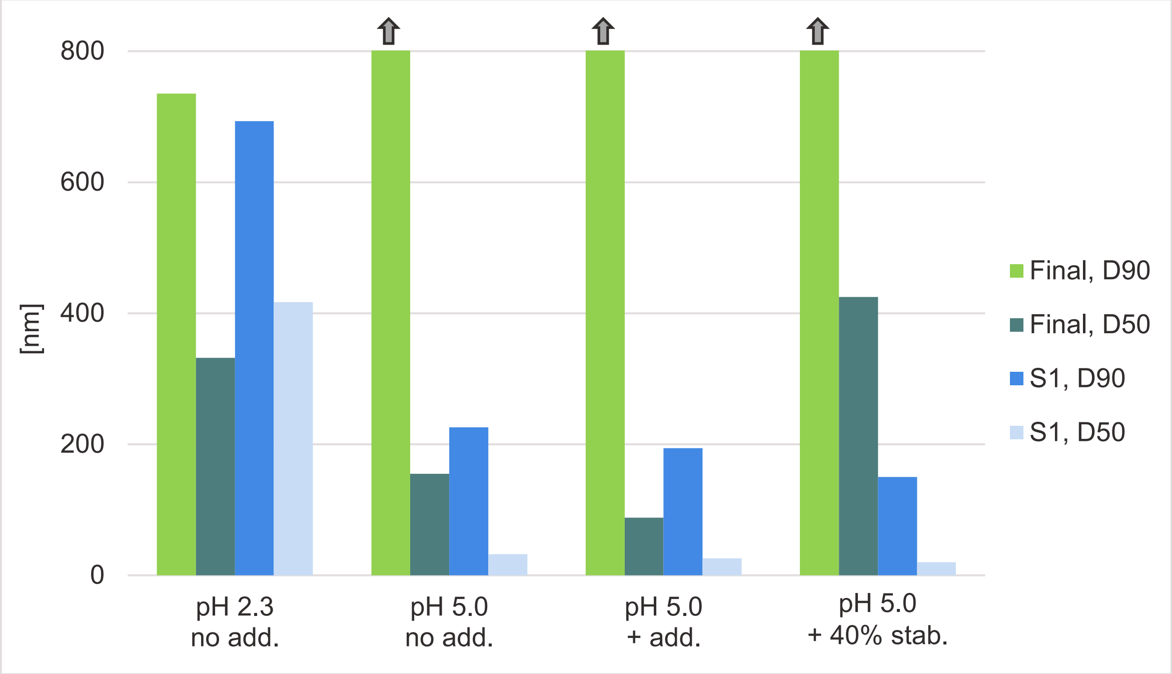
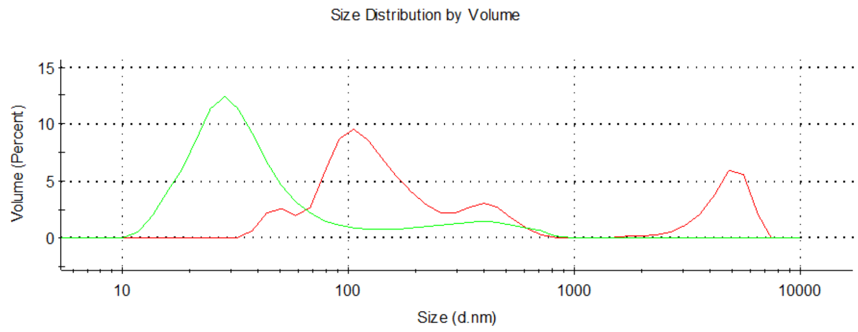
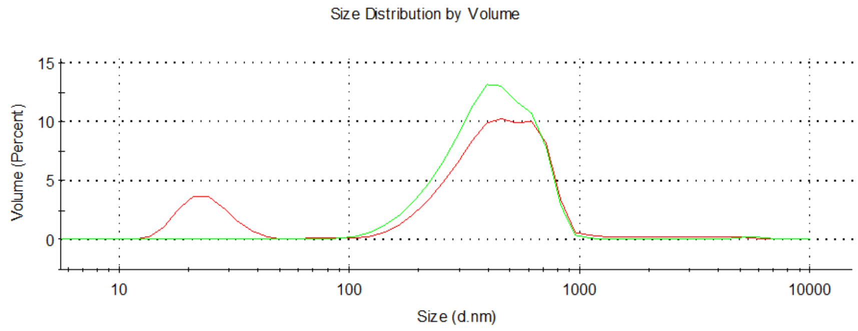


Figure 4.32 *D90 and D50 particle size in dispersions polymerized with Stabilizer 3 and Initiator 1, at 85°C and pH 2.3 with no additions, along with dispersions polymerized at pH 5.0 with no additions; the addition of Substance A and Initiator 3; and 40% more stabilizer. The final D90 values of the three dispersions polymerized at pH 5.0 from left to right: 4 900 nm; 3 300 nm; 5 100 nm.*

As seen in *Figure 4.32*, the particle size of S_1 in all three dispersions executed at pH 5.0 were relatively low. Considering the low solids content of the dispersions, of approximately 10%, the polymerization was not successful during the first 120 min of the polymerization and the dispersion was presumably containing large amounts of unpolymerized monomers (Reed & Alb, 2014). At pH 2.3, a remarkable observation about the D50 values is seen in *Figure 4.32*, where the value of S_1 was greater than the value of the final dispersion. This is explained in *Figure 4.33*, where the final dispersion at pH 2.3 has a peak at very low particle size, indicating the dispersion was containing small particles.



pH 5,0: S1 and Final



pH 2.3: S1 and Final

Figure 4.33 *Particle size distribution by volume, in dispersions polymerized with Stabilizer 3 and Initiator 1, at 85°C and pH 5.0 (above) and pH 2.3 (below). The red curve shows the PSD of the final dispersion and the green curve shows the PSD of the* S_1 *sample.*

At pH 2.3, the dispersion showed clear phase separations (*Figure 4.34*) and was considered unstable. At pH 5.0 with additional amounts of stabilizer, the polymerizations were more successful, and no phase separations were observed.

Figure 4.34 *Dispersions polymerized with Stabilizer 3 and Initiator 1, at 85°C and pH 2.3 (left) and pH 5.0 with 40% more stabilizer (right). Clear phase separations were observed in the dispersion polymerized at pH 2.3 (left). Photo: Private.*

However, the dispersions stabilized by Stabilizer 3 were not stable over time. After three to four weeks of storage, the dispersions showed signs of sedimentation and a thick layer was created on the bottom of the bottle, in comparison to the more stable dispersions polymerized by Stabilizer 2.

In conclusion, Stabilizer 3 did not stabilize the dispersions very well on its own and was presumably inhibited by impurities or inorganic salts (Braun, 2009), and the initiator did not polymerize the monomers sufficiently enough.

4.6 Particle stability and zeta potential

An important factor of the dispersion was the long-term stability. Visual observations can immediately detected if the dispersion did not polymerize or if the stabilizer did not stabilize properly, see number 1 and 3 in *Figure 4.35*, where distinct phase separations are seen.

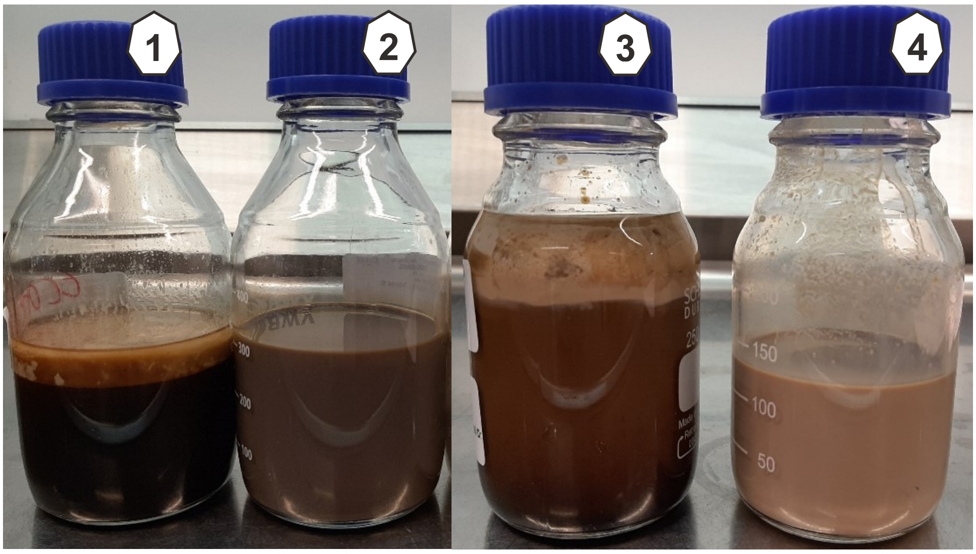


Figure 4.35 *Visual phase separations and color varieties in an assortment of dispersions. 1) Polymerized with Stabilizer 2 and Initiator 2 at pH 5.5; 2) Polymerized with Stabilizer 2 and Initiator 1 at pH 5.0 with 40% more stabilizer; 3) Polymerized with Stabilizer 3 and Initiator 1 at pH 2.3; 4) Polymerized with Stabilizer 3 and Initiator 1 at pH 5.0. Photo: Private.*

Usually, the dispersions separated into layers had a lower solids content than the theoretical solids content. In *Figure 4.35*, a notable color variation among the dispersions are shown. The dispersions that have had a more successful polymerization and therefore are considered stable, had a lighter color nuance. Color variations were not a part of the research plan in this work; therefore, the variations were not investigated any further.

4.6.1 Particle stability

No significant decrease over time in average particle size was detected for a selected number of dispersions that were investigated, seen in *Figure 4.36*, where the original particle size was compared to the particle size measured after storage. The dispersions were stored in closed glass bottles in darkness and at room temperature from 11 to 16 weeks, depending on the time of polymerization.

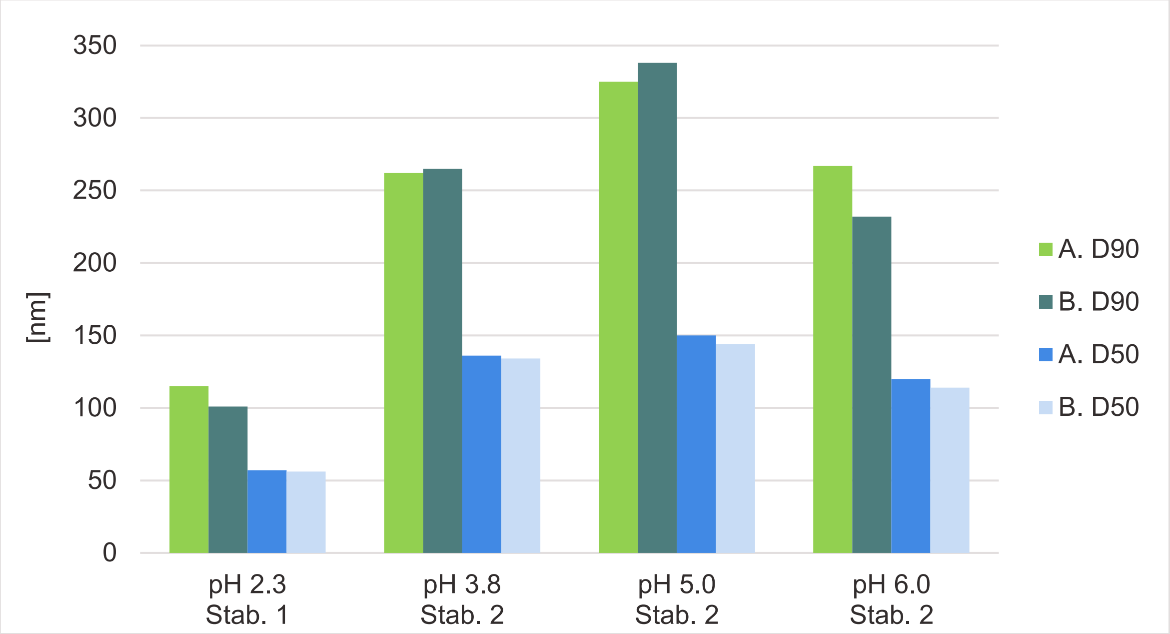


Figure 4.36 *D90 and D50 particle size immediately after polymerization (A) and after 11 to 16 weeks of storage (B), in dispersions polymerized with Stabilizer 1 at pH 2.3, along dispersions polymerized with Stabilizer 2 at pH 3.8; 5.0 and 6.0. All dispersions were initiated by Initiator 1 at 85°C.*

Smaller differences can be detected, presumably due to variations in repeating measurements. Considering this, the molecules did not degrade over this specific timeframe, making the dispersions stable over this period. Furthermore, no sign of sedimentation, due to agglomeration of the particles, was detected.

4.6.2 ζ-potential

The ζ-potential was measured to investigate colloidal stability of the dispersions, see *Figure 4.37*. The measurements were determined at 22°C, where the pH was adjusted between 2.0 and 8.0.

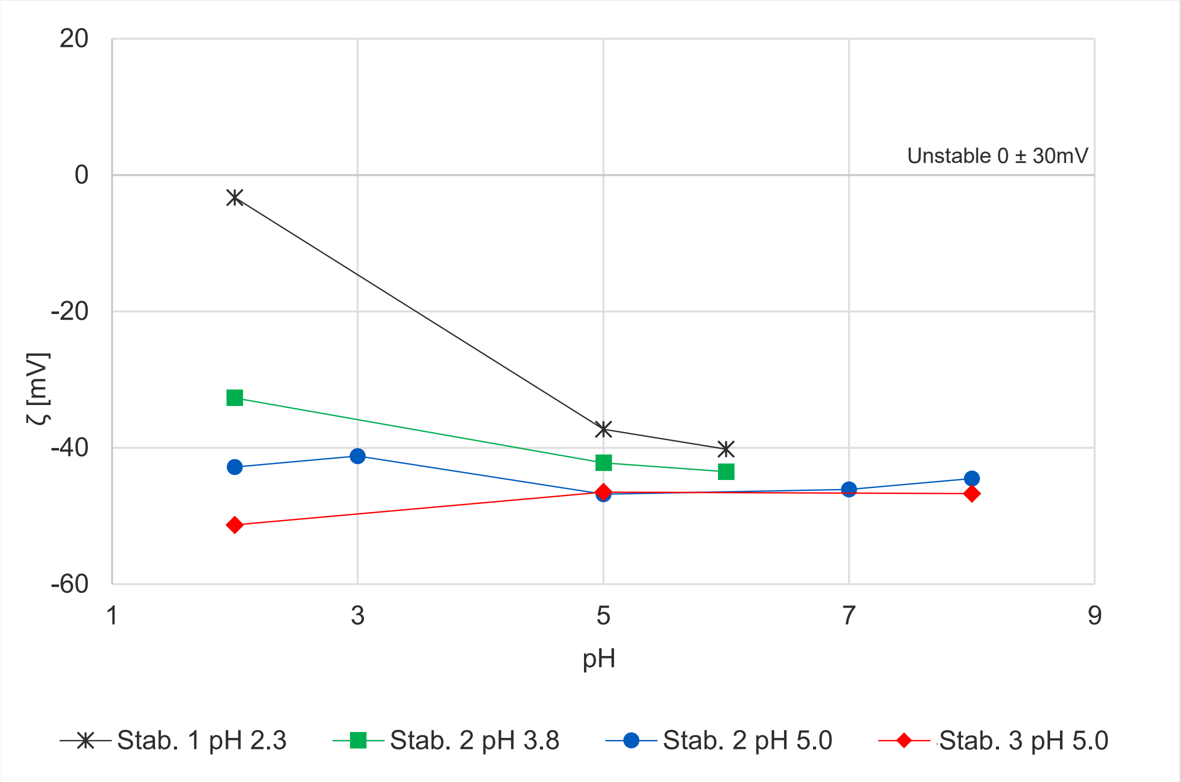


Figure 4.37 *ζ-potential at different pH in dispersions polymerized with Stabilizer 1 at pH 2.3; with Stabilizer 2 at pH 3.8 and 5.0; and with Stabilizer 3 at pH 5.0. All polymerizations were initiated by Initiator 1 at 85°C. The explanations of ζ-potential values are clarified in Table 3.8 in Chapter 3.3, where the dispersion was considered unstable at 0 ± 30 mV.*

The values of pH were chosen according the potential pH range in the area of application for the product. Explanation to different values of ζ-potential was clarified in *Table 3.8* in *Chapter 3.3*: the closer to 0 mV, the more unstable the dispersion was (or more sterically stabilized). As seen in *Figure 4.37*, polymerizations done with Stabilizer 1 gave ζ-potential values closer to zero, than dispersions polymerized with Stabilizer 2 or 3. This indicated that the dispersion had lower electrostatic stabilization (Ishikawa, *et al.*, 2005).

Due to poor distribution data, it was not possible to achieve reliable data for measurements done at higher pH. Considering earlier explained data of average particle size and solids content, the dispersions polymerized with Stabilizer 2 and Initiator 1 at pH 5.0 generated the best average results, compared to the target properties. Further, the ζ-potential was low in the dispersion polymerized at pH 5.0, indicating in good colloidal stability (Ishikawa, *et al.*, 2005).

4.7 Comparison of stabilizers

The differences between the polymerizations executed at pH 5.0 and 6.0, stabilized by Stabilizer 2 and Initiator 1, were small, and according to this research, the best average results concerning target properties were generated at these pH values. Moreover, with an addition of 40% more stabilizer, the properties improved further. Stabilizer 3 did not stabilize the dispersion as efficient as Stabilizer 2. However, compared to the reference polymerization with Stabilizer 1 and Initiator 1 polymerized at pH 2.3, the differences were big between the three stabilizers. The polymerization time was longer for the dispersions stabilized by Stabilizer 2 and 3, with the addition of one hour to the polymerization with Stabilizer 2, respectively two hours with Stabilizer 3, compared to the polymerization time of the dispersions stabilized by Stabilizer 1. All polymerizations discussed in this chapter were executed at 85°C and with Initiator 1.

An additional feed of initiator was added to the polymerizations with Stabilizer 2 and 3, while the reference polymerization with Stabilizer 1 achieved the targeted solids content immediately after the end of the monomer feed, hence no S_1 of the dispersion stabilized by Stabilizer 1 (*Figure 4.38*).

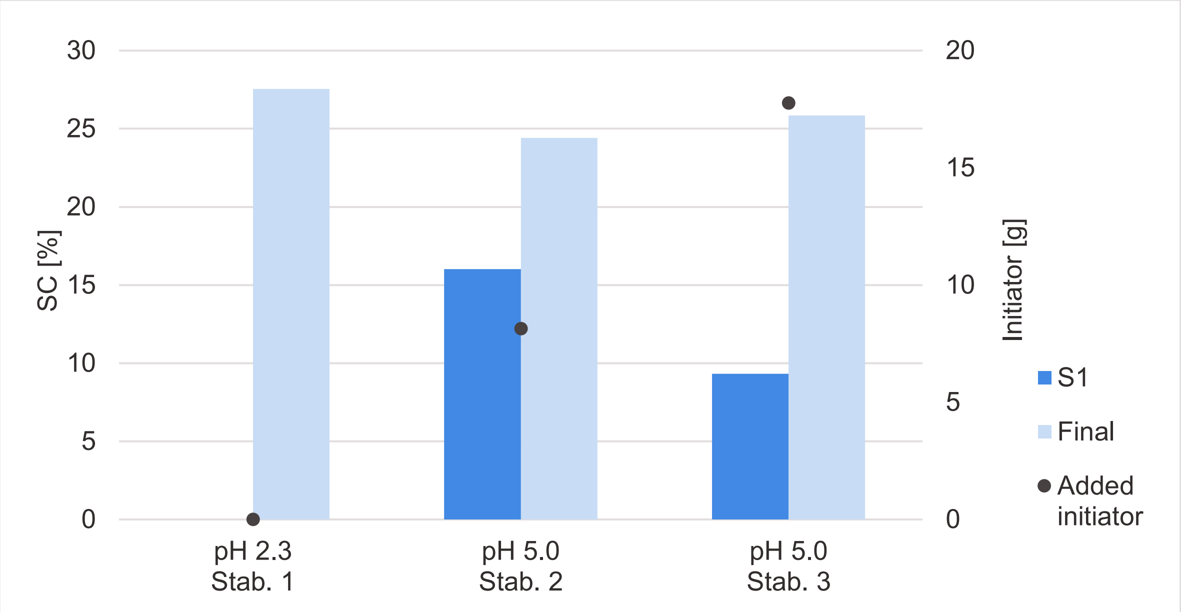


Figure 4.38 *Solids content and additional amount of initiator in dispersions polymerized with Stabilizer 1 at pH 2.3; Stabilizer 2 at pH 5.0 with 40% more stabilizer; and with Stabilizer 3 at pH 5.0 with 40 % more stabilizer. All polymerizations were initiated by Initiator 1 at 85°C. The dispersion polymerized with Stabilizer 1 did not have any* S_1 *data.*

The dispersions stabilized by Stabilizer 1 and 2 showed the same tendencies in the average particle size (*Figure 4.39*).

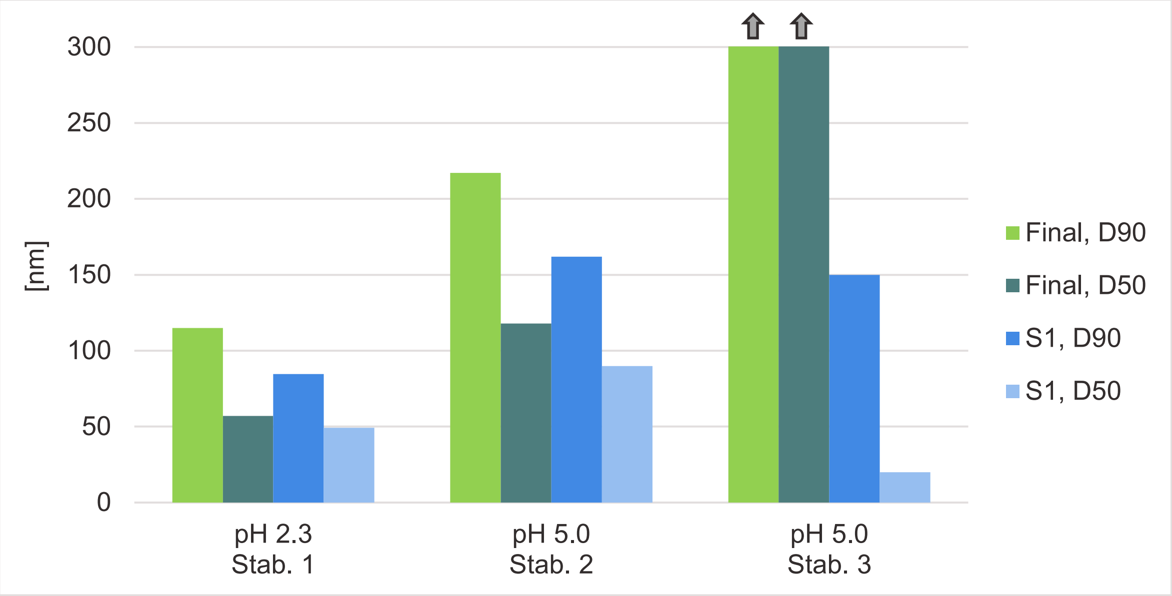


Figure 4.39 *D90 and D50 particle size for dispersions polymerized with Stabilizer 1 at pH 2.3; Stabilizer 2 at pH 5.0 with 40% more stabilizer, and with Stabilizer 3 at pH 5.0 with 40 % more stabilizer. All polymerizations were initiated by Initiator 1 at 85°C. The dispersion polymerized with Stabilizer 3 had a final D90 value of 5 080 nm and D50 value of 425 nm.*

The average particle size values of the polymerizations accomplished at pH 5.0 with Stabilizer 2 were significantly higher compared to the polymerization executed with Stabilizer 1, but no confounding results were generated. The dispersion stabilized by Stabilizer 3 contained large particles and the distribution was broad, as explained in *Chapter 4.5.2*, indicating the stabilizer did not stabilize the particles properly or the initiator was not sufficient enough (Braun, 2009).

The dispersions stabilized by Stabilizer 1 and 2 had narrow particle size distributions, graphs found in *Appendix F*, with no second peaks, indicating no larger particles were found in these dispersions. As seen in *Figure 4.40*, the molar mass of the dispersion polymerized with Stabilizer 1 was lower compared to the molar masses in dispersions polymerized with Stabilizer 2 and 3. Furthermore, this explains the larger average particle sizes for the dispersions polymerized with Stabilizer 2 and 3 (Schmidt, *et al.*, 2017).

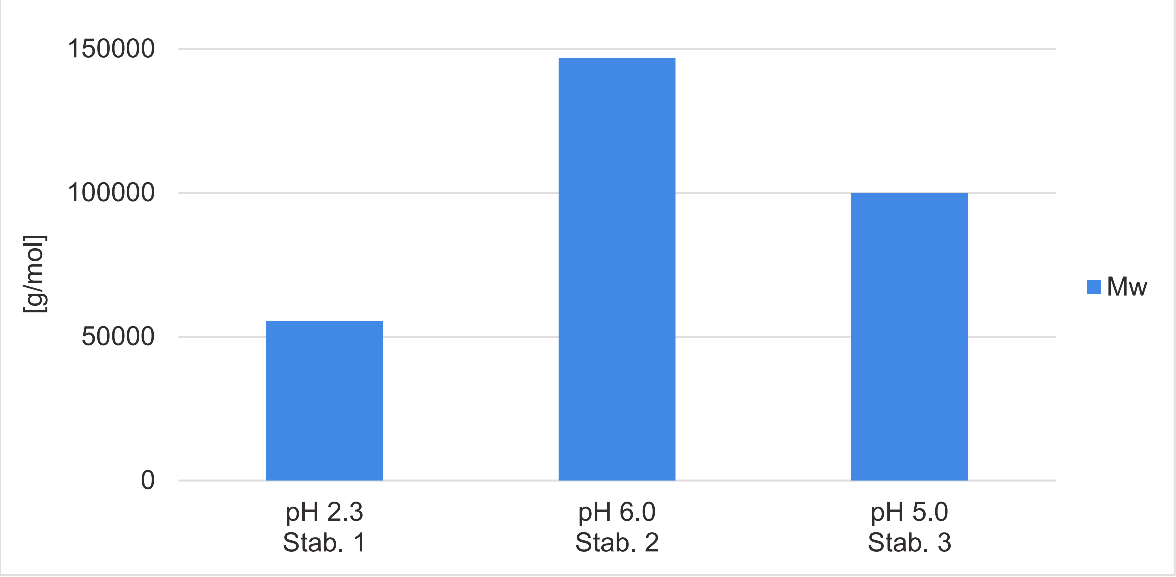


Figure 4.40 *Molar mass of particles in dispersions polymerized with Stabilizer 1 at pH 2.3, Stabilizer 2 at pH 6.0, and with Stabilizer 3 at pH 5.0. All polymerizations were initiated with Initiator 1 at 85°C.*

However, as seen in *Figure 4.41*, the dispersion polymerized with Stabilizer 3 contained lower amounts of residual monomers, compared to similar dispersion polymerized with Stabilizer 2. The decrease in monomer residues was presumably due to the larger amount of initiator in the dispersion polymerized with Stabilizer 3, a more diluted dispersion due to more water in the reaction, and longer polymerization time.

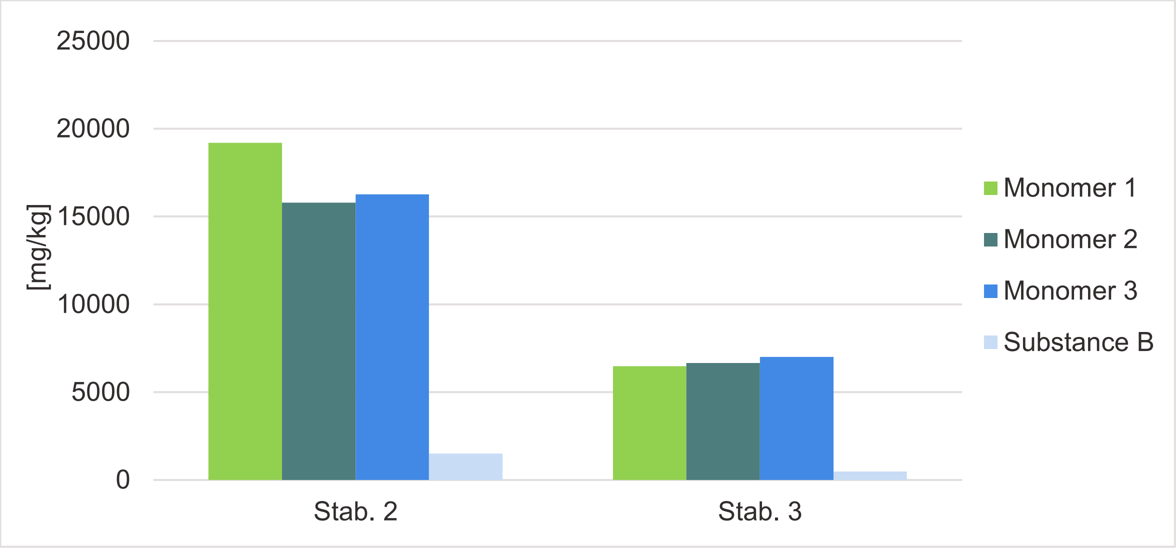


Figure 4.41 *Residual monomers in dispersions polymerized with Stabilizer 2 and 3, both with Initiator 1 at 85°C and pH 5.0. Substance B was a by-product from Monomers 2 and 3.*

5 CONCLUSION

Bio-based and bio-degradable products are constantly developed, and non-renewable material are replaced by bio-friendly components to reduce the impact on the environment. Bio-based stabilizers are found in most plants and protect the plant from, *e.g.*, UV-radiation, fungi and bacteria. Many bio-based polymers, such as cellulose, lignin and hemicellulose, are widely used in the industry today as stabilizers and emulsifiers, among other things. In this thesis, different natural polymers and their potential as stabilizers in mainly latex dispersions were discussed. The focus in this work was on the colloidal stability of a dispersion, *i.e.*, how the stabilizer prevents the aggregation of particles in a dispersion. Furthermore, polymerizations stabilized with two different stabilizers were executed, and the dispersions were analyzed and compared to a reference dispersion. Factors such as pH, temperature and amount of stabilizer have been investigated and discussed.

A reference dispersion with Stabilizer 1, a polysaccharide, was polymerized and the aim of this thesis was to achieve similar properties with Stabilizer 2 (polysaccharides combined with a lignin-based polyelectrolyte) and Stabilizer 3 (consisting of the lignin-based polyelectrolyte in Stabilizer 2). The chemical structure of the stabilizers was quite complex, and the chemical composition of the impurities inhibited the polymerization to some extent, which necessitated a second feed of initiator to successfully complete the polymerization.

The polymerization rate was affected by the pH during polymerization using Stabilizer 2 and Initiator 1 at 85°C. Additional feeds of initiator were needed to finalize the polymerizations, indicating the stabilizer might hinder or slow down the polymerization at lower pH. Considering the target properties, better results were generated at more neutral pH, between 5.0 and 6.0. Here, the particle size distribution (PSD) was narrower, and the dispersion did not contain larger aggregates. At lower pH, the solids content was lower, and the PSD was wider. These dispersions often contained a small number of very large particles.

Keeping the pH constant at 5.0 while changing the temperature made the PSD very broad. At 93°C, the dispersions contained small amounts of very large particles, while at 75°C, the dispersion did not contain significantly larger particles. The rate of polymerization was higher at 93°C, compared to polymerizations done at 85°C and 75°C, and there was no need of an additional initiator to reach the solids content target. However, at higher temperature, the dispersions were unstable and visual phase separations were observed.

Additional amounts of stabilizer, both 20% and 40% more, made the PSD narrower. Polymerizations having 20% more stabilizers were done both at pH 5.0 and 6.0 at 85°C, with slightly lower D50 and D90 values in the dispersion polymerized at pH 5.0. The dispersions containing 40% more stabilizer, polymerized at 85°C and pH 5.0, had the lowest particle size of all successful polymerizations, with a D90 value of 217 nm and D50 of 118 nm, considering the target values of D90 < 200 nm and D50 < 100 nm.

The relatively large amount of residual monomers in the dispersions was a disadvantage. The dispersions cannot contain any hazardous substances due to their further area of applications in surface sizing. The reference dispersion polymerized with Stabilizer 1 did not contain any residual monomers. To reduce the amount of monomer residues, an additional initiator, named Initiator 3, was added to the polymerization after the theoretical solids content was achieved. This improved the rate of polymerization and significantly reduced the amount of monomer leftovers. However, the dispersion still contained approximately 5 000 mg monomers/kg dispersion, in comparison to almost 25 000 mg/kg for a dispersion that did not contain Initiator 3. Furthermore, dispersions polymerized at lower pH had lower amounts of residues, due to the additional amount of initiator to meet the solids content of 25% and a more diluted dispersion.

Since Stabilizer 2 consisted of two main compounds, a few dispersions stabilized with only one of the compounds were done. This stabilizer, Stabilizer 3, was more alkaline than Stabilizer 2, with a pH of 8.3 compared to 5.0, and as polymerizations done with Stabilizer 2, these polymerizations worked better at more neutral pH at 85°C. However, the dispersions had a very broad PSD, and all samples contained small amounts of very large particles. The dispersion polymerized at pH 5.0 with Stabilizer 3 contained residual monomers as well. After weeks of storage, the dispersions started to show signs of sedimentation, indicating the dispersions were not stable over time.

The dispersions polymerized with Stabilizer 2 and 3 at pH 5.0 showed negative ζ-potential, between -40 to -52 mV. The ζ-potential was lower compared to the potential of the reference dispersion polymerized with Stabilizer 1, where the further from 0 mV the better colloidal stability. Furthermore, no degradation over time in the stability of the particle size were detected in dispersions polymerized with Stabilizer 2. The dispersions were stored between 11 and 16 weeks before the particle size was measured again. Only smaller variations were detected, presumably due to variations in repeating tests.

Impurities found in natural stabilizers are a problem, and might hinder the polymerization to some extent, as it presumably did in this work. However, the stabilizers showed great potential in stabilizing nanoparticle dispersions. More experiments should be done to reduce the amount of residual monomers and to decrease the particle size further. According to this thesis, these bio-based stabilizers worked better at neutral pH and with a larger amount of stabilizer and initiator compared to the amount of monomers. However, only dispersions polymerized with Stabilizer 2 did not sediment over time, indicating these dispersions remained stable.

6 SWEDISH SUMMARY – SVENSK SAMMANFATTNING

Biobaserade stabiliseringsmedel för hydrofoba nanopartikeldispersioner

Nyckelord: Stabiliseringsmedel, stabilitet, dispersion, nanopartikel, polymerisering, partikelstorleksfördelning, ytlimning

Intresset för förnyelsebart och bionedbrytbart material har ökat märkbart det senaste årtiondet. Plastprodukter utvecklas ständigt och komponenter ersätts en efter en av biobaserat material. Naturliga stabiliseringsämnen finns i de flesta växter och skyddar mot bl.a. syre, UV-strålning, sjukdomar och kemiska angrepp. Biobaserade polymerer, såsom cellulosa, lignin, kitosan och hemicellulosa, används i stor utsträckning inom industrin som emulgerings-, stabiliserings- eller förtjockningsmedel. Stabiliseringsmedel är nödvändiga för att upprätthålla produktens egenskaper och för att sakta ner eller förhindra att materialet bryts ner, t.ex. vid syre-exponering. Fokuset i detta arbete var på dispersioners kolloidala stabilitet, d.v.s. hur biobaserade material förhindrar agglomerering av partiklar.

De i detta arbete framställda dispersioner kommer att användas inom ytlimning (*sizing*) av kartong. I ytlimningsprocessen sprids en jämn yta av en dispersion på kartongen för att täppa igen fiber och porer på materialets yta, vilket ökar kartongens styrka och dess ytegenskaper, bl.a. tryckegenskaper. Olika ämnen såsom alginater, cellulosa, kitosan, pektiner, och stärkelse, har diskuterats och deras egenskaper och potential som stabiliseringsmedel har klargjorts.

Stabiliseringsmedlet som användes i detta arbete består av vissa polysackarider kombinerat med en ligninbaserad polyelektrolyt, kallat för *Stabilizer 2*. Ett antal polymeriseringar utfördes med *Stabilizer 3*, som består av den ligninbaserade polyelektrolyten i *Stabilizer 2*. P.g.a. den kemiska sammansättningen av orenheter i dessa stabiliseringsämnen, har polymeriseringen av monomererna till viss mån förhindrats eller saktats ner. I och med detta hade ett extra flöde av initiator tillsatts för att nå en torrhalt på åtminstone 25 % och för att slutföra polymeriseringen. Faktorer såsom pH, temperatur samt mängd av stabiliseringsmedel och initiator varierades, och dess inverkan på polymeriseringsgraden undersöktes. Egenskaper såsom torrhalt, viskositet samt partikelstorleksfördelning (PSD) var viktiga, liksom stabiliteten samt mängden av opolymeriserade monomerer i dispersionen. Resultaten jämfördes med varandra och med en referensdispersion med utmärkta egenskaper, som stabiliserades med ett från tidigare känt stabiliseringsmedel bestående av en specifik polysackarid, *Stabilizer 1*. Målet var att nå liknande egenskaper med *Stabilizer 2*.

Dispersioner polymeriserade med *Stabilizer* 2 vid lägre pH och med en konstant temperatur på 85°C krävde en större mängd initiator för att slutföra polymeriseringen eftersom initiatorn fungerade bättre vid mer neutrala förhållanden. Vid pH 5,0 och 6,0 behövdes det en mindre mängd extra initiator för att nå en torrhalt på 25 % och dispersionerna innehöll inte stora agglomerade partiklar. Här var partikelstorleksfördelningen relativt snäv men medelpartikelstorleken var högre än önskat.

Polymeriseringar med *Stabilizer 2* vid högre temperatur (93 °C) gjorde partikelstorleksfördelningen väldigt bred. Dispersionerna innehöll en mindre mängd av väldigt stora partiklar och viskositeten var högre jämfört med dispersioner polymeriserade vid 85 °C. Däremot polymeriserades monomererna snabbare vid högre temperatur och ingen extra initiator krävdes för att nå en torrhalt på 25 %. Polymeriseringarna vid högre temperatur var dock instabila och dispersionerna var tydligt separerade i faser.

Mängden stabiliseringsmedel inverkade på partikelstorleksfördelningen. Dispersioner innehållande 20 % och 40 % mer stabiliseringsmedel polymeriserades, både vid pH 5,0 och 6,0 vid 85°C. Dispersionen som innehöll 40 % mer stabiliseringsmedel och polymeriserades vid pH 5,0 och 85°C gav lovande resultat med en snäv partikelstorleksfördelning och innehöll inga stora partiklar.

Dispersionerna innehöll stora mängder monomerer efter att polymeriseringen avslutats. Halten monomerer bör vara nära noll med tanke på dispersionernas användningsområde för ylimning av kartong. En extra initiator, kallad *Initiator 3*, tillsattes i slutskedet av reaktionen för att polymerisera de resterande monomererna och enligt vätskekromatografiska analyser minskade mängden restmonomerer i dispersionen med nästan 80 %. Mängden monomerer var oavsett ungefär 5000 mg monomerer/kg dispersion, vilket är för mycket för att dispersionen ska kunna användas inom ytlimning. Dispersioner polymeriserade vid lågt pH innehöll mindre mängd restmonomerer, troligen eftersom mer initiator krävdes för att nå en torrhalt på 25 % samt för att dispersionen var mer utspädd. Vid högre pH nådde dispersionerna snabbare en torrhalt på 25 % och innehöll därför en mindre mängd initiator och vatten, och därmed en större mängd restmonomerer.

Stabiliseringsmedlet som användes i detta arbete, *Stabilizer 2*, bestod av två huvudkomponenter. För att undersöka ämnet närmare utfördes ett antal polymeriseringar stabiliserade med endast den ena komponenten, *Stabilizer 3*. Detta stabiliseringsmedel var mer alkaliskt än *Stabilizer 2*, med ett pH på 8,3 jämfört med 5,0. Initiator tillades i större utsträckning till reaktionen för att slutföra polymeriseringen och dispersionen innehöll en märkbart mindre mängd restmonomerer jämfört med dispersioner polymeriserade under samma villkor med *Stabilizer 2*. Partikelstorleksfördelning för dessa dispersioner var dock väldigt bred och dispersionerna innehöll ett antal väldigt stora partiklar.

Dispersioner som polymeriserats med *Stabilizer 2* och *3* vid pH 5,0 hade god kolloidal stabilitet mellan pH 2,0 och 8,0 baserat på resultat från ζ-potentialmätningar. ζ-potentialen hade ett mer negativt värde jämfört med referensdispersionen, stabiliserat med *Stabilizer 1*, där ju närmare 0 mV desto lägre kolloidal stabilitet har dispersionen. I dispersioner stabiliserade med *Stabilizer 2* noterades ingen förändring av partikelstorleken efter förvaring, denna var så gott som oförändrad efter 11 till 16 veckor av förvaring. Dispersionerna som var stabiliserade med *Stabilizer 3* sedimenterade, vilket tyder på en instabil dispersion. Alla dispersioner förvarades i glasflaskor i rumstemperatur och i skydd från solljus.

Orenheter är ett problem i naturliga stabiliseringsmedel och kan förhindra eller sakta ner polymeriseringsprocessen, vilket förmodligen skedde i dessa experiment. Vidare analyser samt experiment bör göras, främst för att minska på mängden restmonomerer men även för att minska partikelstorleken, för att dispersionerna ska kunna användas inom ytlimning. Experimenten bör även upprepas för att få mer tillförlitligt data. Enligt detta arbete polymeriserades dessa dispersioner bättre vid neutralt pH och med större mängder initiator och stabiliseringsmedel.

REFERENCES

Ahmad, H. & Tauer, K., 2003. Effects of chain transfer agent on the radical polymerization of styrene in non-aqueous dispersion. *Colloid and polymer science,* Volume 281, pp. 686-869.

Akhtar, M., Dickinson, E., Mazoyer, J. & Langendorff, V., 2002. Emulsion stabilizing properties of depolymerized pectin. *Food hydrocolloids,* 16(3), pp. 249-256.

Antonietti, M. & Tauer, K., 2003. 90 Years of Polymer Latexes and Heterophase Polymerization: More vital than ever. *Macromolecular Chemistry and Physics,* 204(2), pp. 207-219.

Asua, J. & Schoonbrood, H., 1999. Reactive surfactants in heterophase polymerization. *Acta Polymerica,* 49(12).

Bel Haaj, S., Thielemans, W., Magnin, A. & Boufi, S., 2014. Starch Nanocrystal Stabilized Pickering Emulsion Polymerization for Nanocomposites with Improved Performance. *ACS Applied Materials & Interfaces,* 6(11), pp. 8263-9273.

Bowen, W. & Williams, P., 1996. The osmotic pressure of electrostatically stabilized colloidal dispersions. *Journal of Colloid and Interface Science,* 184(1), pp. 241-250.

Braun, D., 2009. Origins and Development of Initiation of Free Radical Polymerization Processes. *International Journal of Polymer Science,* Volume 2009.

Chattopadhyay, D., Chakraborty, M. & Mandal, B. M., 2001. Dispersion polymerization of aniline using hydroxypropylcellulose as a stabilizer: role of rate of polymerization. *Polymer International,* 50(5), pp. 538-544.

Cheng, S., Zhao, W. & Wu, Y., 2015. Optimization of synthesis and characterization of oxidized starch-graft-poly(styrene-butyl acrylate) latex for paper coating. *Starch,* 67(5-6), pp. 493-501.

Chevalier, Y. & Bolzinger, M.-A., 2013. Emulsions stabilized with solid nanoparticles: pickering emulsions. *Colloids and surfaces A: Physiochemical and engineering aspects,* Volume 439, pp. 23-34.

Daemi, H., Barikani, M. B. & Barmar, M., 2013. Compatible compositions based on aqueous polyurethane dispersions and sodium alginate. *Carbohydrate Polymers,* 92(1), pp. 490-496.

Dai, Z. *et al.*, 2011. Chemical interaction between carbon fibers and surface sizing. *Journal of Applied Polymer Scicence,* 124(3).

Doelker, E., 2005. Cellulose derivatives. In: *Advances in Polymer science, vol. 107.* Geneva: Springer, pp. 199-265.

Draget, K., 2009. Alginates. In: *Handbook of hydrocolloids (second edition).* Trondheim: Woodhead Publishing Series, pp. 807-828.

Draget, K. I. & Taylor, C., 2009. Chemical, physical and biological properties of alginates and their biomedical implications. *Food hydrocolloids,* 25(2), pp. 251-256.

Fujii, S. *et al.*, 2009. Ferritin as a bionano-particulate emulsifier. *Journal of colloid and interface science,* 338(1), pp. 222-228.

Gregorová, A., Cibulková, Z., Košíková, B. & Šimon, P., 2005. Stabilization effect of lignin in polypropylene and recycled polypropylene. *Polymer degradation and stability,* 89(3), pp. 553-558.

Guerrini, L., Alvarez-Puebla, R. A. & Pazos-Perez, N., 2018. Surface modifications of nanoparticles for stability in biological fluids. *Materials,* 11(7).

Güleç, H. A., Sarioğlu, K. & Mutlu, M., 2005. Modification of food containing surfaces by plasma polymerisation technique. Part I: Determination of hydrophilicity, hydrophobicity and surface free energy by contact angle method. *Journal of Food Engineering,* 75(2), pp. 187-195.

Gundersen, S. & Sjöblom, J., 1999. High-and low-molecular-weight lignosulfonates and Kraft lignins as oil/water-emulsion stabilizer studied by means of electrical conductivity. *Colloid and Polymer Science,* 277(5), pp. 462-468.

Horozov, T. S. & Binks, B. P., 2006. Particle-stabilized emulsions: A bilayer or a bridging monolayer?. *Angewandte Chemie International Edition,* 45(5).

Iijima, M. & Kamiya, H., 2009. Surface modification for improving the stability of nanoparticles in liquid media. *Powder and Particle Journal,* Volume 27, pp. 119-129.

Ishikawa, Y., Katoh, Y. & Ohshima, H., 2005. Colloidal stability of aqueous polymeric dispersions: Effect of pH and salt concentration. *Colloids and Surfaces B: Biointerfaces,* 42(1), pp. 53-58.

Ivanov, M. & Ivanov, D., 2012. Nanodiamond nanoparticles as additives to lubricants. In: *Ultrananocrystalline Diamond.* 2nd ed. Illinois: Elsevier Inc..

Katainen, J. *et al.*, 2006. Adhesion as an interplay between particle size and surface roughness. *Journal of Colloid and Interface Science,* 304(2), pp. 524-529.

Kirschweng, B., Tátraaljai, D., Földes, E. & Pukánszky, B., 2017. Natural antioxidants as stabilizers for polymers. *Polymer Degredation and Stability,* Volume 145, pp. 25-40.

Klemm, D., Heublein, B., Fink, H.-P. & Bohn, A., 2005. Cellulose: Fascinating biopolymer and sustainable raw material. *Angewandte Chemie International Edition,* 44(22).

Kumar, A. P., Depan, D., Tomer, N. S. & Singh, R. P., 2009. Nanoscale particles for polymer degradation and stabilization - Trends and future perspectives. *Progress in Polymer Science,* 34(6), pp. 479-515.

Leroux, J. *et al.*, 2002. Emulsion stabilizing properties of pectin. *Food hydrocolloids,* 17(4), pp. 455-462.

Marie, E., Landfester, K. & Antonietti, M., 2002. Synthesis of chitosan-stabilized polymer dispersions, capsules, and chitosan grafting products via miniemulsions. *Biomacromolecules,* 3(3), pp. 475-481.

Mewis, J. & Vermant, J., 2000. Rheology of sterically stabilized dispersions and latices. *Progress in organic coatings,* 40(1-4), pp. 111-117.

Mezdour, S. *et al.*, 2008. Oil/water surface rheological properties of hydroxypropyl cellulose (HPC) alone and mixed with lecithin: Contribution to emulsion stability. *Colloids and Surfaces A: Physiochemical and Engineering Aspects,* 331(1-2), pp. 76-83.

Monteiro, M. J. & de Barbeyrac, J., 2001. Free-Radical Polymerization of Styrene in Emulsion Using a Reversible Addition−Fragmentation Chain Transfer Agent with a Low Transfer Constant: Effect on Rate, Particle Size, and Molecular Weight. *Macromolecule,* 34(13), pp. 4416-4423.

Nan, F. *et al.*, 2014. Uniform chitosan-coated alginate particles as emulsifiers for preparation of stable pickering emulsions with stimulus dependence. *Colloids and surfaces A: Physiochemical and engineering aspects,* Volume 456, pp. 246-252.

NanoComposix, 2019. *Zeta Potential Measurements.* [Online] Available at: https://nanocomposix.com [Accessed 24 October 2019].

Paine, A. J., 1990. Dispersion polymerization of styrene in polar solvents. IV. Solvency control of particle size from hydroxypropyl cellulose stabilized polymerizations. *Journal of Polymer Science Part A: Polymer Chemistry,* 28(9).

Paine, A. J., 1990. Dispersion polymerization of styrene in polar solvents: I. Grafting mechanism of stabilization by hydroxypropyl cellulose. *Journal of Colloid and Interface Science,* 138(1), pp. 157-169.

Paine, A. J., Luymes, W. & McNulty, J., 1990. Dispersion polymerization of styrene in polar solvents. IV. Influence of reaction parameters on particle size and molecular weight on Poly(N-vinylpyrrolidone)-stabilized reactions. *Macromolecules,* 23(12), pp. 3104-3109.

Panzella, L. & Napolitano, A., 2017. Natural phenol polymers: recent advances in food and health applications. *Antioxidants,* 6(2).

Parfitt, G. & Barnes, H., 1997. The dispersion of fine particles in liquid media. In: *Mixing in the Process Industries.* 2nd ed. London: Elsevier Ltd..

Pei, X. *et al.*, 2016. Pickering polymerization of styrene stabilized by starch-based nanospheres. *Polymer Chemistry,* Volume 7, pp. 3325-3333.

Phan, T. T. V. *et al.*, 2019. Chitosan as a stabilizer and size-control agent for synthesis of porous flower-shaped palladium nanopraticles and their applications on photo-based therapies. *Carbohydrate Polymers,* Volume 205, pp. 340-352.

Reed, W. F. & Alb, A. M., 2014. *Monitoring Polymerization Reactions: From Fundamentals to Applications.* New Orleans: Jogn Wiley & Sons.

Rescignano, N. *et al.*, 2014. Use of alginate, chitosan and cellulose nanocrystals as emulsion stabilizers in the synthesis of biodegradable polymeric nanoparticles. *Journal of colloid and interface science,* Volume 445, pp. 31-39.

Reusch, W., 2015. *Free radical polymerization,* East Lansing, Michigan: LibreTexts Chemistry.

Rinaudo, M., 2006. Chitin and chitosan: Properties and applications. *Progress in Polymer Science,* 31(7), pp. 603-632.

Rosenberg, E. & Ron, E., 1999. High- and low-molecular-mass microbial surfactants. *Applied microbiology and biotechnology,* 52(2), pp. 154-162.

Schmidt, B. *et al.*, 2017. Lignin-based polymeric surfactants for emulsion polymerization. *Polymer,* Volume 112, pp. 418-426.

Smeets, N. M. *et al.*, 2010. The effect of different catalytic chain transfer agents on particle nucleation and the course of the polymerization in *ab initio* batch emulsion polymerization of methyl methacrylate. *Journal of Polymer Science Part A: Polymer Chemistry,* 48(5), pp. 1038-1048.

Stevens Creek, B., 2014. *Liquid Cromatography: Efficient LC Solutions for any Application and Budget.* [Online] Available at: https://www.agilent.com/en/products/liquid-chromatography?gclid=EAIaIQobChMI-Zr42bbn5QIVTaqaCh2BFgvbEAAYASAAEgKTuvD_BwE&gclsrc=aw.ds [Accessed 13 November 2019].

Stevens Creek, B., 2015. *Agilent 1100 Series GPC-SEC Analysis System by Agilent Technologies.* [Online] Available at: https://www.selectscience.net/products/agilent-1100-series-gpc-sec-analysis-system/?prodID=10592#tab-2 [Accessed 13 November 2019].

Valles, E. M. & Macosko, C. W., 1979. Structure and viscosity of poly(dimethylsiloxanes). *Macromolecules,* 12(3).

Verkempinck, S. *et al.*, 2018. Emulsion stabilizing properties of citrus pectin and its interactions with conventional emulsifiers in oil-in-water emulsions. *Food Hydrocolloids,* Volume 85, pp. 144-157.

Vijayakumar, S. & Saravanan, V., 2015. Biosurfactants -Types, sources and applications. *Research journal of microbiology,* 10(5), pp. 181-192.

Villain, F., Coudane, J. & Vert, M., 1995. Thermal degradation of polyethylene terephthalate: study of polymer stabilization. *Polymer Degradation and Stability,* 49(3), pp. 393-397.

Whistler, R. L., 1993. Chapter 11-Hemicelluloses. In: *Industrial Gums: Polysaccharides and their derivatives.* 3rd ed. West Lafayette: Academic Press, pp. 295-308.

Yang, D., Qiu, X., Zhou, M. & Lou, H., 2007. Properties of sodium lignosulfonate as dispersant of coal water slurry. *Energy Conversion and Management,* 48(9), pp. 2433-2438.

Yun, J.-K., Yoo, H.-J. & Kim, H.-D., 2007. Preparation and properties of waterborne polyurethane-urea/sodium alginate blends for high water vapor permeable coating materials. *Journal of Applied Polymer Science,* 105(3), pp. 1168-1176.

Zhang, J., Xiao, H. & Yang, Y., 2015. Preparation of hemicellulose-containing latex and its application as absorbent toward dyes. *Journal of Materials Science,* Volume 50, pp. 1673-1678.

Zhulina, E. B., Borisov, O. V. & Priamitsyn, V. A., 1990. Theory of steric stabilization of colloid dispersions by grafted polymers. *Journal of Colloid and Interface Science,* 137(2), pp. 495-511.

APPENDIX

Appendix A

Polymerizations executed and clarification of the compounds used.

Table A1 *Polymerizations executed in this thesis work. All polymerizations were done with constant amount of monomers, fed to the reactor at constant rate if nothing else is stated. Subst. A = Substance A; Init. 3 = Initiator 3*

Test No.	pH	[°C]	Recipe	Stabilizer	Initiator	Subst. A	Init. 3
Ref.	2.3	85	Standard	1	1	-	-
2	2.3	85	Standard	2	1	-	-
5	1.8	85	Standard	2	1	-	-
6	2.8	85	Standard	2	1	-	-
7	3.2	85	Standard	2	1	-	-
8	3.8	85	Standard	2	1	-	-
9	6.0	85	Standard	2	1	-	-
10	5.5	85	Standard	2	2	-	-
11	2.3	85	Standard	2	2	-	-
12	5.0	93	Standard	2	1	-	-
13	5.0	75	Standard	2	1	-	-
14	5.0	85	Standard	2	1	-	-
15	5.0	93	+40% initiator	2	1	-	-
16	5.0	85	+20% stabilizer	2	1	-	-
17	5.0	93	+20% stabilizer	2	1	-	-
18	6.3	85	+20% stabilizer	2	1	-	-
19	5.0	85	Standard	2	1	-	-
20	7.0	85	Standard	2	1	-	-

Test No.	pH	[°C]	Recipe	Stabilizer	Initiator	Subst. A	Init. 3
21	5.0	85	Different feeding rates	2	1	-	-
22	6.0	85	+Additives	2	1	x	-
23	6.0	85	+Additives	2	1	-	x
24	6.0	85	+Additives	2	1	x	x
25	3.8	85	+Additives	2	1	x	x
26	5.0	85	+40% stabilizer	2	1	-	-
27	2.3	85	Standard	3	1	-	-
28	5.0	85	Standard	3	1	-	-
29	5.0	85	+Additives	3	1	x	x
30	5.0	85	+40% stabilizer	3	1	-	-

The polymerization process was carried out according to following standard example:

1. Start the N_2 flow to the reactor
2. Add water into the reactor
3. Add stabilizer to water at room temperature
4. Dissolve catalyst in water and add to the reactor. Prepare the catalyst right before use
5. Uniform mixing at 100 rpm and heat to given temperature °C in 60 min
6. Adjust pH according to the recipe with 30% H_2SO_4 or 30% NaOH. Mix for 5 min and check that pH is stable at 25°C
7. Dilute initiator in water to 3.5% solution
8. Prepare the monomer mixture[1]
9. Measure pH and viscosity at 25°C
10. Feed monomers and initiator to the reactor during 120 min at constant rate. Initiator feed is started 3 min before the monomer feed
11. Measure PDS, viscosity and solids content after 120 min
12. If solids content not reached, continue the initiator feed at constant rate until the solids content is approximately 25%, but not longer than 120 min. Measure the solids content every 30 – 40 min [2]
13. After the feed ends, mix at given temperature for 45 min

14. Close the N_2 flow and cool the product to room temperature
15. Adjust solids content with water, if necessary
16. Adjust pH to 4.5. Mix for 15 min and check that pH is stable (at 25°)
17. Filter the product through 100 µm filter cloth

[1] Substance A is added to the monomer mixture.

[2] Initiator 3 is added after the theoretical solids content is reached, followed by an additional mixing time of 60 min before cooling the reactor.

Appendix B

Data from SEC analyses [g/mol].

Table B1 *Data to graphs plotted in Figure 4.20 in Chapter 4.4.1 and in Figure 4.40 in Chapter 4.7*

Test No.	Mw [g/mol]
Ref.	55 400
2	170 000
9	147 000
24	104 000
28	100 000

Appendix C

Data to solids content [%], viscosity [mPas], particle size D50 and D90 [nm], and additional amount of initiator [g]. η = Viscosity, SC = Solids content.

Table C1 *Data to graphs plotted in Figure 4.1 – 4.3 in Chapter 4.2*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
2	16.3	2.9	25.7	13.6	328	176	224	123	16.1
5	17.3	2.6	22.7	10.6	4380	218	265	108	17.8
6	6.6	2.9	25.4	12.1	284	162	200	114	14.7
7	5.9	3.1	26.1	13.1	277	152	180	104	13.8
8	8.3	4.0	27.2	16.5	262	136	177	103	9.6
9	11.3	9.6	26.5	23.4	267	120	220	112	2.1
19	21.9	8.4	26.8	20.8	267	144	211	118	3.7
20	19.5	6.4	27.4	19.3	280	154	208	109	6,4

Table C2 *Data to graphs plotted in Figure 4.7 – 4.9 in Chapter 4.3.1*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
19	21.9	8.4	26.8	20.2	267	144	211	118	3.7
16	14.9	6.6	25.6	19.1	255	138	218	99	5.0
26	8.3	4.8	24.4	16.0	217	118	162	90	8.1
21	17.6	11.0	21.7	22.6	268	148	206	117	0

Table C3 *Data to graphs plotted in Figure 4.11 – 4.13 in Chapter 4.3.2*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
13	368	4.7	29.5	15.3	555	228	322	44	14.8
12	1 990	15.2	28.6	26.1	341	174	238	142	0
15	1 680	11.3	27.1	24.0	5 360	174	239	129	0
17	13.6	10.0	23.2	23.6	293	144	219	120	0

Table C4 *Data to graphs plotted in Figure 4.16 – 4.18 in Chapter 4.4.*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
9	11.3	9.6	26.5	23.4	267	120	220	112	2.1
18	13.4	6.1	26.8	19.2	263	151	216	116	6.7
22	24.8	6.9	27.7	20.3	366	160	213	109	5.5
23	11.4	7.8	27.0	20.0	299	153	581	298	5.8
24	21.1	6.5	25.3	19.8	4 600	162	194	103	4.3

Table C5 *Data to graphs plotted in Figure 4.21 – 4.23 in Chapter 4.4.2*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
25	8.7	4.7	30.9	16.3	333	160	168	88	11.8
24	21.1	6.5	32.1	19.8	4 600	162	194	103	4.3

Table C6 *Data to graphs plotted in Figure 4.25 – 4.27 in Chapter 4.5.1*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
10	2.4	2.8	14.7	14.6	399	116	9.3	5.6	17.0
11	2.7	3.4	13.4	14.7	461	272	9.5	6.4	17.0

Table C7 *Data to graphs plotted in Figure 4.30 – 4.32 in Chapter 4.5.2*

Test No.	η Final [mPas]	η S1 [mPas]	SC Final [%]	SC S1 [%]	D90 Final [nm]	D50 Final [nm]	D90 S1 [nm]	D50 S1 [nm]	Extra init. [g]
27	2.2	1.8	9.4	8.9	735	332	693	417	16.3
28	35.6	2.8	23.2	9.8	4 890	155	226	32.4	15.5
29	47.0	2.3	21.4	9.4	3 330	88	194	26	17.8
30	193.3	1.7	25.9	9.3	5 080	425	150	20	17.8

Table C8 *Data to graph plotted in Figure 4.36 in Chapter 4.6.1.*
A = immediately after polymerization, B = after x weeks of storage

Test No.	D90 A [nm]	D50 A [nm]	D90 B [nm]	D50 B [nm]	Storage [weeks]
Ref.	115	57	101	56	16
8	262	136	265	134	14
9	267	120	232	114	14
14	325	150	338	144	11

Appendix D

Data from HPLC analyses [mg/kg]. Mon. = Monomer, Sub. = Substance.

Table D1 *Data to graph plotted in Figure 4.5 in Chapter 4.2*

Test No.	Mon. 1 [mg/kg]	Mon. 2 [mg/kg]	Mon. 3 [mg/kg]	Sub. B [mg/kg]
2	4 441	5 580	6 134	3 214
16	19 201	15 786	16 259	1 510
9	7 979	10 740	9 053	1 190
23	24 157	15 917	19 345	1 075

Table D2 *Data to graph plotted in Figure 4.10 in Chapter 4.3.1*

Test No.	Mon. 1 [mg/kg]	Mon. 2 [mg/kg]	Mon. 3 [mg/kg]	Sub. B [mg/kg]
16	19 201	15 786	16 259	1 510
26	9 447	9 787	9 516	471

Table D3 *Data to graph plotted in Figure 4.24 in Chapter 4.4.2*

Test No.	Mon. 1 [mg/kg]	Mon. 2 [mg/kg]	Mon. 3 [mg/kg]	Sub. B [mg/kg]
9	7 979	10 740	9 053	1 190
25	3 703	5 556	5 209	648

Table D4 *Data to graph plotted in Figure 4.41 in Chapter 4.7*

Test No.	Mon. 1 [mg/kg]	Mon. 2 [mg/kg]	Mon. 3 [mg/kg]	Sub. B [mg/kg]
14	19 201	15 786	16 259	1 510
28	6 471	6 665	7 014	489

Appendix E

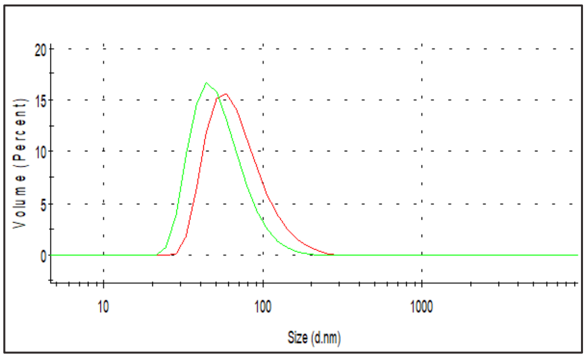
ζ-potential analyses [mV]. n/d = not defined.

Table E1 *Data to graph plotted in Figure 4.37 in Chapter 4.6.2*

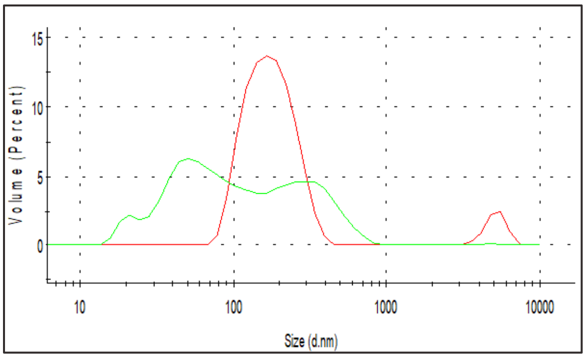
Test No.	pH 2	pH 3	pH 5	pH 6	pH7	pH 8
Ref.	-3.3	n/d	-37.3	-40.2	n/d	n/d
8	-32.7	n/d	-42.2	-43.5	n/d	n/d
14	-42.8	-41.2	-46.8	n/d	-46.1	-44.5
28	-51.3	n/d	-46.5	n/d	n/d	-46.7

Appendix F

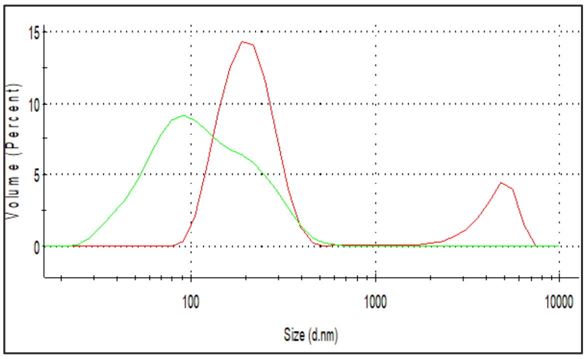
Particle size distribution by volume [%]. Green: S_1. Red: Final dispersion.



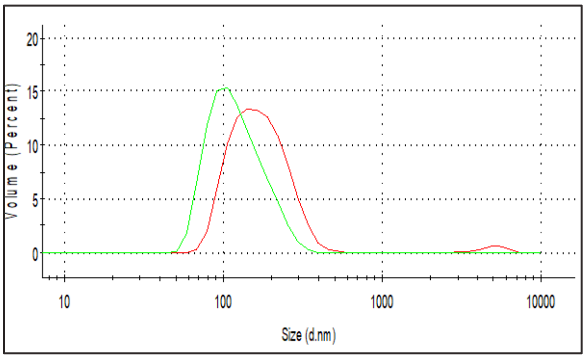
Ref.



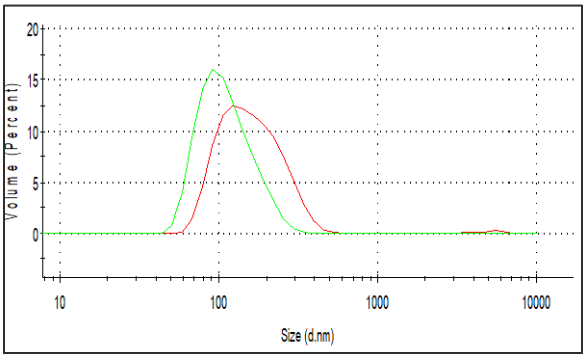
Test 2



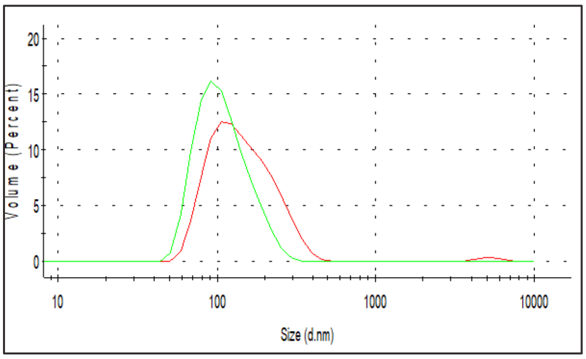
Test 5



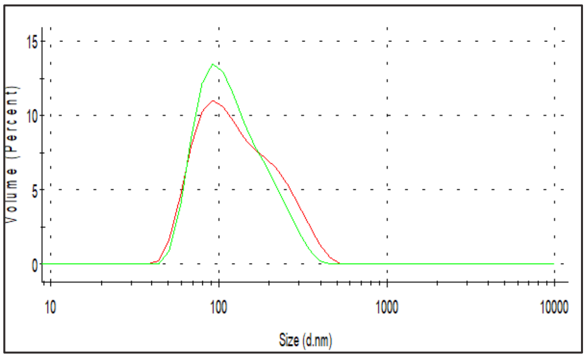
Test 6



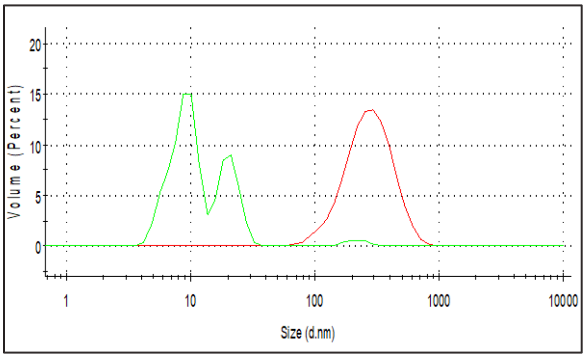
Test 7



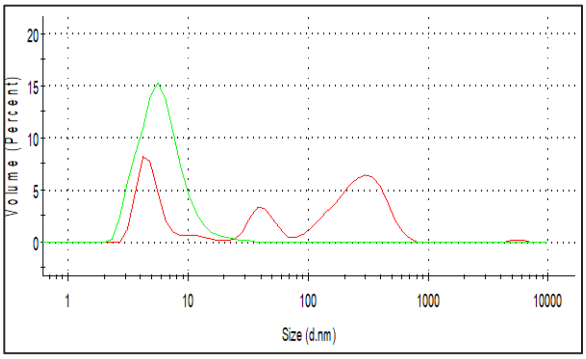
Test 8



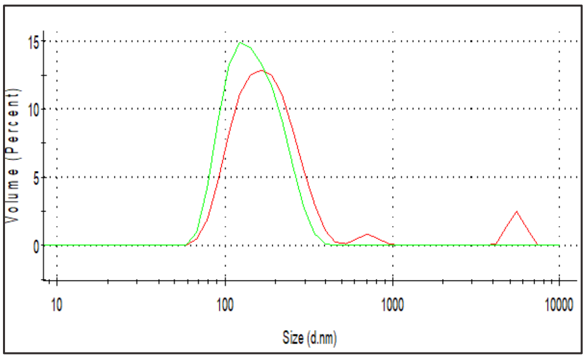
Test 9



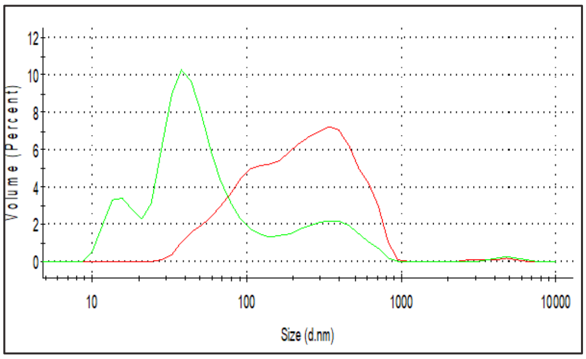
Test 10



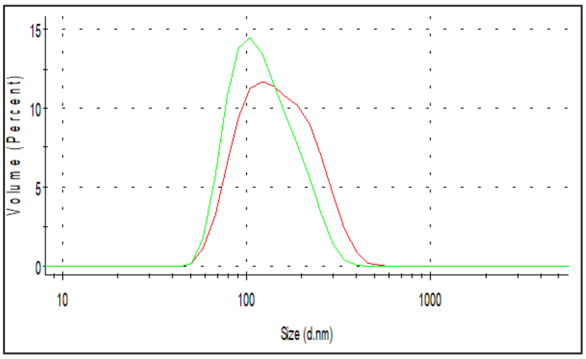
Test 11



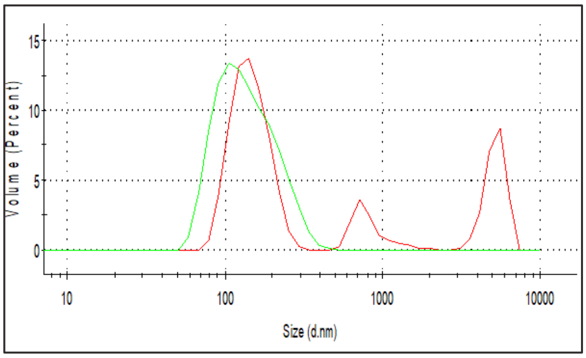
Test 12



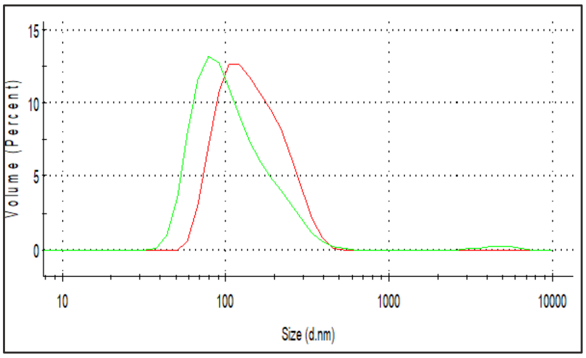
Test 13



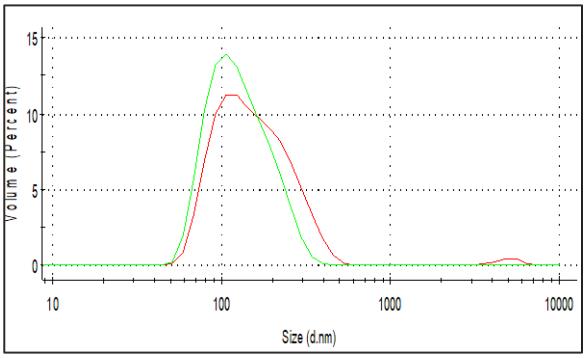
Test 14



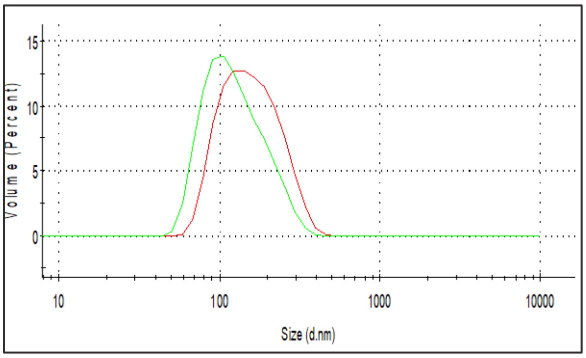
Test 15



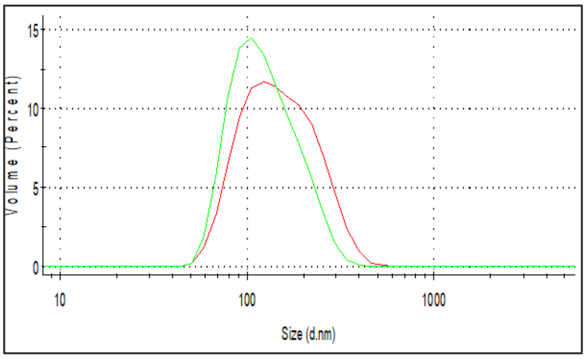
Test 16



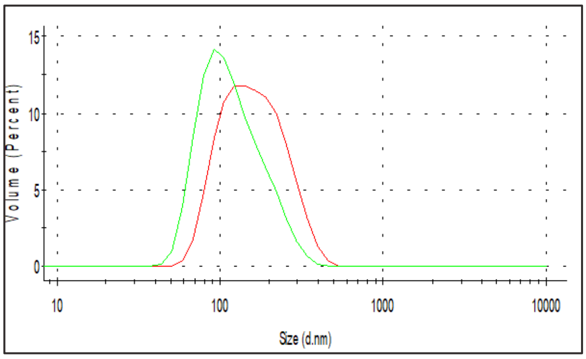
Test 17



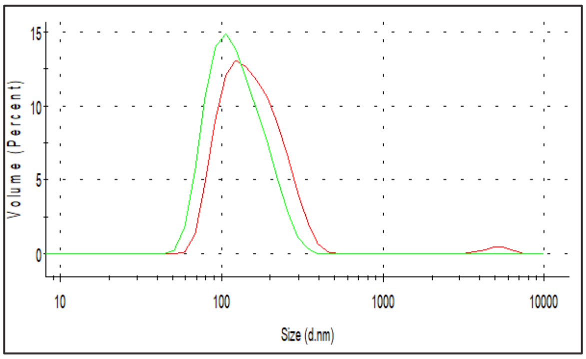
Test 18



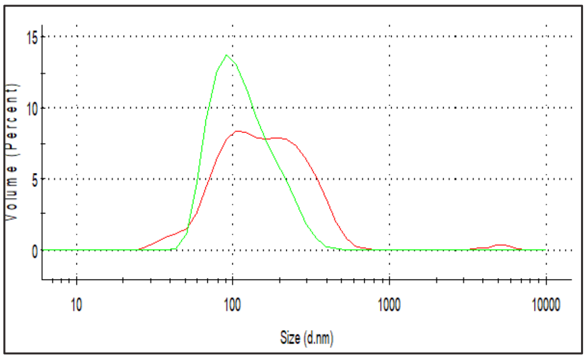
Test 19



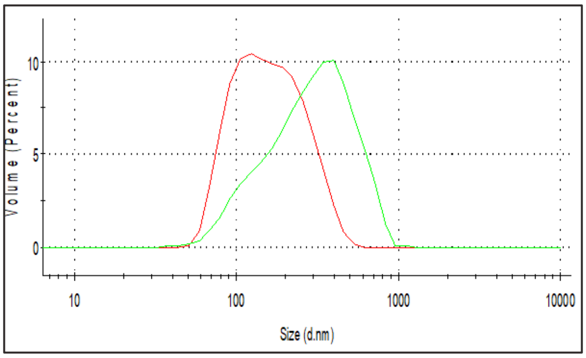
Test 20



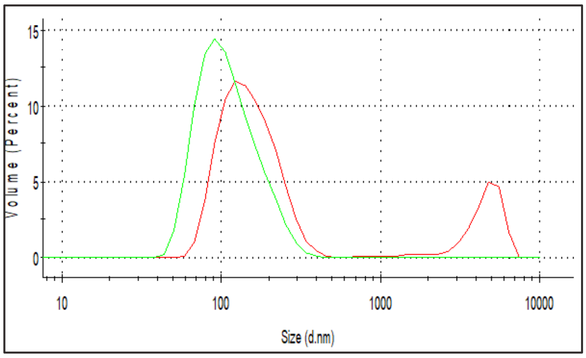
Test 21



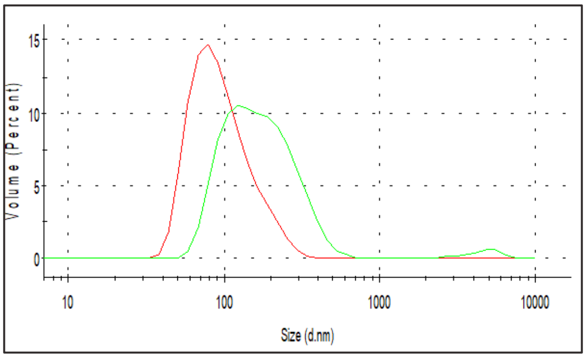
Test 22



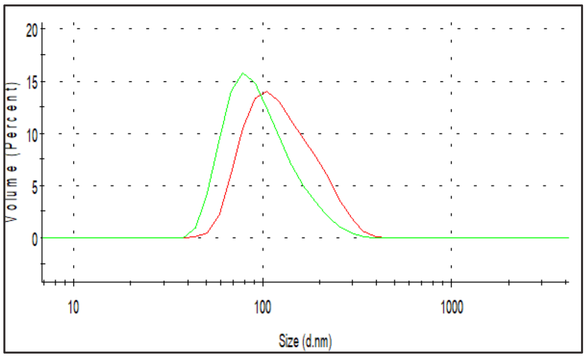
Test 23



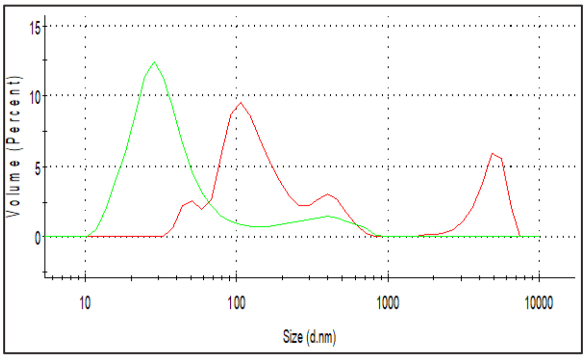
Test 24



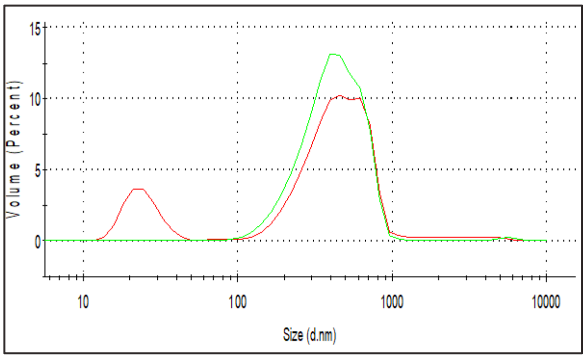
Test 25



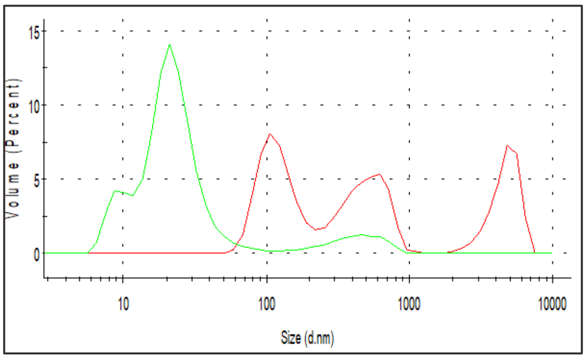
Test 26



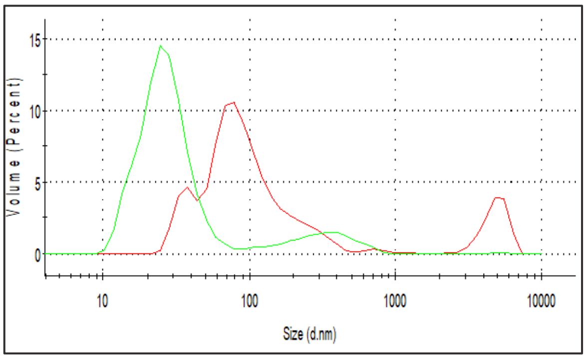
Test 27



Test 28



Test 29



Test 30