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Masterthesis

Optimization and development of processing aids for PVC foam applications

PROMOTOR :
Prof. dr. ir. Jozefien DE KEYZER

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Lénaïc Arnold
Scriptie ingediend tot het behalen van de graad van master in de industriële wetenschappen: chemie

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PREFACE

I choose to do an internship at the modifier division of Kaneka Belgium as part of my education in chemical industrial engineering at the University of Hasselt. During this internship I focused on improvement and development of processing aids for PVC applications.

I had an incredible learning experience and a delightful time at Kaneka Belgium. First of all I would like to thank my external promoter dr. ir. Sofie Sannen for her excellent guidance and support during this internship. She was always willing to share her experience and know-how in order to make me a better scientist. I would like to thank you for freeing up your time for me and for your thorough feedback on my master's thesis. In addition I also wish to thank all the colleagues who were willing to listen to my brainstorm sessions and give input in order to steer me on the right path.

I would also wish to thank my internal promoter Prof. dr. ir. Jozefien De Keyzer for her rapid, constructive and clear feedback on my assignments for this master's thesis. The information and knowledge shared through here lessons in plastic engineering were of great help during my research.

Furthermore I would like to thank my parents for the help and support. They gave me the opportunity to study and build a future of my own. For which I will always be grateful.

Finally I would like to thank my girlfriend Celien Claes who was always a listening ear and who supported me unconditionally during my internship. Her kind words have, as always, served me well.

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GLOSSARY

Abbreviation	**Description**	**Units**
AIBN	Azobisisobutyronitrile	-
$A_{\text{internal standard}}$	Intensity peak area for internal standard	-
A_{monomer}	Intensity peak area for monomer	µV*sec
ASG	Apparent specific gravity	g/cc
BHT	Butylated hydroxytoluene	-
CMC	Critical micellar concentration	g/l
Cp	Combined specific heat capacity	J/kg*°C
D	Diffusion coefficient or Particle diffusivity	m^2/s
d	Diameter of particle	m
f_{monomer}	Monomer factor related to FID detector	-
FRP	Free radical polymerization	-
GCL	Gas containing limit	-
H_{vap}	Heat evaporation of water	J/kg
k_B	Boltzmann constant	J/K
$\dot{m}a$	Air mass flow	kg/s
$\dot{m}f$	Feed mass flow	kg/s
$m_{\text{internal standard}}$	Mass of internal standard added	µg
m_{latex}	Mass latex weighed	g
M_w	Molecular weight	g/mol
PBA	Physical blowing agent	-
phr	Parts per hundred resin	-
pPVC	Plasticized polyvinyl chloride	-
PS	Particle size	Å
PSD	Particle size distribution	-
PVC	Polyvinyl chloride	-
PW	Process water	-
$\dot{Q}$	Heat transfer	J/s
RMC	Residual monomer content	µg/g
SEM	Scanning electron microscope	-
T	Absolute temperature	K
TA	Transfer agent	-
T_g	Glass transition temperature	°C
TMP	Tetramethyl piperidine	-
T_{ref}	Reference temperature	°C
uPVC	Unplasticized polyvinyl chloride	-
UV	Ultraviolet light	-
η	Dynamic viscosity of medium	kg/m*s
η_{Sp}	Specific viscosity	-
η_{Sp} ref	Reference specific viscosity	-

ABSTRACT

Optimization and development of processing aids

Kaneka Belgium develops and produces additives for PVC to improve its properties. Processing aids are added to improve fusion of the PVC resulting in better processability. PVC has poor processability characteristics other than slow fusion such as melt fracture, poor melt strength and extensibility. Processing aids improve melt rheology thanks to their high molecular weight chains. This master's thesis aims to improve the production process of a processing aid as well as develop a new processing aid. Properties of former processing aid should remain the same whilst production efficiency increases. Development of a processing aid resulting in a low-density PVC foam product with good surface finish is a desired outcome.

Processing aids are produced via free radical emulsion polymerization. Changes in recipe such as solid content, emulgator type, reaction time and post-initiation methods aim to improve the production process. To ensure properties remain within range, evaluation of parameters such as molecular weight, particle size distribution and shear viscosity are performed. In attempt to develop a new processing aid, parameters such as chain transfer agent, monomer composition and functional groups are changed along with blending of processing aids. Die swell and Brabender tests are performed to evaluate melt rheology of the new processing aid.

Alterations to the former processing aid resulted in an improved production efficiency. First developments towards the new processing aid were conducted.

ABSTRACT IN DUTCH

Kaneka Belgium ontwikkelt en produceert additieven voor PVC. *Processing aids* worden toegevoegd om fusie van PVC te promoten wat resulteert in betere procesverwerking. PVC heeft nog andere slechte procesverwerkingseigenschappen zoals smeltbreuk, slechte smeltsterkte en rekbaarheid. Dankzij de hoogmoleculaire ketens verbeteren *processing aids* de smeltreologie. Deze master thesis streeft naar verbetering van het productieproces van een *processing aid* alsook de ontwikkeling van een *processing aid*. Eigenschappen moeten behouden blijven terwijl productie-efficiëntie verbeterd. Ontwikkeling van een *processing aid* dat resulteert in een PVC schuim product met lage dichtheid en goede oppervlakteafwerking is een gewenst resultaat.

Processing aids worden via vrij radicaal emulsie polymerisatie geproduceerd. Wijzigingen in receptuur zoals vaste stof gehalte, emulgator type, reactietijd en postinitiatiemethoden dienen om het productieproces te verbeteren. Parameters zoals moleculair gewicht, deeltjesgrootteverdeling en afschuifviscositeit worden geëvalueerd om te verzekeren dat eigenschappen behouden worden. Om een nieuw *processing aid* te ontwikkelen worden parameters zoals ketenoverdracht stoffen, monomeer compositie en functionele groepen gewijzigd samen met mengen van *processing aids*. Extrusie en Brabender tests worden uitgevoerd om de smelt reologie te evalueren.

Wijzigingen in het receptuur van de *processing aid* resulteerden in verhoogde kost efficiëntie. De eerste ontwikkelingen omtrent de *processing aid* zijn uitgevoerd.

1 INTRODUCTION

CONTEXT

Kaneka Corporation is a leading and technology driven chemical company which has its headquarters in Osaka and Tokyo Japan. Kaneka, established in 1949, produces chemical intermediate products used for end products with applications in various fields. These fields consist of chemicals, functional plastics, expandable plastics, electronic products and synthetic fibres. Kaneka has sites in VS, Singapore, Malaysia, China, Vietnam, India, Taiwan, South-Korea, Australia and Belgium. Worldwide Kaneka employs more than 8400 people.

Kaneka Belgium NV is the first subsidiary of Kaneka Corporation and was founded in 1970. The site is located in Westerlo-Oevel and is known for its a) high performance polymers, b) liquid polymers and c) expanded polymers.

a) High performance polymers have excellent characteristics and consist of impact modifiers, specialty additives, acrylic binders, elastomers and processing aids. The high performance polymers are used for industrial applications, building and construction industry, flexible and rigid packaging, engineering plastics, plastisols, automobile and electrical industry.
b) Liquid polymers are used for production of sealants, glues, coatings and paints. Characteristics such as high gel percentage, weatherability and heat resistance are obtained by using liquid polymers produced by Kaneka.
c) Expanded polymers such as expandable polypropylene and polyethylene foam particles are produced at Kaneka. Due to the outstanding mechanical, cushioning and energy absorbing capabilities of these materials they can be implemented into automobile industry, technical products, recyclable containers, protecting packaging etc…[1, 2].

BACKGROUND INFORMATION

Polyvinyl chloride (PVC) is a polymer which is made out of vinyl chloride monomers. It is known for a wide range of applications such as construction, medical, automobile, electrical, piping, packaging, flooring, …. PVC is the world's second most produced thermoplastic after polyolefin. Many processing techniques are available for PVC such as extrusion, injection moulding, blow moulding and calendering [1, 2].

Manufacturing of PVC foam applications needs a lot more ingredients than plain PVC. The PVC formulation consists of lubricants, stabilizers, plasticizers, fillers, impact modifiers and acrylic processing aids. Each of these ingredients contribute to the properties of the final product. Lubricants reduce PVC sticking to the processing unit whereas stabilizers improve durability and plasticizers reduce viscosity and increases flexibility of the polymer chains. Fillers reduce production costs, impact modifier increase impact strength and processing aids improve surface finish, melt strength and form a continuous matrix of polymer [3, 4].

Processing aids are polymers which can be produced out of multiple monomers. The monomers most often have acrylate as a functional group. Processing aids are often produced via emulsion polymerisation and are known for their high molecular weight M_w (1-10 million g/mol). The high molecular weight provides a high melt strength. The long flexible chains (processing aids) entangle the short stiff PVC chains to promote PVC fusion as shown in Figure 1 and Figure 2. PVC resin grain fuse into primary particles and into micro domains. Fusion occurs by shearing, friction and heat. This ensures a continuous polymer matrix [3-9].

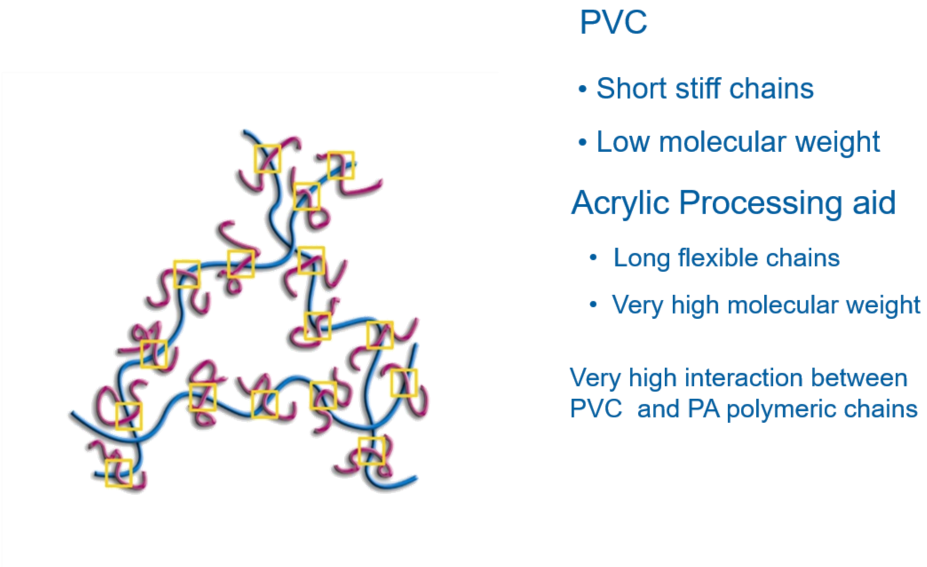


Figure 1: PA (long blue flexible chains) entangled PVC (short purple stiff chains) network [10]

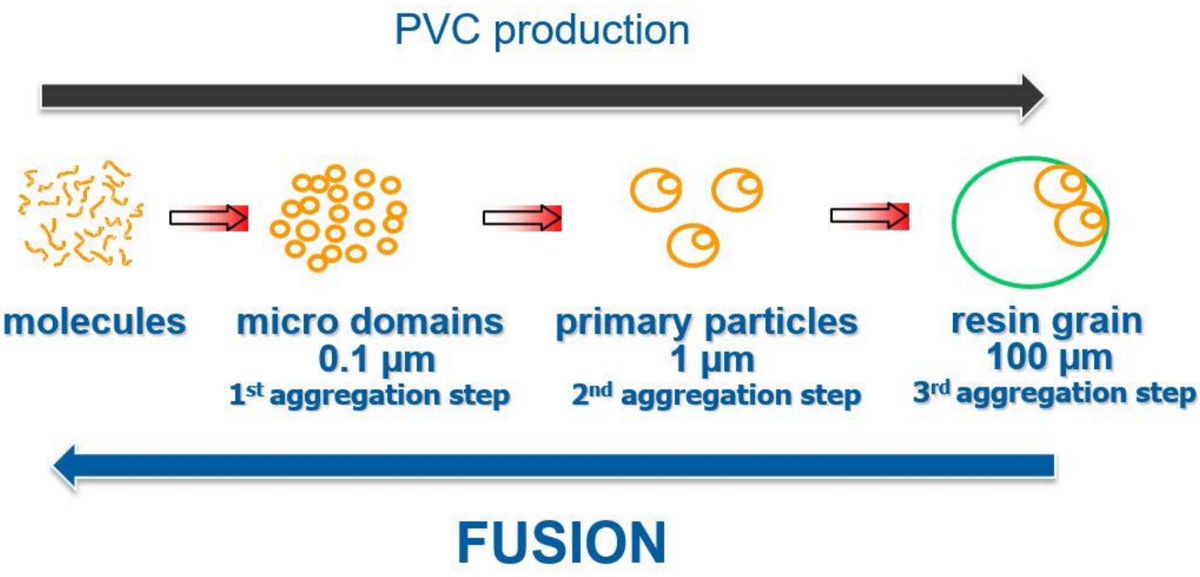


Figure 2: Production and fusion of PVC resin grains [10]

Processing aids are added to products to produce a wide variety of applications, such as profiles, film & sheets, bottles, foamed PVC, pipes and injection-moulded PVC. Foamed PVC uses processing aids in combination with gas bubbles (CO_2 and NO_2) to produce low density products without compromising mechanical strength.

PROBLEM STATEMENT

The production department request an improved production process for an existing processing aid X. This means implementation of modifications to processing aid X without losing quality of the product. Changing the emulsifier in the recipe of processing aid X could impact the particle size and molecular weight of the processing aid negatively. Increasing the solid content during production could lead to heat removal and mixing problems. Decreasing polymerization time could increase residual monomers in the product which are not environment friendly. Strategies in reducing the residual monomers could shorten the molecular weight of the processing aid which is crucial for its function. Is it possible to introduce modifications that improve the production process without compromising quality of the processing aid X?

In addition research to develop a new processing aid Y is requested. Which strategies are viable to produce a new processing aid Y that leads to PVC foam applications with improved surface finish and reduced density? What properties of the processing aids are important for PVC foam applications? How are these properties obtained?

OBJECTIVES

The objective of this master's thesis is to improve the production process of an existing process aid X and to develop a new processing aid Y.

Improvement of the existing processing aid X is established by changing emulsifier type and concentration. The emulsifier storage capacity can be optimized by using a higher surfactant concentration which means less transport costs. In addition to surfactant change, a decrease in polymerization time, reduction of residual monomers and increase in solid content are desired results. A decrease in polymerization time improves the production rate. Reduction of residual monomers improves environmental impact and solid content increase improves product per batch rate. All properties need to be comparable with an in-house standard.

Development of a new processing aid Y is done by researching literature, patents and using in-house knowledge. Obtaining properties such as high melt strength and high die swell in combination with good PVC fusion properties is the objective. An approach on development of a new processing aid Y consists of monomer composition changes, implementation of functional groups, blending of processing aids, increased molecular weight, glass transition temperature change and tacticity increase.

STRATEGY

Lab scale emulsion polymerization experiments are carried out with modifications to the recipe of the processing aid. Modifications will be implemented systematically. Properties of the processing aid will be analysed in the lab. These properties being molecular weight, particle size and particle size distribution, solid content, viscosity, … . The In addition tests such as Brabender gelation test, Rheotens test and die swell test are performed to evaluate the fusion behaviour, melt strength and die swell of the processing aid. Evaluation of these properties is crucial to ensure the quality of the processing aid.

Optimization of the processing aid X requires different modifications. At first, an emulsifier change will be implemented and preservation of properties are desired. In addition a change in dosage rate of emulsifier is evaluated as well. Second, a solid content increase increases product per batch ratio but viscosity problems are the limiting factor. A viscosity increase is the result of the solid content increase which leads to mixture and heat removal issues. Solid content increase can lead to scales which are unwanted and will be monitored as well as third experiment. Scales are undesired coagulation of polymer particles which are collected through filtration of the latex product. In the fourth place influence of polymerization time will be tested. The last experiment for processing aid X explores alternative methods for residual monomer reduction will be implemented. Dosage of peroxide, type of peroxide, pH change, and reaction time are variations between the experiments. These variations may have an undesirable scission effect which shortens the molecular weight of the processing aid.

Development of processing aid Y is approached via research and experimental work. Research and experiments with different monomer types, blending of processing aids, changes in glass transitions temperature, tacticity changes, high molecular weight and implementation of functional groups are done to develop processing aid Y. Patent research and in-house knowledge will be the base for the development strategy of the new processing aid.

The following chapters will introduce the principles of emulsion polymerization and explain in depth which modifications are implemented and how the samples are measured.

2 LITERATURE

The subject and goal of this thesis is improvement and development of processing aids. In order to achieve this goal some fundamental knowledge of processing aids is required. Subjects such as free radical polymerization, emulsion polymerization, additives of polyvinyl chloride and processing aids are important to grasp in order to interpret the results of the experiments carried out. Processing aids are polymers made with free radical emulsion polymerization. Thus, the core steps of polymerization are explained. These steps are known as initiation, propagation and termination. The importance of working oxygen free, due to oxygen's retardation and inhibition effect on the polymerization reaction, will also be mentioned. The merits of emulsion polymerization and an explanation of its ingredients with their functions are included in the literature. A broad spectrum of additives is used for polyvinyl chloride including processing aids. Therefore, an overview of such additives follows with more in depth information concluding the processing aids.

2.1 POLYMERIZATION

Polymerization is a chemical reaction in which monomer molecules (building blocks) are linked together to form a long-chain polymer. A polymer chain consists of repeat units (monomers) and the number of repeat units is called the degree of polymerization. A distinction can be made between two polymerization classes depending on the way the polymer chains are constructed. The different classes are known as step-growth reactions and as chain-growth reactions. Step-growth reactions use monomers with functional groups to grow into a polymer chain. The monomers are bifunctional or multifunctional and react to form dimers, trimers, oligomers and eventually polymers. In order to achieve a high molecular weight a high extent of reaction is needed. Whereas step-growth polymerization needs functional groups chain-growth polymerization requires free-radicals or ions as a reactive site. Chain-growth polymerization is a technique in which unsaturated monomers add onto these reactive sites present on a growing polymer chain. The growth of the chain only occurs at the end of the chain. The reactive sites are originally created via initiators. These reactive sites are regenerated after addition of monomer onto the reactive site of the growing chain. This thesis focusses on free radical chain-growth polymerization to produce new processing aids. All experimental work is executed with free radical polymerization technique. Other methods such as living free radical polymerization are thus not implemented in this work.

2.1.1 Free radical chain-growth polymerization

Chain-growth reactions are known for a rapid consecutive addition of monomers to the active site at the end of the polymer chain. The unit added to the growing chain takes over the active site from the growing chain. The active site is a radical and is readily available for further addition of monomer. Free radical polymerization (FRP) is the most used kind of chain polymerization amongst anionic, cationic and coordination polymerization. FRP undergoes three different stages: initiation, propagation and termination to produce the polymer chain. This process of polymerization takes place at the expense of double bonds present in the monomer [3-7, 9, 11, 12].

2.1.1.1 Initiation step

The initiation step involves the creation of the free-radical active site. The formation of this active site consists of two steps. The first step is addition of an initiator which produces primary free radicals. The second step is reaction of the primary free radical with a monomer to produce an active site on the monomer. Formation of free radicals can be done by homolytic scission of a single bond or by redox initiation where transfer of a single electron to or from an ion or molecule takes place. Homolytic scission can be achieved through thermolysis or by photolysis. Thermolysis produces radicals via application of heat. Initiators containing peroxide- or azo-groups undergo thermolysis in a convenient temperature range of 50-100°C. An example of an initiator of this kind is t-butyl peroxide. See Figure 3 for a homolytic scission of t-butyl peroxide through thermolysis.

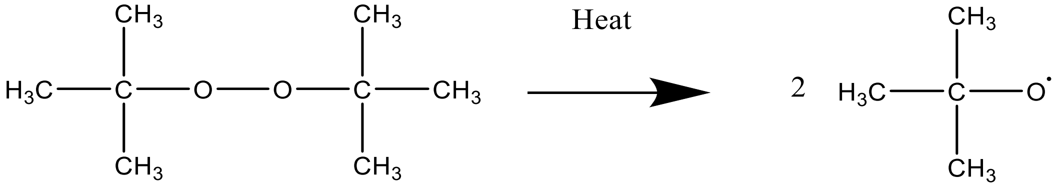


Figure 3: Thermolysis of t-butyl peroxide [9]

Decomposition rates increase with elevated temperatures. The medium which surrounds the formed free radicals influence decomposition rates as well. Not all radicals formed have the opportunity to react with a monomer molecule. The formed radical can react with another radical which leads to an inefficient use of initiator. These recombination reactions are not wanted and are provoked with the use of viscous medium which encages the formed radicals from monomer molecules.

Photolysis utilizes irradiation of the initiator with light of a suitable wavelength (example: UV-light) in order to obtain dissociation and produce primary free radicals. Photolysis makes it possible to start initiation without the use of elevated temperatures and is able to stop the reaction instantaneously by simply blocking out the light. Azobisisobutyronitrile (AIBN) is an example of an initiator which can undergo photolysis and is shown in Figure 4.

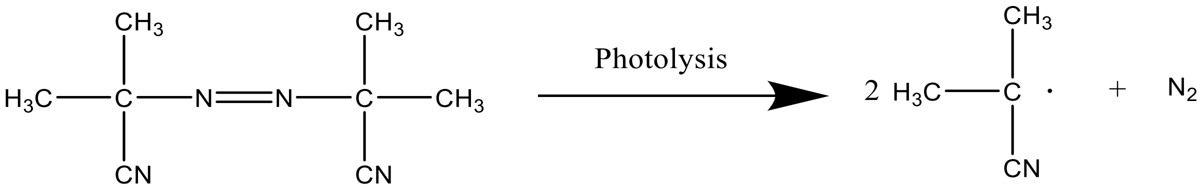


Figure 4: Photolysis of AIBN [9]

Redox initiation can be implemented at lower temperatures than thermolysis or photolysis. Electron transfer between oxidant and reductant produces free radicals. Peroxide compounds like cumyl hydroperoxide and potassium peroxodisulphate are oxidizing agents which yields radicals in combination with reductants like Fe^{2+} and sodium pyrosulfite due to redox reactions. See Figure 5 and Figure 6 for examples of the mentioned redox systems.

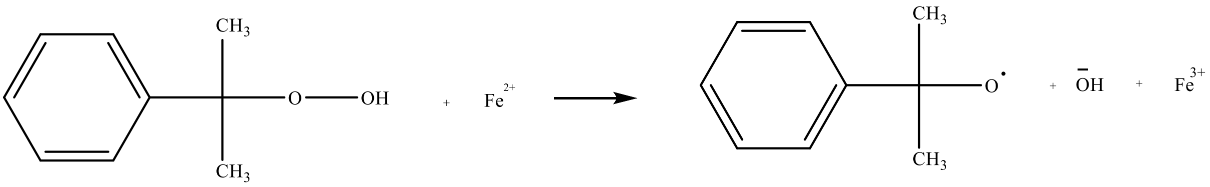


Figure 5: Redox system of cumyl hydroperoxide and ferrous ion [9]

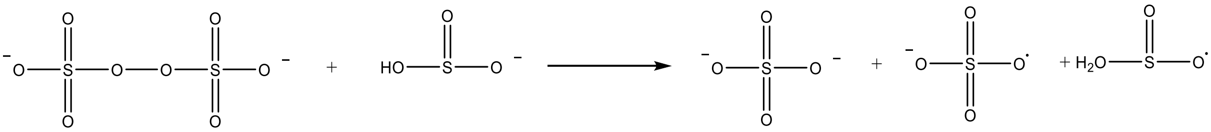


Figure 6: Redox system of peroxodisulphate and pyrosulfate [9]

Radicals formed by thermolysis, photolysis or redox initiation are called primary free radicals. These primary free radicals will be able to react with the π-bond of the monomer and will result in a monomer radical. This reaction can occur in two ways as shown in Figure 7.

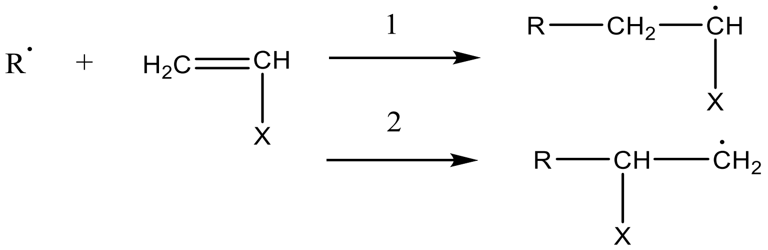


Figure 7: Two initiation options of primary radical reaction with pi-bond of monomer [9]

The first reaction takes place more predominantly due to the lack of steric hindrance of the X-group [3-9, 11, 12].

2.1.1.2 Propagation step

Addition of a monomer molecule to a monomer radical is known as a propagation reaction. These successive additions of monomer produce growing polymer chains at a fast rate. Within a few seconds thousands of monomer additions can take place and π -bonds are converted to σ-bonds which releases heat due to the exothermic nature of the reaction. Addition of monomer can occur in two ways as shown in Figure 8. Head-to-tail additions occur predominantly due to the steric effect in head-to-head additions. Head-to-head additions occur more rarely than the head-to-tail additions though an occasional head-to-head reaction can take place. If the substituent group X is small a higher head-to-head linkage can be expected. Notice the similarity with Figure 7.

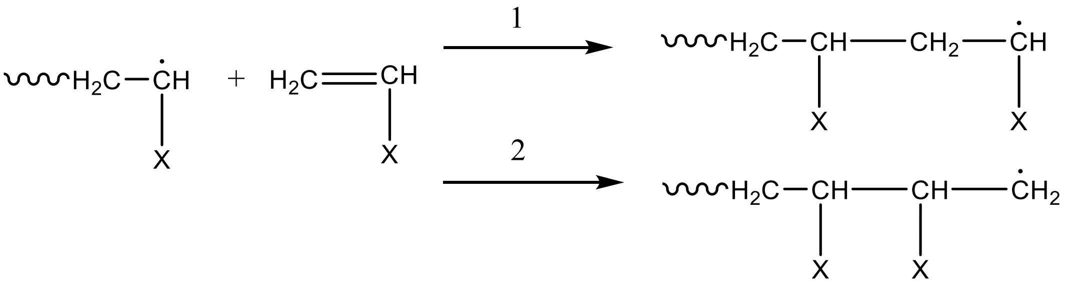


Figure 8: Two options of propagation 1=head to tail addition and 2=head to head addition [9]

Reactivity of monomer and the growing chain determine the rate of propagation. Other factors such as resonance, polar effects and steric hindrance are important for the reaction rate. Whilst these factors have an influence on the reactivity of monomers the influence of reactivity of the propagating polymer radicals are of greater importance for the propagation rate. Resonance stabilization of the propagating radical dictates the reaction rate. For example, a comparison is made between polystyrene radicals and vinyl acetate radicals. Comparing these radicals leads to the conclusion that several resonance hybrids of the polystyrene radicals are possible which explains the higher stabilization effect of the radical. Resonance structures of polystyrene radicals are shown in Figure 9.

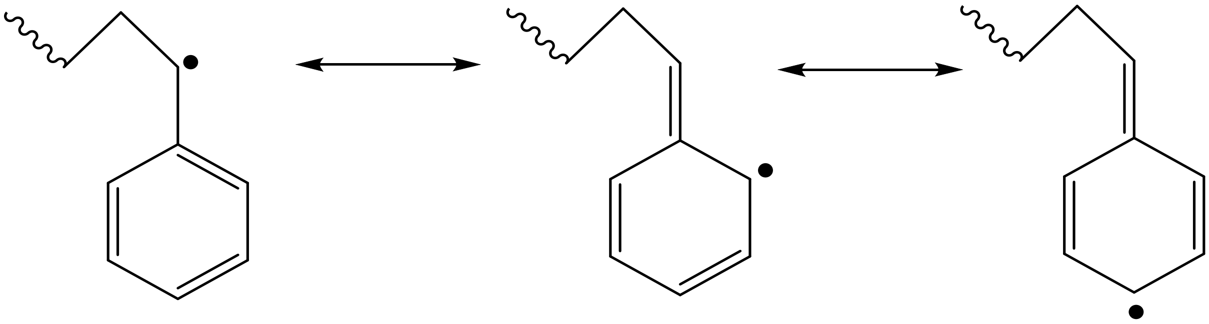


Figure 9: Resonance hybrid forms of polystyrene [8]

Vinyl acetate radicals lack this resonance stabilization effect because of oxygen’s limitation to accommodate only eight electrons. The lack of stabilization causes vinyl acetate radicals to be more reactive than polystyrene radicals.

Propagation rates increase with increase in temperature which are aided through the exothermic reaction. Increased propagation rates cause a lack of steric control over the manner of monomer placement during chain growth and causes the radical to be free in mobility. If the temperature is decreased the mobility of the growing radical is impeded and stereo regularity of the polymer chain is gained. A lower temperature results in a greater amount of syndiotactic arrangements due to trans-trans placement requiring less energy [3-9, 11, 12].

2.1.1.3 Termination step

Termination ends the growth of the propagating polymer chain in three possible ways. Combination, disproportionation and chain transfer reactions can cause a 'dead' chain.

Combination reaction also known as coupling reaction combines the two polymer radicals to form a σ-bond resulting in one large polymer chain. Notice that through combination of two polymer radicals, with a polymerization degree of n and p respectively, a large polymer chain is obtained. An example of a combination reaction is shown in Figure 10.

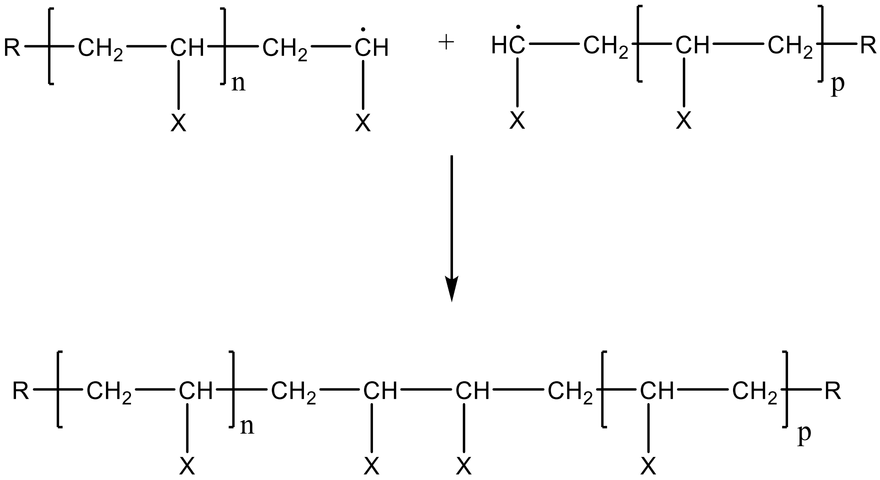


Figure 10: Combination reaction for termination [9]

In contrast to combination reactions two polymer chains are formed when termination takes places via disproportionation reaction. One polymer chain has an unsaturated end-group and the other polymer has a saturated end group as shown in Figure 11. A hydrogen atom is abstracted from one growing chain by another.

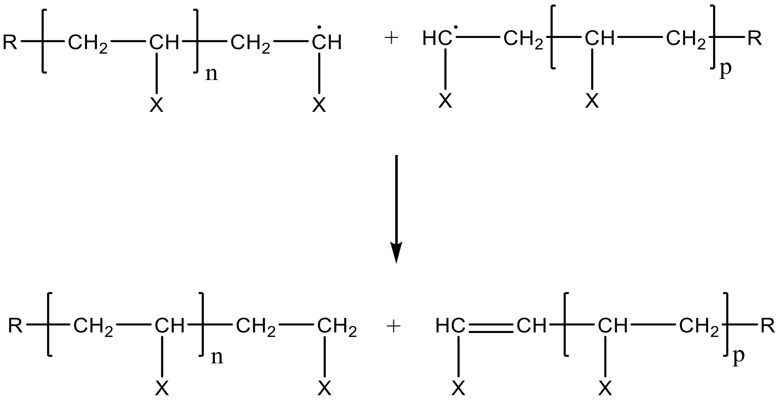


Figure 11: Disproportionation reaction for termination [9]

Notice that combination reactions lead to polymers with a higher molecular weight compared to disproportionation. Disproportionation reactions require more energy and this manner of termination will occur more often at higher temperatures. Not only temperature but also monomer types have an influence on the termination type. Some monomers tend to terminate via disproportionation because of steric hindrance effects.

Termination via chain transfer produces a dead polymer chain and a new radical which is able to initiate the growth of a new chain. Chain transfer reactions cause premature termination of the growing polymer chain. A molecule reacting with the growing polymer will break its single bond to create a new radical and a dead chain. The molecule TA acts as a transfer agent and transports a radicular atom to the radical polymer.

Figure 12: Transfer chain reaction [9]

Initiators, solvents and monomers can all function as a transfer agent. The strength of the bonds within the transfer agent determine the ease of chain transfer reactions. Labile atoms present in halogen compounds and mercaptans make them susceptible for chain transfer reactions. Prevention of chain transfer reactions is needed to produce a polymer chain with a high molecular weight [3-9, 11, 12].

2.1.1.4 Inhibition and retardation

During storage and transport of monomers an inhibitor is added to prevent premature polymerization. These inhibitors such as substituted phenols are added in small amounts. An inhibitor is highly efficient in preventing polymerization. It is a substance which is able to react with the free-radical active site producing stable species (radical or non-radical) that are unable to reinitiate polymerization. An inhibitor will react so rapidly that no free radicals can escape which causes an induction time until the inhibitor is completely consumed.

The difference between an inhibitor and a retarder is the efficiency of slowing down the polymerization rate. A retarder will slow down polymerization and yields species that slowly reinitiate polymerization. A retarder will not cause an induction period. Free radical polymerizations are usually performed under an inert atmosphere since oxygen functions as inhibitor and a retarder [6].

2.2 POLYMERIZATION TECHNIQUES

Free radical polymerization can be achieved in numerous ways. Different techniques such as bulk-, solution-, suspension- and emulsion polymerization can be implemented. Each of these polymerization techniques have their advantages and disadvantages. Bulk polymerization also known as mass polymerization is a simple technique in terms of formulation. The reaction mixture only consists of initiator and monomer. No solvent is used for bulk polymerization. This means that a pure polymer is produced without contaminations (solvent residues). Pure polymer translates to high optical clarity. Another advantage of bulk polymerization is the exclusion of solvent cost. Even though bulk polymerization is a simple technique, it is not without its disadvantages. The mixture becomes more viscous as the exothermic reaction proceeds. This means precautions are necessary to prevent difficulties with mixing and heat transfer. In extreme situations these difficulties can lead to thermal degradation of polymer product. High viscosity and heat transfer limitations lead to low molecular weights and to a broad molecular weight distribution. The polymerization can be carried out in a solution in order to limit the drawbacks of bulk polymerization. This is called a solution polymerization.

The monomer and produced polymer are both soluble in the solvent. The function of the solvent is to reduce viscosity by diluting the mixture. Lower viscosity leads to better mixture capabilities. The solution is able to absorb the heat released from the exothermic polymerization reaction. Improvements in mixture behaviour and heat transfer are possible due to addition of solvent. However, purification steps are necessary to remove the excess solvent from the polymer product. Removal of solvent takes an extra processing step which is cost and time inefficient. The produced polymer is not pure due to solvent residues that are difficult to remove completely. It is not possible to obtain very high molecular weight products due to the chain transfer reactions occurring with the solvent. Suspension and emulsion polymerization both have a reaction mixture containing water, initiator and monomer. Emulsion polymerization has one component more, an emulsifying agent. The difference between both polymerization methods is that the initiator is hydrophobic for suspension polymerization and is hydrophilic for emulsion polymerization. This difference leads to initiation happening in the aqueous phase for emulsion polymerization whereas monomer droplets are the source of initiation for suspension polymerization. However in both systems the monomers used are hydrophobic [13]. Suspension and emulsion polymerization have monomer dispersed in a continuous aqueous phase which facilitates heat removal. The heterogeneous system of suspension and emulsion polymerization yields better agitation properties due to the low viscosity. Superior heat removal and agitation properties lead to higher monomer conversions compared to bulk polymerization. Suspension and emulsion polymerization are techniques which are able to produce core/shell structures. These core/shell structures have a rubbery core embedded in a thermoplastic matrix which make them excellent impact modifiers. Despite these advantages these polymerization techniques have drawbacks to consider. Reactor productivity is lower compared to bulk and solution polymerization due to the system containing up to 50 % water. This means that the amount of product per volume reactor is lower. Furthermore, removal of water is needed to obtain the final product which increases the production costs[14].

Emulsion polymerization

The use of emulsion polymerization has a lot of advantages compared to bulk and suspension polymerization methods. Emulsion polymerization has the unique advantage of being able to produce high molecular weight polymers at high polymerization rates. Generally, there is a trade-off between molecular weight and polymerization rate for bulk and solution polymerization.

Emulsion polymerization is a technique leading to colloidal polymer particles dispersed in a continuous medium, known as a latex. Components such as water, surfactant, initiator and monomer are needed to carry out an emulsion polymerization. The initiator used is usually water-soluble and the monomer is partially water-soluble.

Water acts to maintain a low viscosity and provide good heat transfer. In addition, isolation of the polymerization compartments is achieved. This plays an important role in terms of molar masses acquired.

The function of the surfactant, also known as emulgator, is to act as a colloidal stabilizer. It consists of a hydrophobic and hydrophilic part. The hydrophobic part of the surfactant is a nonpolar tail whereas the hydrophilic part is a polar or ionic head. The surfactant will absorb onto the monomer droplets dispersed in water stabilizing them and decreasing surface tension. The hydrophobic tail will enclose the monomer whilst the hydrophilic head faces outwards to the water.

Depending on the concentration of the surfactant micelle formation can occur. Micelle formation is the formation of ordered surfactant clusters as shown in Figure 13. Usual dimensions for micelles are 2-10 nm and each micelle consist of 50-150 surfactant molecules.

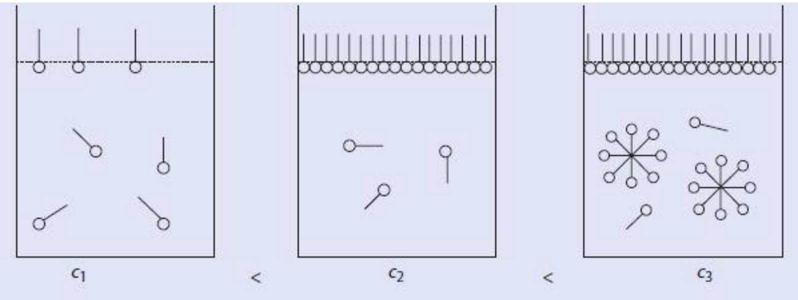


Figure 13: Schematic of micelle formation [3]

The critical micelle concentration (CMC) is the concentration surfactant needed at a specific temperature for micelle formation and indicates the transition to a constant surface tension. In Figure 14 a graph with surface tension on the y-axis and surfactant concentration on the x-axis demonstrates the critical concentration where surface tension remains constant. Once the surfactant concentration equals or surpasses the concentration C2 micelle formation occurs. The CMC of most surfactants ranges between 0.001-0.1 mol/l.

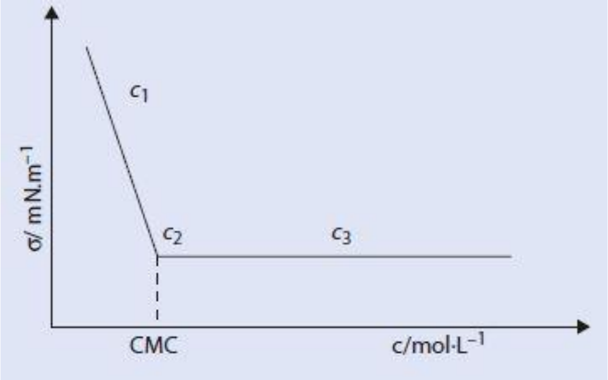


Figure 14: Plot of surface tension as function of concentration surfactant and representation of CMC [3]

Monomer droplets only contain a small part of the surfactant. The diameter of monomer droplets ranging 1-100 µm results in a large volume to area ratio compared to the micelles. In addition, the concentration of monomer droplets (10^{12} – 10^{14} /l) are much lower than the concentration of micelles (10^{19}-10^{21} /l).

Most initiators are water soluble and produce radicals that are too hydrophilic to enter the organic phase. Therefore, no reaction will occur with the organic monomer droplets and instead reaction of the radical occurs in the aqueous phase with the water-soluble monomer. The reaction forms oligoradicals (monomer radicals) which become hydrophobic enough after some additions of monomer units. When the oligoradical achieves its Z-mer length it can enter into the organic phase of the system. Surfactant molecules will surround the oligoradical with their hydrophobic tails and face the hydrophilic groups outwards in order to stabilize the growing particle. The formed micelle is swollen with monomer. The process of formation of polymer particles by precipitation of oligoradicals is called homogeneous nucleation whereas heterogeneous/micellar nucleation has radicals entering pre-existing micelles. Micellar nucleation occurs predominantly when the surfactant concentration exceeds the CMC. Homogenous nucleation happens when surfactant concentration is lower than the CMC. Figure 15 shows a schematic representation of emulsion polymerization including micelles, monomer stabilized droplets, initiator, oligomers and stabilized polymer particles swollen with monomer.

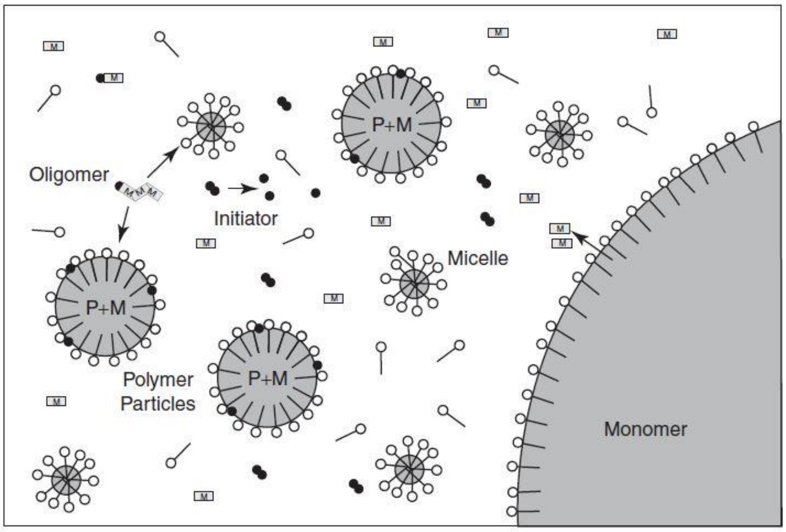


Figure 15: Schematic representation of emulsion polymerization [6]

The oligoradical is able to grow fast and form a polymer chain due to the monomer-rich environment within the micelle. Monomer diffuses from monomer droplets into the aqueous phase and replenishes monomer used in the micelles for chain growth. These newly formed particles are very small but suffer a tremendous increase in surface area upon particle growth. Redistribution of surfactant molecules from micelles which have not been initiated or from surfaces of the disappearing monomer droplets will adsorb onto the surface of the growing polymer particles, maintaining the colloidal stability of the particles. The polymerization is completed when all the monomer is converted into polymer. The latex formed consists of submicron polymer particles dispersed in the aqueous phase [3, 6, 15]

Emulsion polymerization can be divided into three stages. Interval I can be defined as particle formation stage. Particle growth stages are covered in interval II and III. A distinction between intervals can be made when the rate of polymerization and the surface tension are plotted as function of the conversion. This plot is shown in Figure 16.

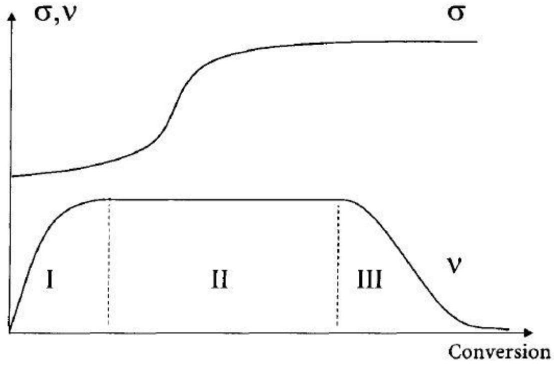


Figure 16: Plot of rate of polymerization and surface tension as function of conversion [15]

During interval I the polymer particle is formed. It is important to stabilize the growing latex particles to prevent agglomeration. Stabilization is accomplished by surfactant molecules absorbing onto the surface of the particles. Micelles containing no polymer will disappear and the concentration of surfactant is able to decrease under the CMC. The decrease in free surfactant leads to an increase in surface tension as visible in Figure 14. Formation of new latex particles is prohibited due to the increase in surface tension as shown in Figure 16. Interval I, latex particle formation, is completed after about 10-20 % conversion.

From this point on begins interval II where the number of latex particles remains the same. During interval II polymerization only occurs in the latex particles which are enriched with monomer diffusing from the monomer droplets. The concentration of monomer stays constant within the latex particles and so does the polymerization rate as shown in Figure 16.

Interval III starts when polymerization reaches 60-80 % conversion. The monomer droplets are depleted and are no longer present. All monomer molecules are present in the latex particles. As the polymerization proceeds monomer concentration within the latex particles decreases and so does the polymerization rate as shown in Figure 16. At the end of interval III all monomer is depleted and an emulsion consisting of polymer particles is the remaining result.

It is possible to observe an increase in polymerization rate at interval III due to the Trommsdorff effect. A decrease in termination rate is caused by the raised viscosity of the polymerization system. The rise in viscosity is linked to the growing polymer chains. Termination reactions normally are very rapid but due to the viscous mixture of polymer chains mobility of the large molecules is prohibited, preventing effective collisions between two radicals [3, 6, 15].

Figure 17 shows a schematic representation of the emulsion system during each interval.

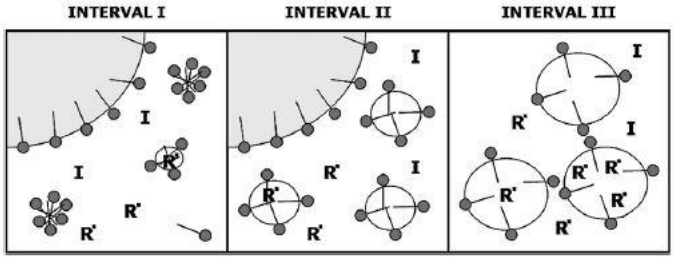


Figure 17: Schematic overview of interval I, II and III for emulsion polymerization [16]

The formed latex particles are dried through a spray drying process to obtain the final product as a powder.

2.3 POLYVINYL CHLORIDE

Polyvinyl chloride also known as PVC is prepared from vinyl chloride monomer. Vinyl chloride monomer is a colourless gas with a boiling point of -14°C. It is kept under pressure to obtain a liquid state. PVC is not soluble in its own monomer. The PVC polymer contains between 700 and 1500 repeat units of vinyl chloride monomer as shown in Figure 18. PVC is synthesised predominantly via suspension polymerization (80 %). Remaining techniques used are bulk polymerization which accounts for 8% and emulsion polymerization which accounts for 12 %.

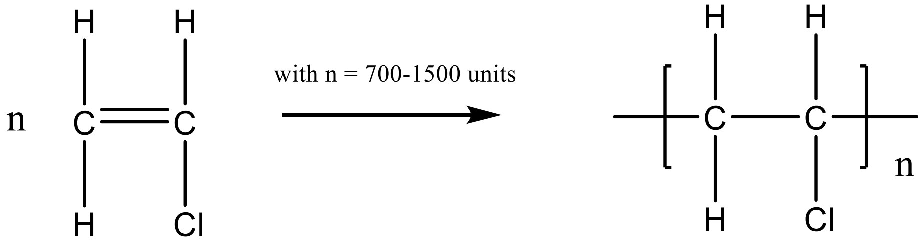


Figure 18: Reaction of vinyl chloride monomer to PVC [17]

The PVC has short stiff chain lengths. The small repeat number of monomer means that the molecular weight (M_w) of PVC is in the range of 44 000 - 94 000 g/mol. PVC is relatively inexpensive to produce and can be applied in a wide scope of applications. Its application varies from piping, electric cables, construction, clothing, furniture, flooring, sheets. Thanks to its wide application range PVC is one of the most produced synthetic thermoplastic polymers. It exists in two basic forms known as rigid PVC and flexible PVC. Flexible PVC is obtained by addition of high amounts of plasticizer and therefore has the abbreviation of pPVC. Unplasticized PVC is known as uPVC, the rigid PVC form. PVC polymer chains are linear and are mainly arranged in a head-to-tail configuration. The structure is atactic with some degree of syndiotacticity. The atactic structure means that the substituents are placed randomly around the chains. The syndiotactic structure means the substituents have alternatively positions along the chain which gives PVC a few percent crystallinity. The glass transition temperature of PVC is 82°C [18-20]. Table 1 shows material properties of uPVC and pPVC.

Table 1: Material properties of uPVC and pPVC [18]

Properties	**uPVC**	**pPVC**
Density g/cm³	1.30-1.45	1.10-1.35
Tensile strength MPa	31-60	10-25
Elongation at break %	2-4	150-400
Specific heat J/g·K	0.8-0.9	1.0-2.0

2.4 ADDITIVES

Addition of additives is crucial for processing PVC resins and including desired properties. A typical PVC formulation consists of fillers, colourants, stabilizers, blowing agents, plasticizers, lubricants, impact modifiers, processing aids and PVC resin. Addition of filler material reduces cost whereas colourants are used to obtain the desired appearance of the product. Stabilizers increase the resistance of the PVC product to heat and ultraviolet light. Blowing agents are necessary to introduce a cellular structure for foam applications. Plasticizer is added to make the brittle PVC softer and more flexible. Lubricants are needed to prevent sticking of PVC melt to the die walls. Impact modifiers are able to increase durability of PVC products whilst processing aids are vital for circumventing processing restrictions linked to PVC. Depending on the required properties of the product different variations in additives and quantity are used. Other additives such as flame retardants and antistatic agents are used for specific applications but are not relevant to this work and are seen as unusual additives. The term phr means parts per hundred resin and is used for the amount of additive added per hundred parts of base polymer in the compounding mixture [18].

2.4.1 Fillers

The main function of filler material is to reduce cost. The use of filler is occasionally interpreted as a synonym for cheapening extender, which is not completely correct. Whilst the main focus of filler material is to reduce cost additional functionality can be introduced as well. This functionality can be reinforcement of uPVC via glass fibres as filler material or flame-retardant properties by adding antimony trioxide as filler. Ideally a combination of cost reduction, increased output (no processing difficulties) and improved properties are the desired result of incorporation of fillers. In practice a compromise has to be made so that some features are secured in expense of others.

The most used filler material is calcium carbonate. Other components such as silicates, sulphates and alkaline-earth metals are also usable as filler material. PVC prices are valued on weight therefore addition of filler material with a higher density than PVC is profitable. Reasons for calcium carbonate being used predominantly as filler are the availability, ease in processing and low cost. Calcium carbonate has other properties such as good resistance to thermal decomposition and absence of water. Thermal resistance is necessary during PVC processing steps. Also lack of water eliminates contamination of the PVC formulation which could have negative effects on the final properties of the PVC product. A low-cost filler may seem adequate for cost reduction purposes but other features such as low output, absorption of plasticiser, poor surface finish, extra pigment requirement may cancel out the benefit of its low cost [21].

2.4.2 Colourants

Colourants can be divided into dyes and pigments. Dyes are colouring materials which are soluble in the base polymer. On the other hand, pigments are insoluble and form particulates in the polymer composition. Colourants are generally added in small amounts to the polymer, in the range of fractions of a phr to a few phr. For a colourant to be useful it must have a sufficient intensity to impart it in the desired degree to the material.

Dyes are mostly used to colour polymer in transparent shades. Metal-complexes can be used as dye such as coumarin, anthraquinone and azo-compounds. Dyes are organic components. Pigments are made of inorganic metal oxides or of organic compounds such as isoindolines and dioxazines. An important inorganic metal oxide used as a white pigment is titanium oxide. Since organic pigments have cleaner and brighter shades than organic pigments but organic pigments have a lower tendency to migrate out of the PVC a combination is used of both pigments is used.

2.4.3 Stabilizers

PVC is susceptible to thermal- and photochemical degradation. Degradation is rapid and is accelerated in the presence of oxygen. Incorporation of heat stabilizers is necessary to protect PVC compositions from the high temperatures occurring during processing steps. PVC has a decomposition temperature that is lower than its melting temperature. Due to the instability of the PVC chains elevated temperatures initiate a self-accelerating dehydrochlorination reaction.

The function of the stabilizer is to neutralize hydrochloric acid and prevent further degradation by introducing nucleophilic substitution reactions. Antioxidant and UV-absorbing additives are used against photochemical degradation. Neighbouring hydrogen and chlorine atoms form hydrochloric acid and produce a double bond between the carbon atoms to which they were originally attached. This reaction continues and forms conjugated double bonds within the polymer as shown in Figure 19. These conjugated double bonds are the cause of unwanted colour development.

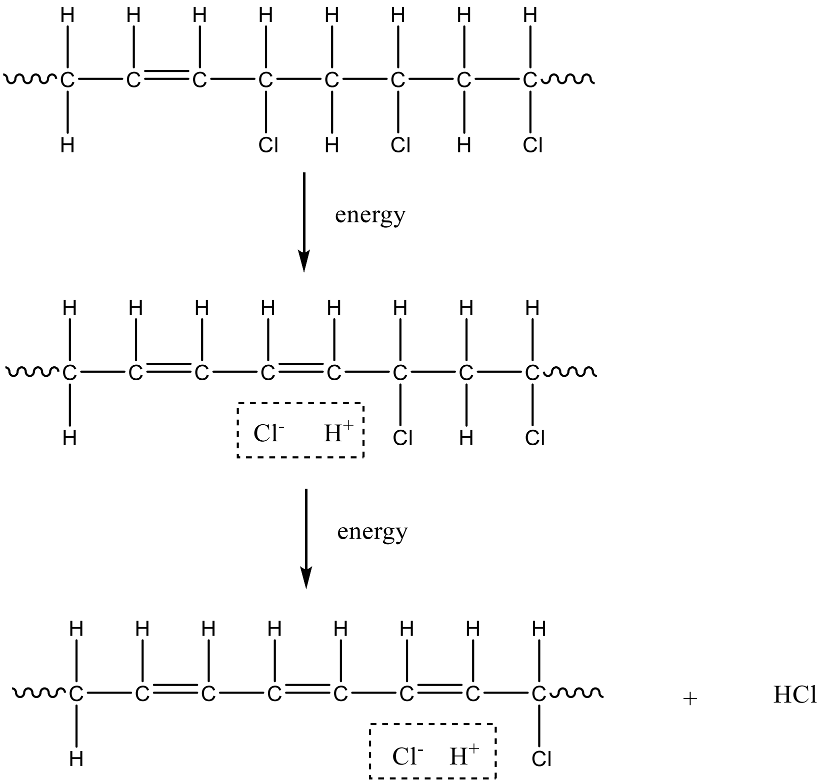


Figure 19: Degradation of PVC liberating HCl [19]

2.4.3.1 Heat stabilizers

Heat stabilizers can be divided into two main groups metal and non-metal containing stabilizers.

The latter group is usually used in combination with metal containing stabilizers in order to achieve a synergetic effect. Organic phosphites and epoxy compounds are examples of non-metal containing stabilizers.

Metal containing stabilizers range from lead, tin stabilizers to metallic stearates. Tin stabilizers are very effective and introduce a long-term stability to the PVC product, but toxicity and high cost limit their use. Lead stabilizers on the other hand are relatively cheap and achieve long-term stability as well. Drawback of using lead are staining of PVC and toxic properties. Barium, cadmium and zinc stearates are effective stabilizers but introduce unwanted deposition of metal parts onto the process unit which is known as plate-out.

2.4.3.2 UV-stabilizers

UV-stabilizers such as titanium dioxide can absorb the UV-radiation and release radiation in the visual light spectrum. The exited polymer transfers its energy to the UV-stabilizer whereby the polymer is able to return to its original state. The breakdown of polymer is diverted but the UV-stabilizer needs to lose its radical and does so by emission of heat or of light of a longer wavelength a shown in Figure 20. Notice that the UV-stabilizer reacts catalytically which means that they are endlessly reusable if migration out of polymer is excluded.

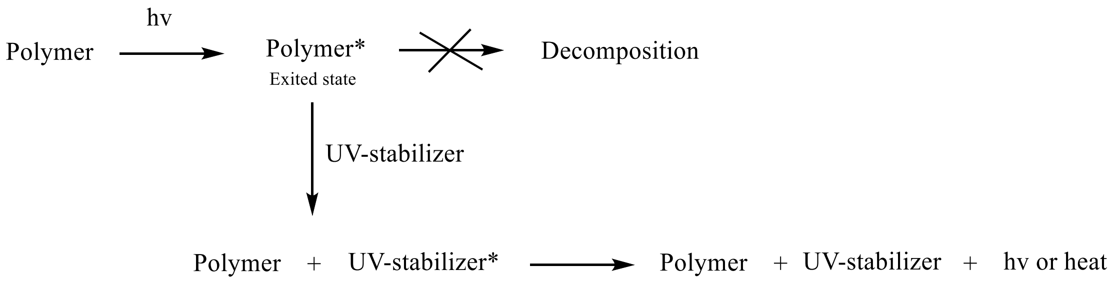


Figure 20: UV-stabilization schematic [3]

Another method of protecting polymers from UV-light is addition of antioxidants to catch free radicals formed by photodecomposition. Primary antioxidants intercept free radicals preventing oxidation and breakdown of polymer. Secondary antioxidants reduce the formation of peroxides.

Primary antioxidants are often sterically hindered phenols. For example, butylated hydroxytoluene (BHT) can be used as a primary antioxidant. Transfer of a hydrogen atom saturates the radical and terminates the reaction chain. The formed BHT radicals react with other radicals and forms dimers which are effective antioxidants.

Secondary antioxidants such as sterically hindered phosphites, thioethers and amines are used to reduce peroxides. Amines are able to decrease the overall radical concentration in the polymer by reacting with peroxy- and polymer radicals. An example of a sterically hindered amine is tetramethylpiperidine (TMP). As shown in Figure 21 these antioxidants react stoichiometrically and not catalytically. This means that antioxidants are consumed and after fully depletion undesired oxidation of polymer can start anew.

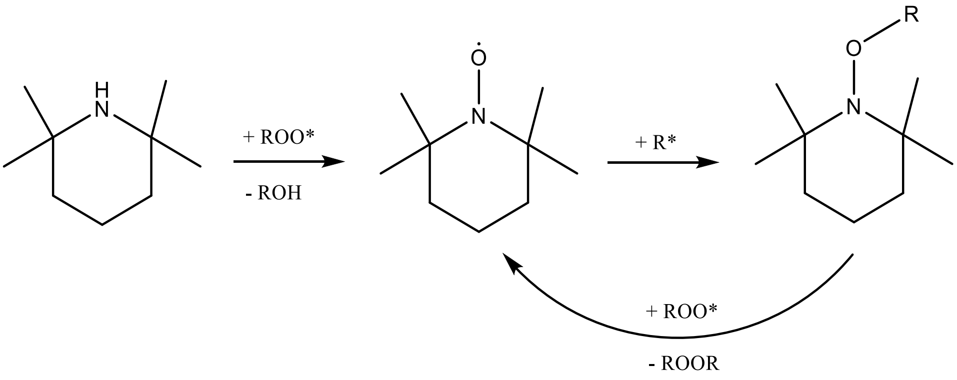


Figure 21: TMP as example of a sterically hindered amine used as secondary antioxidant [3]

Protection of the polymer material is dependant of peroxide formation and amount of antioxidant added. Increasing the amount of additive extents the durability of the polymer but is limited by the solubility of the additive. If the solubility level is exceeded formation of additive crystals will occur and the additive migrates out of the polymer. Oversaturation of stabilizer can bring entail negative effects such as absorption of water, oxygen or other gases.

2.4.4 Blowing agents

The blowing agents are crucial components of PVC formulations for the production of foams. The PVC formulation is melted, and gas bubbles are introduced into the melted material. Introduction of gas bubbles can be done mechanically, chemically or physically.

Mechanical introduction of gas bubbles is executed by rigorous stirring of melt which enfolds gas or by injecting gas directly into the polymer melt.

Chemical blowing agents are compounds that introduces gas within the polymer melt due to reaction. Azodicarbonamide is an example of a chemical blowing agent which undergoes a thermal degradation reaction at elevated temperature releasing nitrogen, carbon dioxide and ammonia gases which form a cellular foamed structure.

Physical blowing agents (PBA's) are known for having a low boiling point. PBA's undergo evaporation after heating to form foam.

Desired properties for blowing agents are having a good shelf life (stable at room temperature); being compatible with the polymer composition; having good dispersibility within the polymer melt; producing harmless gasses; having a controllable rate of gas production; having a controllable exothermic decomposition; have no negative influence such as colour or odour alternation on the properties.

An ideal blowing agent retains its liquid form during fusion of the PVC blend in order to prevent gas escaping prematurely. A supersaturation of the blowing agent in the melt is caused by a pressure drop when exiting the die as shown in Figure 22.

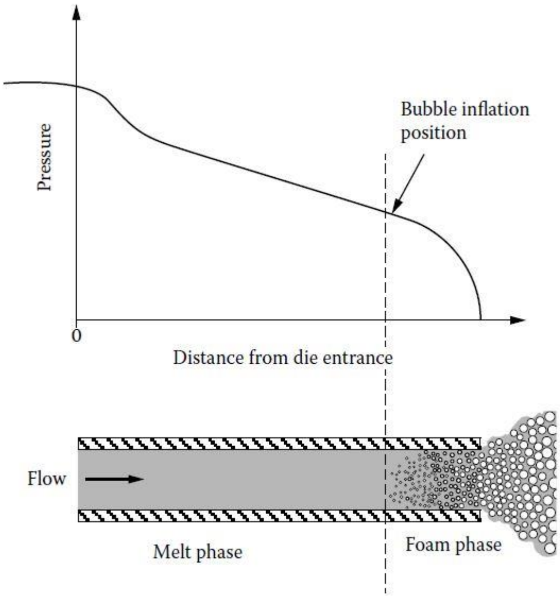


Figure 22: Axial pressure profile along a die of constant cross section: a pressure drop is followed by bubbles nucleating [22]

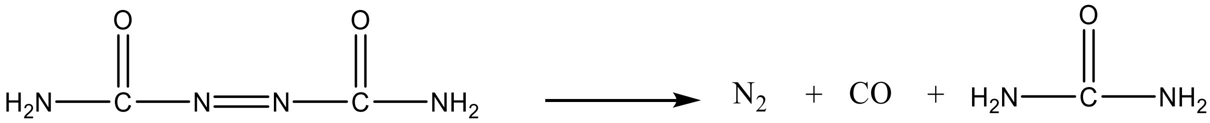
The gas will separate from the melt and form bubbles until the gas pressure inside equals the surface tension of the walls. The cellular foam structure is cooled rapidly in order to prevent collapsing of the cells. Increasing blowing agent concentration results in lower density foams. A decrease in foam density is limited with addition of a blowing agent. After surpassing the limit of blowing agent addition also known as the gas containment limit (GCL), an increase in foam density is caused by the rupturing of cellular structures. Adjustments of blowing agent concentrations can improve surface quality and density of the foam dramatically.

2.4.4.1 Physical blowing agents

Physical blowing agents dissolved in the melt expand at elevated temperatures. Microbubble nucleation and growth are produced due to the expansion. Bubbles are nucleated at different times which leads to gas bubbles with different dimensions. Properties such as strength-to-weight ratio are influenced by bubble size distribution. An example of a physical blowing agent is the evaporation of pentane used for polystyrene foam.

2.4.4.2 Chemical blowing agents

Azodicarbonamide is an organic compound which produces gases under thermal degradation. An inorganic chemical blowing agent is sodium bicarbonate. The latter example decomposes over a wider temperature range compared to azodicarbonamide which is an undesired property. In Figure 23: Thermal degradation of azodicarbonamide as chemical blowing agent Figure 23 a thermal degradation of the chemical blowing agent azodicarbonamide shown.



$$H_2N-\overset{\overset{O}{\|}}{C}-N=N-\overset{\overset{O}{\|}}{C}-NH_2 \longrightarrow N_2 + CO + H_2N-\overset{\overset{O}{\|}}{C}-NH_2$$

Figure 23: Thermal degradation of azodicarbonamide as chemical blowing agent [18]

2.4.5 Plasticizers

Plasticizers are added to a polymer to change its properties. Plasticizers are non-volatile and low molar mass compounds added as additives to achieve a higher mobility for the polymer chains. The additive has so called ‘lubricating effects’ on the polymer chain. The polymer molecules are surrounded by low molar mass plasticizers which increases the ease of movement for the chains. Addition of plasticizer lowers the glass transition temperature and therefore softens the stiff polymers. The polymer first brittle is now flexible. PVC is a polymer where large quantities of plasticizers are added to in order to decrease the glass transition temperature. As mentioned in section Polyvinyl chloride, PVC can be classified in uPVC where no or little plasticizer is present and pPVC where large quantities are added to. PVC without plasticizer has a glass transition temperature of 81°C. Required plasticizers properties are being compatible with the polymer resin; being non-toxic; perform good at low temperatures; having non-flammability and non-volatility properties as well as good heat and light stability. A compromise in properties has to be made for the desired product. Mixtures of plasticizers make it possible to include good properties. Plasticizers are divided into two groups, primary and secondary plasticizers. Primary plasticizers are highly compatible with PVC resin. This group of plasticizers are able to be added up to at least 150 phr. Secondary plasticizers are generally used in mixtures with primary plasticizers due to lower compatibility properties. Phthalate compounds are the most used plasticizers. Phosphates, epoxies and chlorinated paraffins are also uses as plasticizers.

2.4.6 Lubricants

Lubricants are added to polymers in order to improve processability. PVC formulations are known for their high melt viscosity which impedes processability. PVC sticks to the metal wall of the die due to its high melt viscosity. Lubricants avoid sticking and reduce melt pressure in the processing unit. Dispersions of additives are improved with addition of lubricants and friction is lowered by the long hydrocarbon chains. Lubricants can be divided into two groups, the so called internal and external lubricants. During PVC fusion intermolecular friction occurs which is reduced by internal lubricants. Due to the polar structure of internal lubricants a high compatibility with PVC polymer is obtained. External lubricants are used to prevent adhesion of PVC polymer to the metal surface of the processing unit.

2.4.7 Impact modifiers

Addition of impact modifiers make it possible to improve the durability of the polymer. Impact strength and toughness are improved and are especially important at lower temperatures where PVC is brittle. Impact modifiers are elastomeric copolymers which improves PVC’s impact strength through absorption of impact energy. In order to achieve thorough absorption of impact energy a good dispersion of the impact modifier is needed. Adhesion between the impact modifier and polymer melt must be strong in order to obtain good durability properties. Adhesion via physical cross-linking or chemical bonding are preferred. Example of an impact modifier is a methacrylate/butadiene/styrene copolymer.

2.4.8 Processing aids

Processing aids are used to improve processability and melt characteristics of polymers. Acrylic and styrene copolymers are used mostly as processing aids. Processing aids will be discussed further in chapter 2.6.2 due to being the main subject of this thesis.

2.5 FUSION PROCESS

In order to process PVC a homogeneous melt is desired. Fusion of PVC grains is a breakdown of PVC agglomerates (100-180 µm) into smaller fragments called primary particles (1 µm). The agglomerates are classified as stage III particles which after fusion form primary particles known as stage II particles as shown in Figure 24.

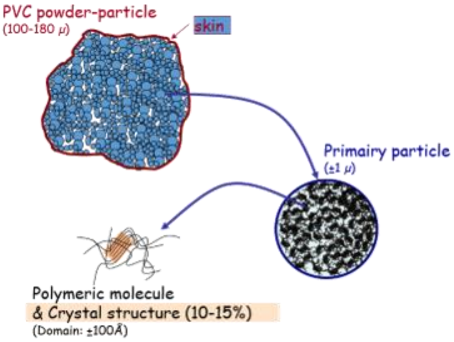


Figure 24: Schematic representation of fusion process of PVC [10]

Primary particles are polymer chains which form crystalline zones that are tied together with tie molecules as shown in Figure 25.

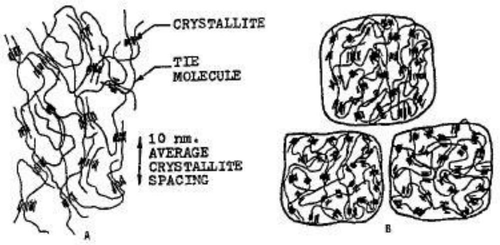


Figure 25: Representation of the PVC structure with A) the crystalline zones connected with tie molecules and B) the primary particles which are formed out of the crystallites and tie molecules [23]

Diffusion between molecular chains of two different primary particles is not possible due to the entanglement caused by the crystallites. Fusion is achieved through application of heat, friction and shear. When temperatures exceed the glass transition temperature of PVC, chain motion takes place inside the PVC grains. The fusion of these heterogeneous crystallites takes place at glass transition temperatures and beyond. PVC chains motion improves after fusion of the crystallite zones and they are now able to interact with other polymer chains. A homogeneous melt is formed and fusion is completed. The homogeneous melt cools down an forms secondary crystallites which connects the primary particles and forms a homogenous melt as shown in Figure 26.

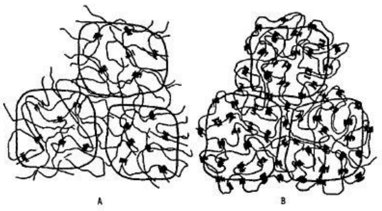


Figure 26: Representation of primary particles where A) displays the interaction between primary particles through free polymer molecules and B) represents the structure after cooling and the formation of secondary crystallites [23]

2.6 MANUFACTURING PROCESS

After choosing the additives for the required PVC formulation the PVC formula is blended in order to obtain a well dispersed formulation. After blending, many shaping steps are possible depending on the requirements of the finished product. Shaping steps such as extrusion, injection moulding, calendaring, blow moulding, foam extrusion and others are used for production of the final product. This thesis focusses on development of processing aids for PVC foam products. Thus foam extrusion will be elaborated on more in depth than previous mentioned shaping steps.

2.6.1 Foam extrusion

Foam extrusion is an extension of the traditional extrusion application. Extrusion includes mechanisms such as melting, mixing, homogenization and shaping. The extrusion line contains different components such as an extruder, cooling/shaping unit and a puller unit. During extrusion the PVC granulates are converted into a continuous melt. The PVC melt is than forced through a die with the help of an extrusion screw. The die has a uniform cross-section in order to produce pipes, tubing, window profiles and etc. After extrusion the product passes a cooling and shaping unit. This unit corrects the dimensions of the extrudate and fixes it in place by cooling. After shaping the product is subjected to a puller unit which allows the product to be cut and sized in its final shape. Figure 27 shows an overview of the extrusion line.

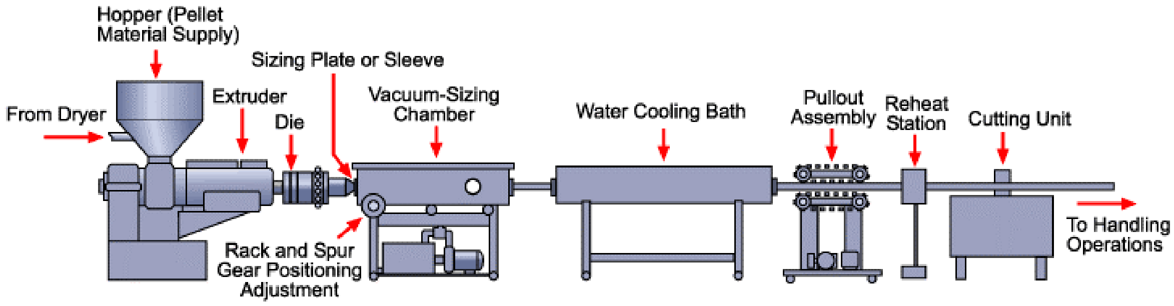


Figure 27: Schematic overview of an extrusion line [24]

The extruder includes a hopper unit which contains PVC granulates and feeds the barrel containing the extrusion screw. A schematic overview of an extruder is shown in Figure 28. The extrusion screw rotates and forces the PVC granulates in the direction of the die. The screw transports the PVC but also causes friction in order to melt the PVC granulates. The extruders is equipped with heating systems to aid melting and control temperature. A homogeneous melt is produced and fusion of PVC is obtained.

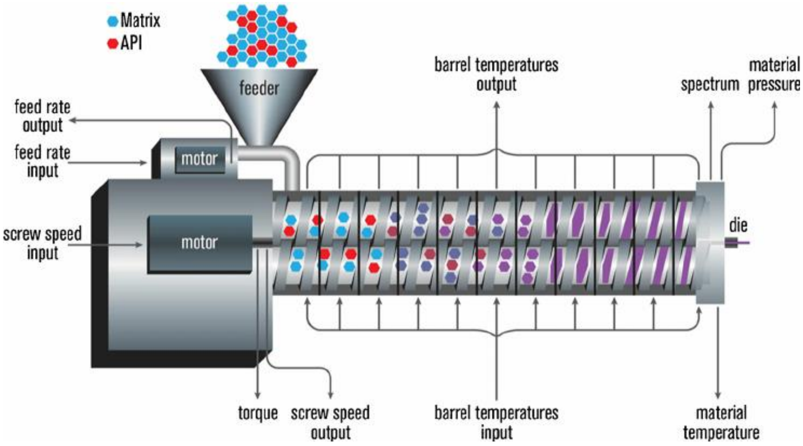


Figure 28: Schematic overview of an extruder [25]

The extrusion screw can be divided into three sections based on its dimensions and functions. The channel depth of the rotating screw is large in the beginning and narrows down towards the end. Figure 29 shows a schematic overview of an extrusion screw with its sections.

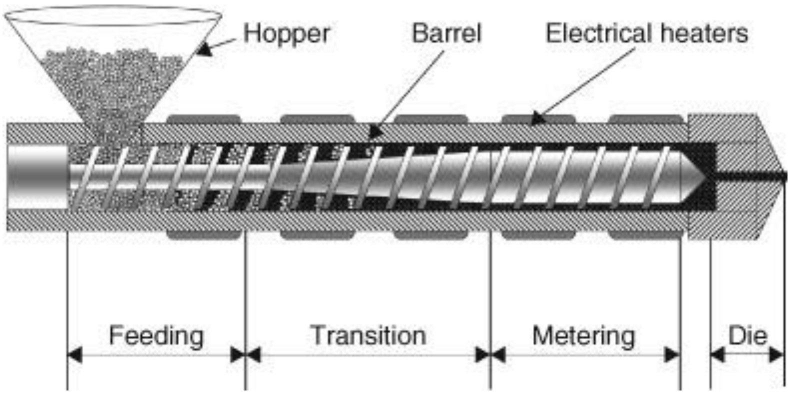


Figure 29: Schematic overview of an extrusion screw with its sections [26]

The first section called the feeding section and has the largest channel depth. This section transports the PVC granulates from the hopper to the transition or compression zone. Here, the PVC undergoes melting and releases trapped air. Further down the screw line the metering section is reached. Here, the melt will be homogenized. Pressure is generated in the metering zone to force the homogenized melt through the die.

Melting, mixing, homogenization and shaping are mechanisms that can be adapted for use in foam operations. Conditions and states in the foam extrusion process are shown in Table 2 .

Table 2: Conditions and states in the foam extrusion process [22]

Location	**Prior extrusion**	**In extrusion**	**At the die tip**	**Post extrusion**
Materials	Resin, blowing agent	Gas/melt	Gas/polymer	Air/polymer
Mechanisms	Feeding	Melting, mixing, cooling	Foaming	Aging
State	Solid, liquefied	Molten	Gas/melt	Gas/solid
Conditions	Low pressure, low temperature	High pressure, high temperature	Low pressure, high temperature	Low pressure, low temperature

Thermoplastic foams are produced with densities ranging from 3-50 % of polymer depending on the application of the end product. Chemical blowing agents decompose in order to release gas in the melt. As the pressure reduces through the die, foam is formed by the releasing gas. Chemical blowing agents are usually used for higher density foams. Physical blowing agents are injected into the extruder to form lower density foams. These blowing agents have a plasticizing effect leading to a reduction in melt viscosity. Reduction of melt temperature is necessary in order to prevent excessive expansion, cell rupture and collapse of the cellular structure. Lower melt temperatures means lower production rates. With the use of a second extruder this problem can be mitigated. Its function is to work in tandem with the primary plasticising extruder. The function of the added extruder is to cool down the melt temperature so that foam can be produced at elevated production rate without introduction of ruptured cells.

An extruder screw provides control of melt temperature and provides good mixing of the polymer. These properties are essential for good foam extrusion results. Adjustments of temperatures within the barrel zone are necessary for providing the optimum melt temperature for the polymer. In addition timing of the decomposition of blowing agent has to be controlled as well. Different designs for extruder screws are available such as single screw or twin screw extruders. When the PVC melt reaches the transition zone care must be taken to avoid premature decomposition of the blowing agent due to elevated temperatures. Meanwhile low temperature leads to poor mixing of the extrudate. Reduction of temperature gradients are necessary for a good cellular foam structure and can be achieved by good screw design and proper barrel temperatures [22]. A foam extruder line with secondary extruder in tandem is shown in Figure 30.

Figure 30: A photo of XPS foam production 150 mm/200 mm tandem line [22]

2.6.2 Injection moulding

Injection moulding is a batch process in contrast to extrusion. Injection moulding is widely used for its low postprocessing costs and for its flexibility in product dimensions. During injection a mould is filled with a certain amount of polymer melt. A reciprocating extrusion screw forces the melt into the mould to give it a shape. Figure 37 shows different steps of injection moulding process.

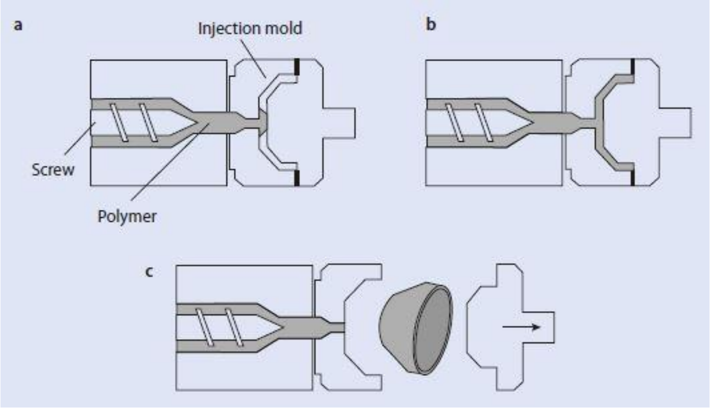


Figure 31: Simplified injection moulding process. (a) Start of the polymer melt injection. (b) End of the injection. (c) Demoulding and ejection [3]

Depending on the product’s dimensions different amounts of material are injected. The amount injected is known as the shot weight. The mould is equipped with channels for cooling water. Cooling down the product is the most time consuming step of injection moulding but is necessary so the product can be ejected without deforming. Amorphous polymers are ejected after cooling down below their glass transition temperatures whereas semi-crystalline polymers are brought below their melting temperatures. Meanwhile elastomers are heated and undergo a cross-linking reaction in the mould. The time needed for the product to harden depends on the geometry of the part, the rate of the crystallization and the shot weight. The hardening process ranges between one second and several minutes. Cooling down the melt is the most time consuming step which limits the output rate of product. Limiting the output increases process costs. For large scale production processes it is possible to automate the injection moulding process [3].

2.6.3 Calendering

Calendering is a technique which produces calendered sheets (broad strips of polymer) with the help of rollers. These sheets are semi-finished products which are processed further on. The PVC end products are used for flooring, curtains, roof-lining material and films. Calendering is an expensive manufacturing method, due to machinery costs, which is only viable for high output operations. The reason that calendering equipment is so expensive is due to high quality rollers used. These rollers need to resist pressure generated by the high viscous polymer melt. The pressure is able to deform rollers which deforms the dimensions of the calendered sheets.

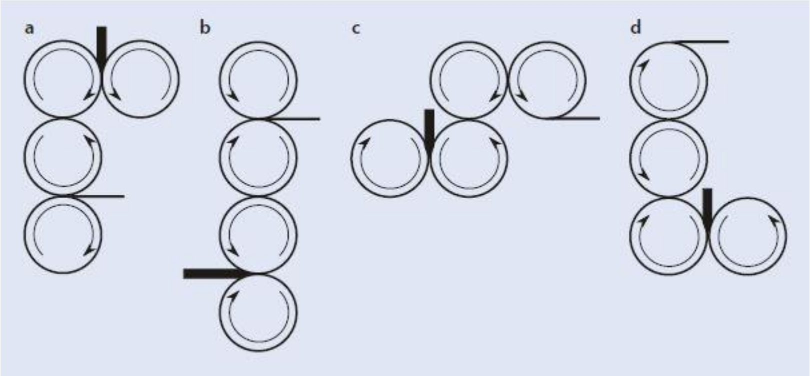


Figure 32: Roller configurations for a four-roll calender. (a) F-calender. (b) I-calender. (c) Z-calender. (d) L-calender [3]

Rolls are used to distribute additives through the PVC in order to form a homogeneous PVC melt. The plastic material passes through an extruder which makes the material malleable. The malleable materials passes over a series of heated rollers through narrow gaps. The narrow gap is adjustable to vary thickness of the material. The first rollers are fed with an excess of material which can’t pass through the gaps. The melt that can’t pass through the gaps is subjected to the rotation movement of the rollers which mixes the melt. Guides ensure the melted material stays on the rollers. After passing the first rollers the material is transported via rollers differing in rotation speed and temperature. After passing the last rollers the material is cut in pieces and stacked or wound up to a roll. The final product vary in thickness between 0.1 and 1 mm [3].

2.6.4 Blow moulding

Blow moulding is a manufacturing method used to produce hollow thermoplastic parts. It consists of two steps that are similar to injection moulding and extrusion. The first step uses extrusion with a ring die to produce a tube-like preform. This preform is known as a parison. The second step is similar to injection moulding. The parison is put into a mould and a needle is inserted into the top end of the hot and malleable tube. The mould is closed sealing the parison. Compressed air forces the malleable tube to confine to the contours of the mould. A schematic overview of the blow moulding process is shown in Figure 33.

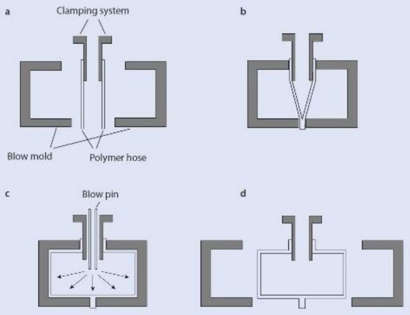


Figure 33: Process steps during blow moulding hollow objects. (a) Introducing the preform into the form and onto the mandrel. (b) Form closure. (c) Inflation of the preform to the final form. (d) Opening the blowing mould and demoulding [3]

2.7 PROCESSING AIDS

Mostly processing aids are produced from acrylic copolymers. Choice in comonomers and in their polymerization sequence are of great importance for the processing aid. Methyl methacrylate is a monomer which has great compatibility properties with PVC but trades in mobility due to the higher glass transition temperature. Acrylate monomers have lower mobility but a lower glass transition temperature compared to methyl methacrylate. The combination of these monomers are able to promote fusion of PVC. These processing aids are usually produced via emulsion polymerization. This method allows for production of extremely high molecular weights. The molecular weights surpass even 1 million which is a different magnitude than the typically 40 000-80 000 range for PVC.

2.7.1 Promotion of fusion

Processing aids coat the surface of the PVC agglomerates at the early stage of PVC fusion. Due to the coating friction between agglomerates is promoted which aids the breakdown of the structure [10, 27]. In the molten stage further promotion of fusion is caused by the entanglement of the short PVC chains and the long processing aids chains as shown in Figure 34.

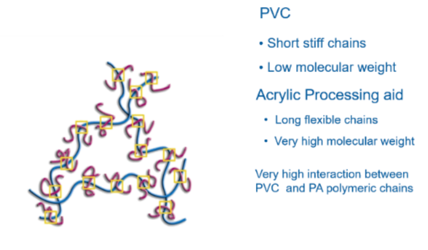


Figure 34: PVC and PA entangled network [10]

Without processing aids long processing times and high temperatures would be needed in order to obtain a homogeneous melt. This however is not possible due to the fact that PVC undergoes thermal degradation under these conditions. Poor mechanical properties of the final product are caused by improper fusion of the PVC melt. Processing aids accelerate the fusion process of PVC. Testing the breakdown of the agglomerate structure into primary particles is done by a Brabender gelation test. A rotating roller is kept a certain speed and the torque maintaining the rotating speed is recorded. The torque is plotted as a function of time or as a function of temperature. The last torque peak in a torque versus temperature curve signifies the part where breakdown of primary particles occurs. This torque peak is shifted to lower temperatures thanks to the addition of processing aids. A torque versus time curve shows that addition of processing aid leads to a reduction of time of fusion. A scanning electron microscope (SEM) can be used to show the difference between fusion with and without processing aids. A formulation with insufficient processing aid results in unmelted primary particles visible with the SEM. The chemical composition and molecular weight have a considerable influence on the ability of processing aids to promote fusion. When the molecular weight of the processing aid is increased the ability to accelerate fusion of the PVC grains is decreased.

2.7.2 Modification of melt behaviour

Melt behaviour or melt rheology can be improved by adding processing aids. PVC has poor processability characteristics other than slow fusion. Examples are poor melt strength, poor extensibility and occurring melt fracture. The processing aid does not solely promote fusion but also improves melt rheology thanks to its high molecular weight chains.

2.7.2.1 Die swell

Die swell occurs during extrusion when the polymer melt is forced through a die or capillary. The diameter of the polymer melt exceeds the diameter of the capillary. This phenomenon is also known as extrudate swell or Barus effect. The polymer stream undergoes stress passing through the narrow die which forces the molecules to align as shown in Figure 35.

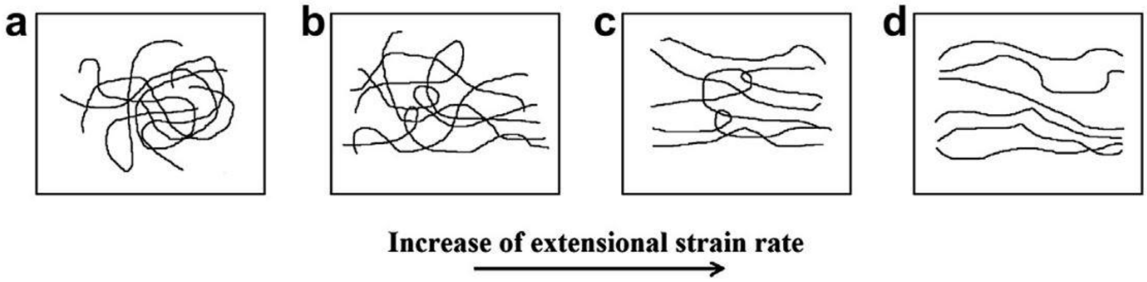


Figure 35: Alignment of polymer chains [28]

The polymer chains enter the die in a spherical conformation which is their most stable form. The narrow die forces alignments of the chains which is restricted due to the physical entanglements. After exiting the die the polymer chains are able to relax and regain a portion of their former shape. An increased retention time leads to more disentanglement and less die swell occurring. Figure 36 demonstrates the die swell phenomenon.

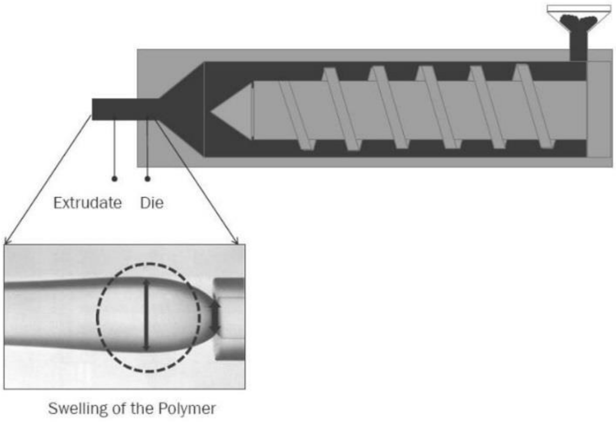


Figure 36: Die swell representation [29]

Control of die swell is very important for blow moulding and blown film techniques. Often die swell is least desired for profile extrusion and injection moulding techniques. The swell of polymer extrudate is greatly influenced by the polymer’s composition, molecular weight and other processing variables such as shear rate, temperature and length of the die. The molecular weight of processing aids (> 1 million) exceeds these of PVC (40 000-80 000). Addition of larger amounts or increase of molecular weight of PVC do result in an increase of the swell ratio of the PVC formulation. Figure 37 show the effect of the molecular weight of processing aid on PVC swell ratio. Die swell can be measured by a capillary rheometer or by small scale extrusions.

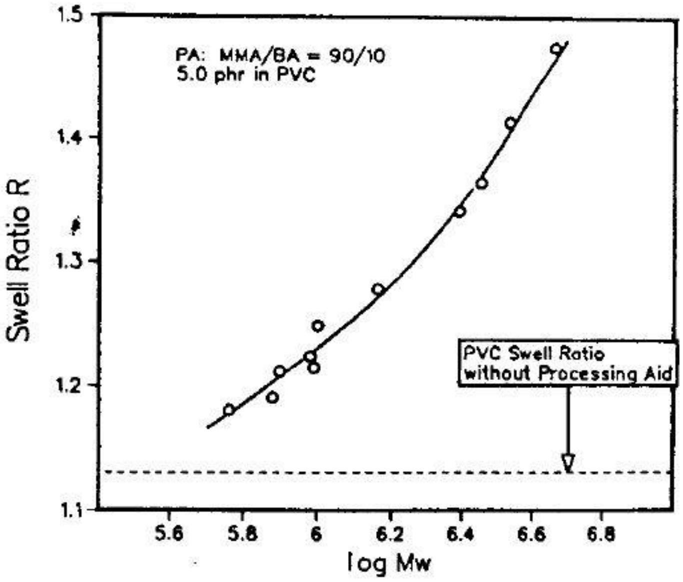
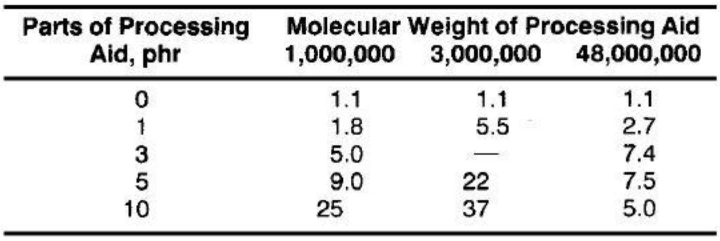


Figure 37: The effect of the molecular weight of processing aid on PVC swell ratio [30]

2.7.2.2 Melt strength

Melt strength is of great importance in blow moulding and film applications. If the melt strength does not meet standards, sagging of the molten polymer causes uneven thickness in the final product. Melt strength is a characteristic that reflects both elasticity and elongational viscosity. The molecular weight of the processing aid is proportional to the ability to improve the melt strength of the PVC formula. Higher molecular weight processing aids are desirable for their melt strength. However disadvantages such as slower fusion, increase in melt viscosity and more than desired increase in die swell ratio. Melt strength can be measured by a Göttfert Rheotens by directly pulling of the hot extrudate. In foam extrusion a high melt strength is desired in combination with a good extensibility. This means being able to undergo large elongational deformations without rupturing. Processing aids are able to increase the extensibility of the PVC formulation. A higher concentration and a higher molecular weight of processing aid improves the extensibility. However at extremely high molecular weight, a reduction of the effect is visible. Table 3 shows the effect of molecular weight and concentration of processing aid on the extensibility of PVC.

Table 3: Effect of processing aid molecular weight on PVC draw ratio at break tested at 172°C [30]



Parts of Processing Aid, phr	Molecular Weight of Processing Aid		
	1,000,000	3,000,000	48,000,000
0	1.1	1.1	1.1
1	1.8	5.5	2.7
3	5.0	—	7.4
5	9.0	22	7.5
10	25	37	5.0

Addition of processing aid to an extruded PVC foam formulation benefits the uniformity of the cell structure. The melt can withstand great extension before breaking which results in reduced cell rupturing and a lower density foam. During thermoforming a higher molecular weight processing aid ensures prevention of rupturing. On the other hand a stiffer polymer melt requires higher temperatures or longer heating time which is undesired.

2.7.2.3 Melt fracture

Melt fracture is a common surface defect that occurs in profile and sheet extrusion. Fracture is linked to shear rate, shear stress, temperature of processing and to the PVC formulation. Melt fracture occurs when the shear stress applied exceeds the critical stress level of the melt. The steady flow is disrupted and melt fracture is visible. The value of the critical stress level can be determined by a capillary rheometer. Manufacturers' production rates are limited by the critical shear rate. Addition of processing aids change the melt rheology to allow increased output without inducing melt fracture.

2.7.2.4 Melt viscosity

The high molecular chains in processing aids increase melt viscosity. This results in an undesired increase in minimum mould filling pressure for injection moulding. The high melt viscosity enables reducing of jetting and improvement of surface appearance. Interaction between the processing aid and the polymer matrix control the effect on processing. The molecular structure, molecular weight and interaction with other additives dictate the efficiency of the processing aid [30].

3 MATERIALS AND METHODS

3.1 MATERIALS

Chemicals for polymerization

In order to produce processing aids, different chemicals are used. Table 4 shows the reagents used during experimental work with a brief summary of their function and description. The reagents are coded since they are sensitive information of the company Kaneka. For example the value of the glass transition temperature T_g for monomer M1 is chosen as reference temperature $T_{ref.}$. The glass transition temperature of other monomers will be compared to the T_{ref}.

Table 4: Polymerization reagents with function, properties and description

Component	Function	Properties	Description
B1	Monomer	$T_g = -5.5 \cdot T_{ref}$	Building block polymer chain
B2	Monomer	$T_g = 2 \cdot T_{ref}$	Building block polymer chain
M1	Monomer	$T_g = T_{ref}$	Building block polymer chain
M2	Monomer	$T_g = 11.5 \cdot T_{ref}$	Building block polymer chain
T	Monomer	N/A	Star polymer formation
H	Monomer	$T_g = 5.7 \cdot T_{ref}$	Functional group implementation
P11	Redox Initiator	N/A	Produces radicals
EH6	Reducing agent	N/A	Reducing agent
F	Recovery reducing agent	N/A	Recovers the reducing agent to increase radical formation
H1	PH regulator	N/A	Regulates pH for redox system
EM15	Emulsifier	N/A	Stabilizes polymer particles
EM30	Emulsifier	N/A	Stabilizes polymer particles
P4	Post initiator	N/A	Reduces residual monomer
PW	Medium	N/A	Process water free of ions

3.2 METHODS

In this chapter the polymerization setup and the experiments will be discussed. By conducting an experiment a latex is produced. The latex is analysed on a broad range of parameters such as solid content, particle size distribution, specific viscosity, residual monomer content, latex viscosity, scales amount and mechanical stability. The produced latex is dried via a spray dry setup which leads to a dried processing aid powder. This powder is analysed for properties such as colour, Brabender gelation, heat stability, die swell, melt strength and apparent specific gravity. In addition a funnel test is performed. Extensive testing of latex as well as powder properties are necessary to ensure the processing aid meets the desired specifications to ensure quality. The importance of each parameter and test will be elaborated on in chapters 3.2.4 and 3.2.5.

3.2.1 Polymerization setup

The polymerization setup in Figure 38 demonstrates the equipment used and will be discussed in this chapter.

The polymerization setup consist of four glass reactors (5 l) placed in a water bath. The water bath is heated using three Julabo ED heaters. The reactors are equipped with a digital overhead stirrer, baffles, reflux cooler and a temperature probe. The overhead stirrer is an IKA-WERKE EUROSTAR. The stirrer is placed approximately 1 cm above the bottom of the reactor. Two types of stirrers are used during experiments: a straight and pitched (45°) blade. Each stirrer is combined with a certain pair of baffles in order to improve mixing. The temperature probes are placed inside of the glass reactor and in the water bath. The temperature is logged via a Yokogawa view recorder. The reflux cooler is supplied with cold water in order to avoid evaporation of the reagents. A FMI Lab pump model QG 105 is used to feed the reactor with emulsifier at a fixed rate. All reactors and vessels containing reagents are kept under a nitrogen flow of 100 ml/min to prevent oxygen introduction into the system. As discussed in section 2.1.1.4, oxygen has undesired retardation and inhibition properties.

Numbering	Equipment
1	Glass reactor
2	Water bath
3	Heater
4	Stirrer & baffle
5	Temperature probe
6	Reflux cooler
7	Yokogawa view recorder
8	FMI Lab pump
9	Vessel for emulsifier
10	Nitrogen supply

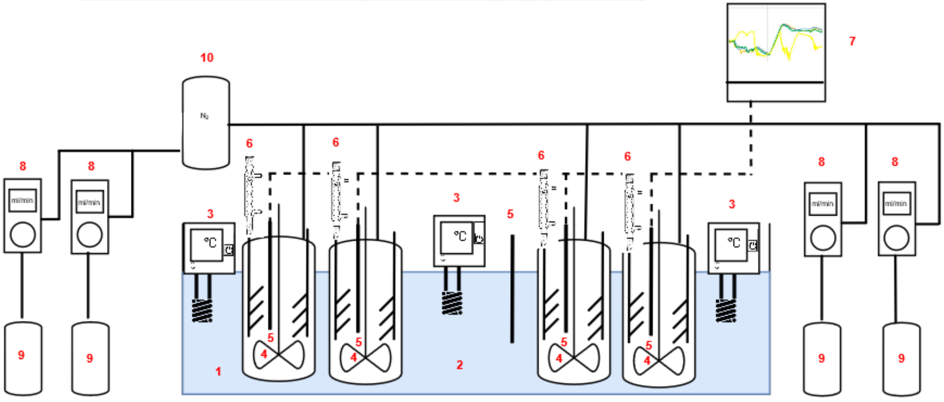


Figure 38: Polymerization setup

3.2.2 Polymerization experiments

The polymerization experiments can be divided into two groups. The first group of experiments are executed to improve the production of the processing aid X. The second group of experiments are carried out to develop a new processing aid Y. The original recipe of processing X is shown in Table 5. The initial charge is added at once. Afterwards, the monomers are dosed with a 700 ml graduated addition funnel. The initiation charge is added when the reactor temperature is reached. The emulsifier is charged in 20 min to approximately 25 min after start of reaction. This emulsifier dosage is necessary to stabilize growing polymer particles. At the end of the reaction post initiator is added in order to react with residual monomer. The post initiator is added in small amounts to prevent scission effect on the high molecular weight polymer chains.

Table 5: Recipe of processing aid X

Charge	**Components**	**Concentration PHR[1]**	**Function**
Initial charge	PW	116.8	Medium
	EM15	x	Emulsifier
	H1	0.0148	pH regulation
	EH6	0.01	Reducing agent
Monomer charge	B1	x	Monomer
	M2	x	Monomer
	T	x	Monomer
Initiation charge	F	x	Recovery reducing agent
	P11	x	Redox initiator
Emulsifier	EM15	x	Stabilizes growing polymer particle
Post initiation charge	P4	x	Reduces residual monomer

Consecutive changes of the recipe were applied to the first group of experiments concerning processing aid X. All the different tests regarding processing aid X are listed in Table 6.

Table 6: Summary of modifications of processing aid X

Test number	**Modification to the recipe**
X1	Emulsifier type
X2	Solid content
X3	Setup
X4	Polymerization time
X5	Post initiation

---

[1] The value of 1 phr equals to 21.50 gram.

Test X1 changes the emulsifier type used. Emulsifier EM15 was exchanged with emulsifier EM30. The emulsifier differs in type and concentration. The emulsifier types differ in CMC which could change the nucleation step. The CMC levels are shown in Table 7.

Table 7: CMC levels of the different emulsifiers EM15 and EM30

	EM15	**EM30**
CMC g/l	1.5	0.4

The new emulsifier has a concentration of 30 m% and is diluted to 15 m% with process water during addition to the reactor. In addition, the dosage rate of the new emulsifier is increased. An increase in dosing rate may influence oxygen introduction into the system and affect the polymerization reaction. The use of higher concentrated emulsifier enables an increased storage capacity on the site and reduces vehicular transport.

Test X2 focuses on the solid content increase. This is achieved through reduction of initial process water. Increasing the solid content results in a higher product per batch ratio. An increased production capacity is the added value. During this test, 4 reactors were used with different solid content. The solid content in the test ranged from 44 % to 50 %. Notice that increasing the solid content results in an increase in viscosity which may impede mixing capacity and heat removal. By this, the increase of the solid content is restricted.

Test X3 implements a different setup. Here, different mixers and baffles are used and scale formation is monitored. Scales are monitored for all the tests. Scales are lost product and could cause productions errors. The scales could block pipelines and pollute reactors.

Test X4 consist of 3 experiments where the overall polymerization time is reduced. The polymerization times 12, 11 and 10 $\cdot$ $\text{time}_{\text{poly}}$ hours are tested. Reducing polymerization time whilst maintaining the same properties of the processing aid results in a higher production rate. The polymerization time cannot be reduced without limitation. The limitation being a desired monomer conversion.

Test X5 focusses on the P4 and P11 addition strategy for post initiation. Different strategies are applied. The strategies contain, changing the P4 and P11 dosages added to the system, changing the timing between dosages and changes in pH level. These strategies are evaluated on the capacity to reduce residual monomers while maintaining the molecular weight. The P4 and P11 additions are known for their scission effect which decreases the molecular weight of the polymer effect. A decrease in residual monomer and a decrease in scission effect are desired results.

The second group of experiments regards to the development of the new processing aid Y. Changes such as increased M_w, different monomer compositions, blending of processing aids, introduction of functionality and increased tacticity are implemented. All the different tests regarding processing aid Y are listed in Table 8.

Table 8: Summary of modifications of processing aid Y

Test number	Modification of recipe
Y1	Reference recipe with increased M_w
Y2	Reference recipe for blending
Y3	Monomer composition
Y4	Decrease in T_g
Y5	Implement functionality
Y6	Increase tacticity

Test Y1 is the reference recipe which implements the new emulsifier and has a solid content of 46 % similarly to the improved processing aid X. The post initiation step is not included in order to acquire a higher molecular weight and improve the melt strength/die swell. The reference recipe is described in Table 9.

Table 9: Reference recipe without post initiation for processing aid Y

Charge	Components	Concentration PHR	Function
Initial charge	PW	103.991	Medium
	EM30	x	Emulsifier
	H1	0.0148	pH regulation
	EH6	0.01	Reducing agent
Monomer charge	B1	x	Monomer
	M2	x	Monomer
	T	x	Monomer
Flush water	PW	2.913	Medium
Initiation charge	F	x	Recovery reducing agent
	P11	x	Redox initiator
Emulsifier	EM30	x	Stabilizes growing polymer particle
	PW	5.010	Medium
Flush water	PW	0.582	Medium

Test Y2 uses the same recipe as test Y1 but with the intention of blending it with another processing aid Z. The blending should offer a bimodal particle size distribution. The blending should combine high melt strength on account of the high molecular weight of recipe Y2 but at the same time improve mobility and fusion due to the lower molecular weight of processing aid Z.

Test Y3 uses another monomer composition for the recipe. The use of a different monomer can impact the relaxation time of the polymer chain. If the relaxation time differs, a difference in die swell is to be expected. The glass transition temperature is kept the same as in recipe Y1.

Table 10: Monomer composition for test Y3

Charge	Components	Concentration PHR	Function
Monomer charge	B2	x	Monomer
	M2	x	Monomer
	B1	x	Monomer

Test Y4 is based on the reference recipe with an increase in B1/M2 ratio in order to decrease the glass transition temperature. Monomer B1 is increased with 25 % and monomer M2 is decreased with 6.25 % in order to increase the ratio B1/M2. Monomer T is excluded as well in this recipe.

Table 11: Monomer composition for test Y4

Charge	Components	Concentration PHR	Function
Monomer charge	B1	x	Monomer
	M2	x	Monomer

Test Y5 introduces functionality by implementing monomer H. This monomer contains a functional group which improves compatibility with the PVC matrix.

Table 12: Monomer composition for test Y5

Charge	Components	Concentration PHR	Function
Monomer charge	B1	x	Monomer
	M2	x	Monomer
	H	x	Monomer

Test Y6 aims to increase tacticity from the polymer chain. An increase in monomer T should provide a higher tacticity, which aims to increase the melt strength. The original concentration of monomer T is multiplied by ten for this test.

Table 13: Monomer composition for test Y6

Charge	Components	Concentration PHR	Function
Monomer charge	B1	x	Monomer
	M2	x	Monomer
	T	x	Monomer

3.2.3 Spray dry setup

The latex undergoes a spray drying process to obtain a powder form of the processing aid. This chapter aims to explain the procedure of this process. Figure 39 shows the setup.

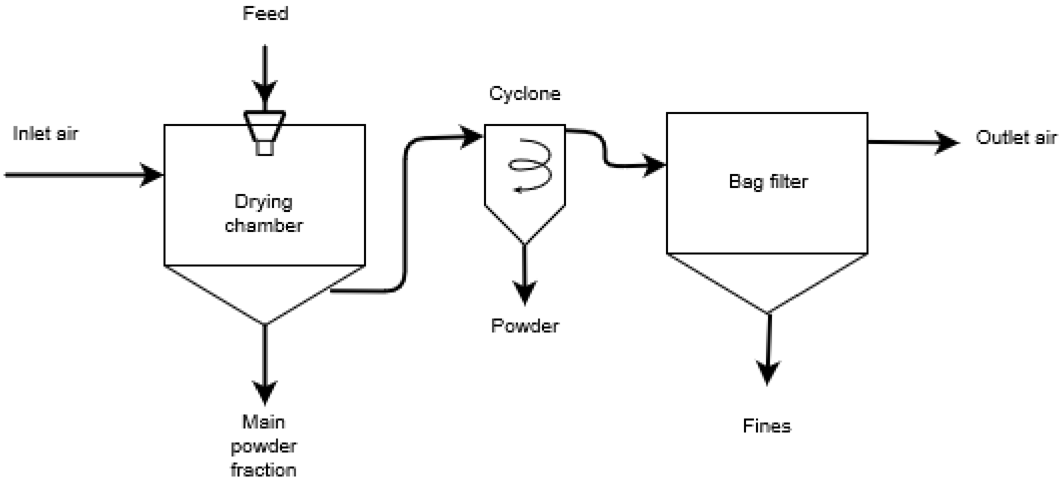


Figure 39: Spray dry setup

The latex is fed to the drying chamber through a peristaltic pump. The feed is send through a atomizer wheel at the top of the drying chamber. It is possible to control the rpm of the atomizer to affect the droplet size of the feed. Inlet air is heated before entering the drying chamber. Nebulizing the latex exposes more surface area to the warm air which improves heat transfer. 80 % of the dried latex is collected as a main powder fraction below the drying chamber. A cyclone collects the remaining 20 % of the latex as fine powder. Finally a bag filter catches potential remaining powder so that clean outlet air leaves the system.

The high specific heat capacity C_p and heat evaporation H_{vap} of the process water demands a higher efficiency of the spray dry process. Equation 1 shows a heat transfer equation mentioning the combined (latex & water) heat capacity and heat evaporation. Increasing the rpm of the atomizer as well as decreasing the flow of the feed to the drying chamber are steps taken to ensure sufficient heat transfer is possible for the drying process. A higher rpm produces a finer mist improving heat transfer between the warm inlet air and the latex due to an increase in surface area A. Decreasing the feed-rate $\dot{m}_f$ demands less heat transfer $\dot{Q}$.

Equation 1: Heat transfer equation

$$\dot{Q} = \dot{m}_f * Cp * \Delta T + \dot{m}_f * Hvap = \dot{m}_a * Cp * \Delta T$$

With

- $\dot{Q}: Heat\ transfer\ \left[\frac{J}{s}\right]$
- $\dot{m}_f: Feed\ mass\ flow\ \left[\frac{kg}{s}\right]$
- $\dot{m}_a: Air\ mass\ flow\ \left[\frac{kg}{s}\right]$
- $Cp: Combined\ specific\ heat\ capacity\ \left[\frac{J}{kg°C}\right]$
- $Hvap: Heat\ of\ evaporation\ of\ water [J/kg]$

The inlet air has a constant flow which is not altered during the drying process. The inlet and outlet temperature of the air, respectively 135°C and 55°C, is displayed on a monitor. Controlling feed-rate and atomizers rpm is done by setpoints. These setpoints are expressed in percentage output.

3.2.4 Latex sample analysis

Analysis of latex samples is necessary to evaluate the quality of the processing aid. Solid content, particle size distribution and specific viscosity are analysed. These parameters indicate if the experiment went well and shows the influence of modifications. The specific viscosity is a measurement for the molecular weight of the polymer. Other important parameters are the residual monomer content, latex viscosity, amount of scales and mechanical stability. The residual monomer content is analysed for test X5 to evaluate the post initiation strategy. Latex viscosity is monitored in order to ensure mixing during production. The scales amount is monitored as well in order to prevent loss of product and prevent possible production errors. These production errors could mean blocked pipelines or having to clean reactors. The latex undergoes transport through pumps which causes mechanical stress upon the latex. This stress can provoke undesired scales formation. A mechanical stability test tells if the latex is stable enough for transport.

3.2.4.1 Solid content

To determine the solid content of the produced latex a CEM square sample pad, a Sartorius LA3200D scale and a Whirlpool Compact microwave are used. Approximately 3 ml of latex is added to the sample pad. The pad is weighed before and after addition of latex. The wet sample pad is dried in the microwave at 500W for 5 min. Afterwards the dried sample pad is weighed again. The solid content can be determined via Equation 2.

Equation 2: Determination solid content

$$SC\% = \frac{mass_{dried\ sample\ pad} - mass_{sample\ pad}}{mass_{wet\ sample\ pad} - mass_{sample\ pad}}\ x\ 100\%$$

3.2.4.2 Particle size and particle size distribution

The average particle size of the latex is measured via a UV 1800 Shimadzu UV spectrophotometer. This UV-vis spectrophotometer consists of a light source, monochromator, beam splitter, sample compartment and detector. The wavelength used is 546.0 nm The light passes through the cells. If the sample cell contains a compound which absorbs the wavelength a difference in intensity is detected. A higher concentration equals to a lower transmittance.

Kaneka produced a method where solid content, weight and transmittance of the sample is used to calculate the particle size. The method used by Kaneka is based on the Mie theory. The Mie theory is applicable in situations with a particle diameter similar to wavelength of the incident light. Kaneka experimentally obtained the constants used in their calculation. Approximately 0.450 grams of latex is weighed and diluted to 1 litre in order to produce a 0.2% solution. This solution is placed in the sample cell.

The particle size distribution is measured with the Nanotrac Wave II apparatus which is based on the principle of dynamic light scattering. Particles in dispersion undergo Brownian motion. A laser sends light through the dispersion which is scattered by the particles. The frequency shifts are detected by a detector setup at a fixed angle. The observed intensity is the result of interference of the scattered light by each element. Larger particles will move slower than smaller particles. This is shown in Figure 40 and can be deducted from the Stokes-Einstein equation.

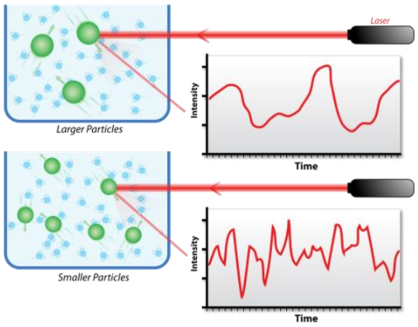


Figure 40: Intensity of the scattered light as function of time for a large and small particle [31]

Equation 3: Stoke-Einstein equation of particle diffusivity

$$D = \frac{k_B * T}{3 * \pi * \eta * d}$$

With

- $D: Diffusion\ coefficient\ or\ Particle\ diffusivity$ $[\frac{m^2}{s}]$
- $k_B: Boltzmann\ constant$ [J/K]
- $T: Absolute\ temperature$ [K]
- $\eta: Dynamic\ viscosity\ of\ medium$ [kg/m·s]
- d: Diameter of particle [m]

The observed intensity is measured in function of time. A correlation function searches for repeating parts in the plot. The produced correlation function contains a parameter known as the decay rate. This parameter can be used to determine the particle diffusivity shown in Equation 3. The relation between particle diffusivity makes it possible to determine the particle diameter [32].

3.2.4.3 Specific viscosity

The use of a viscometer Viscotek model 340 allows measuring the specific viscosity of a solution. The solution consists of 0.1996 g dried latex per l toluene (0.2 %). The latex is dried at 125°C for 1.5 hours in a petri dish. The Viscotek dilutes the dried latex with toluene to the desired concentration of 0.2 %. The polymer chains dissolve in the solution forming spherical particles that affect viscosity. Secondary attractive interactions between the polymer chain and the solvent inhibits motion. Chain entanglement and summation of attractive forces leads to an increased viscosity. This means that the specific viscosity can be correlated to the molecular weight of the latex polymer. The molecular weight is a desired parameter for evaluating the processing aid.

The Viscotek is equipped with a two capillaries marked with a start and finish position. Toluene, as pure solvent, is sent through one capillary at a constant speed. This requires a certain pressure P1. Afterwards a polymer solution is sent across the capillary with a pressure P2. The required pressure P2 is compared to the pressure P1 needed for toluene. Due to the high viscosity of the polymer solution a higher pressure will be required. The ratio of P2 to P1 is a measure for the specific viscosity of the processing aid.

The η_{sp} value measured with the Viscotek is multiplied by a factor of 2.73 to represent the molecular weight of the processing aid. The factor has been established experimentally within Kaneka. A sample was measured multiple times on different days in order to calculate the margin of error on the measurement. The margin of error is ±0.065.

3.2.4.4 Residual monomer content

A Varian CP-3800 gas chromatograph with splitless injection is used to determine the residual monomer in latex samples. A known amount of latex sample (± 0.200g) is added to a vial with 2 ml diethyl ether and 50 µl of an internal standard. The internal standard is a solution of 2808 mg chlorobenzene per litre diethyl ether. The prepared sample is shook for 30 minutes on the Specamill and centrifuged for 15 minutes at 5000 rpm on the Hettich EBA 21 apparatus. By centrifuging the sample, solvent and latex separate from each other. In the solvent layer the extracted monomer molecules are present. 1 µl of this solvent layer is injected into the chromatograph. The chromatograph is equipped with a FID detector which produces an intensity peak for the ionization of the passing components. Each monomer produces a specific intensity per mass which is expressed by factors determined by Kaneka employees every year. These factors are used to calculate the parts per million monomer remaining in the sample.

Equation 4 demonstrates how the residual monomer content is determined.

Equation 4: Calculation of residual monomer content with gas chromatography

$$RMC = \frac{A_{monomer}}{A_{internal\ standard}}\ x\ f_{monomer}\ x\ \frac{m_{internal\ standard}}{m_{latex}\ x\ \frac{100}{SC\%}}$$

With

- RMC: $Residual\ monomer\ content\ [\mu g/g]$
- $A_{monomer}$: $Intensity\ peak\ area\ for\ the\ monomer\ [\mu V * sec]$
- $A_{internal\ standard}$: $Intensity\ peak\ area\ for\ the\ internal\ standard\ [\mu V * sec]$
- $f_{monomer}$: $Monomerfactor\ related\ to\ FID\ detector$
- $m_{internal\ standard}$: $Mass\ of\ internal\ standard\ added\ [\mu g]$
- m_{latex}: $Mass\ latex\ weighed\ [g]$
- $SC\%$: the solid content of the latex

3.2.4.5 Latex viscosity

The viscosity of the latex is an important parameter to ensure good mixing and heat transport during polymerization is provided. The latex viscosity is measured using a fungilab evo expert rotational viscometer. A coaxial TL5 spindle is used for experiments. The viscometer is equipped with a PT100 temperature probe. Temperature differences between experiments have to be avoided in order to compare the results. Temperature influences the viscosity of the latex. The spindle is programmed to undergo different speed steps. These steps are 2, 5, 10, 20 and 100 rpm. The latex undergoes shear stress and shear rate. The torque is measured and the viscosity is displayed. All the data is exported an excel sheet and a viscosity versus shear rate plot is graphed.

3.2.4.6 Scales amount

The latex product is filtered in order to separate scales. These scales are dried and weighed. The amount of scales is expressed in percentage compared to the total monomer added as shown in Equation 5.

Equation 5: Amount of scales expressed in percentage

$$scales\ \% = \frac{mass_{dried\ scales}}{mass_{total\ monomers}}\ x\ 100\ \%$$

3.2.4.7 Mechanical stability

At industrial scale latex is transported via pumps through pipes. The latex undergoes mechanical stress during transport which can lead to undesired coagulation and scale formation. The latex is tested on mechanical stability by weighing approximately 100 g latex and placing it in a metal die. The metal die is kept at a temperature of 55°C and a weight of 7 kg is placed on the latex. A rotational movement is imposed on the latex during 20 min. Afterwards the die is opened and the scales are weighed. The amount of scales formed is expressed via following Equation 6.

Equation 6: Mechanical stability expressed in scales formation %

$$scales\ \% = \frac{mass_{scales}}{mass_{latex}\ *\ solid\ content_{fraction}}\ x\ 100\ \%$$

A high amount of scales formation means the latex has poor mechanical stability.

3.2.5 Analysis of dried processing aid

Dried processing aids are used as additives to PVC formulations. Their goal is to improve melt strength, die swell and PVC fusion. Tests such as Rheotens, die swell and Brabender gelation are used to evaluate these parameters. Changes in recipe of the processing aid could alter the colour which is not desired for some applications. Another concern is the heat stability of the powder. Properties of the powder should not be sensitive to elevated temperatures. Good heat stability increases the shelf life of the processing aid. The powder is tested on caking properties to ensure no lumps are formed during storage. A funnel test is conducted to evaluate the ease of addition through funnels. In addition the average specific gravity is tested.

3.2.5.1 Rheotens

A rheotens test is performed to evaluate the melt strength of a polymer. Producing foamed PVC products require a sufficient melt strength to ensure no gasses leave the polymer melt. The processing aid (4.5 phr) is blended with a PVC formulation known as Contifeed in preparation for the test. The PVC formulation is shown in Table 14.

Table 14: PVC formulation (Contifeed) for Rheotens and Die swell test

Components	**Function**	**Phr**
PVC Solvin 257 RF	PVC	100
R	Stabilizer	x
L1	Internal lubricant	x
L2	External lubricant	x.5
L3	External lubricant	x
D	Plasticizer	x.5
C	Filler	x
TO	Filler	x

The rheotens is equipped with an extruder to produce a polymer melt at a constant flowrate of 800 g/hr. The melt is sent through some counter-rotating pinching wheels. These wheels have the same take-up speed as the velocity of the extruded polymer filament. The pinching wheels accelerate (6 mm/s^2) which elongates the polymer melt until it breaks. The draw-down force is measured during the test and plotted in function of the pull-off speed.

Increasing the pull-off speed causes the diameter of the polymer filament to decrease in such extent that the wheels are slipping. When slipping of the filament occurs periodic fluctuations are visible on the curve.

3.2.5.2 Die swell

The die swell test is performed with the same PVC formulation as in the Rheotens test. The extruder produces a polymer melt which is measured with a laser/cutting unit. Settings used are displayed in Table 15.

Table 15: Settings for die swell test

Extruder		**Laser/cutting unit**	
Screw speed	25 rpm	Output	500 g/hr
Die dimensions	30 x 2 mm	Cutting time	5 s
Hopper cooling	on	Number of measurements per cycle	40
Temperature C1	165°C	Distance laser to die	5 cm
Temperature C2	182°C		
Temperature C3	184°C		
Temperature C4	190°C		
Temperature Die	195°C		

The temperature gradient throughout the extruder is given in Table 15. The polymer filament passing the laser unit is cut every 5 seconds in order to prevent elongation due to the suspended weight of the filament. The die swell is expressed as die swell ratio as seen in Equation 7.

Equation 7: Die swell ratio

$$Die\ swell\ ratio = \frac{D}{D_0}\ x\ 100\%$$

With

$D\colon Diameter\ of\ polymer\ filament\ [mm]$

$D_0\colon Diameter\ of\ die\ [mm]$

3.2.5.3 Brabender gelation

Processing aids are added to PVC formulation to promote fusion. The fusion/gelation behaviour of the PVC formulation is tested with a Brabender Plasti-Corder PL 2000. This apparatus consists of a temperature controlled chamber equipped with mixing blades. The PVC formulation is loaded in this chamber and undergoes shear and friction due to the mixing blades. This mixing induces gelation. The gelation behaviour can be influenced by three parameters. The first parameter is the dosage of PVC formulation to the gelation chamber. More shear and friction is established by increasing the formulation dosage. The second parameter is the temperature of the gelation chamber which influences mobility of the polymer chains. The third parameter is the rotational speed of the mixing blades which induces shear and friction within the formulation.

The PVC formulation used for Brabender gelation is known as NWGII. This formulation is mixed with 2.5 phr processing aid. Settings of the gelation parameters are shown in Table 16.

Table 16: Settings Brabender gelation

Temperature chamber	145°C
Rotation speed mixing blades	45 rpm
Sample charge	53 g

The sample is fed into the chamber using a plunger and subjected to heat and friction during 10 min. The Brabender measures the torque on the mixing blades as well as the temperature during this gelation process. These measurements allow to plot torque versus temperature and torque versus time graphs (Figure 41and Figure 42). The graphs are used to compare the gelation behaviour induced by the processing aids. Point A has the highest torque value. This peak, known as the loading peak, is caused by injecting the powder into the chamber. The minimum torque is represented by point B. This point indicates the start of powder melting. Only primary particles are present at this stage. The mixing blades apply friction and shear causing a temperature increase. The primary particles disappear resulting in an increase in torque demonstrated by point G. Interaction between primary particles cause the torque value to increase to a maximum (point X). The time needed to achieve point X is known as the fusion time. After reaching point X a decrease in torque occurs. The increase in temperature lowers the viscosity of the melt resulting in a decrease in torque. Point E known as the final torque represents a homogeneous melt.

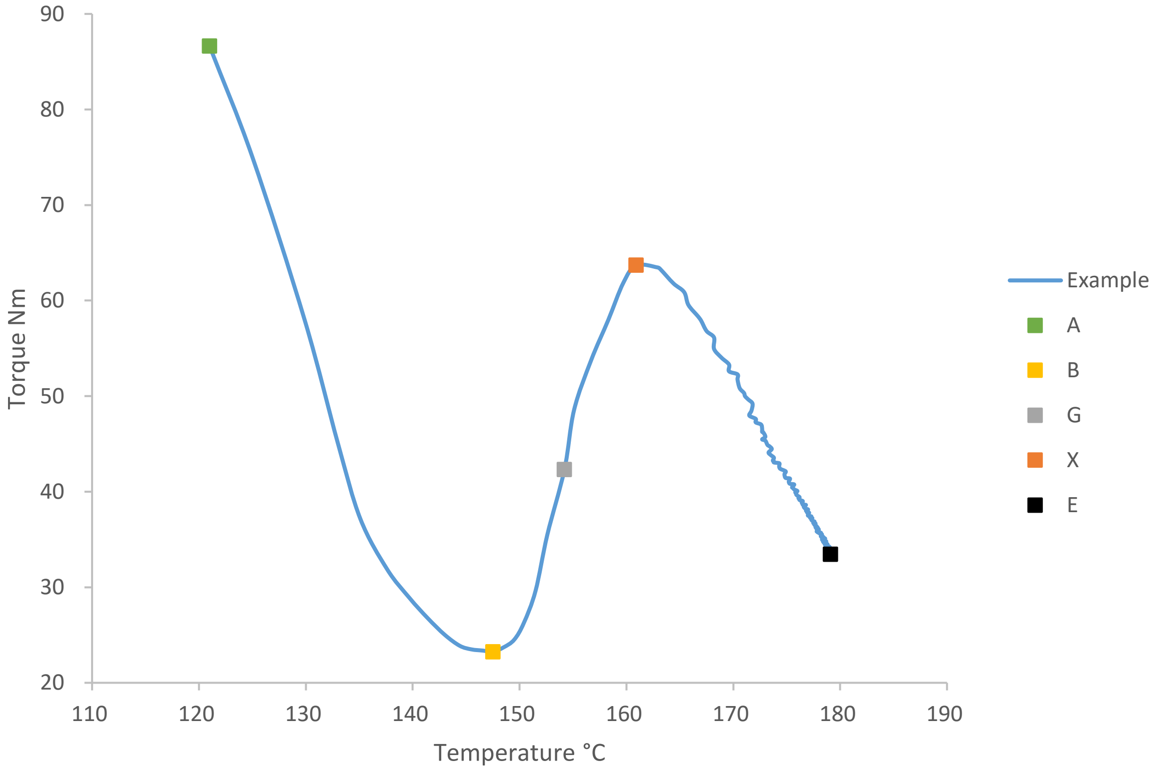


Figure 41: Example of Brabender gelation test with torque (Nm) as function of temperature (°C)

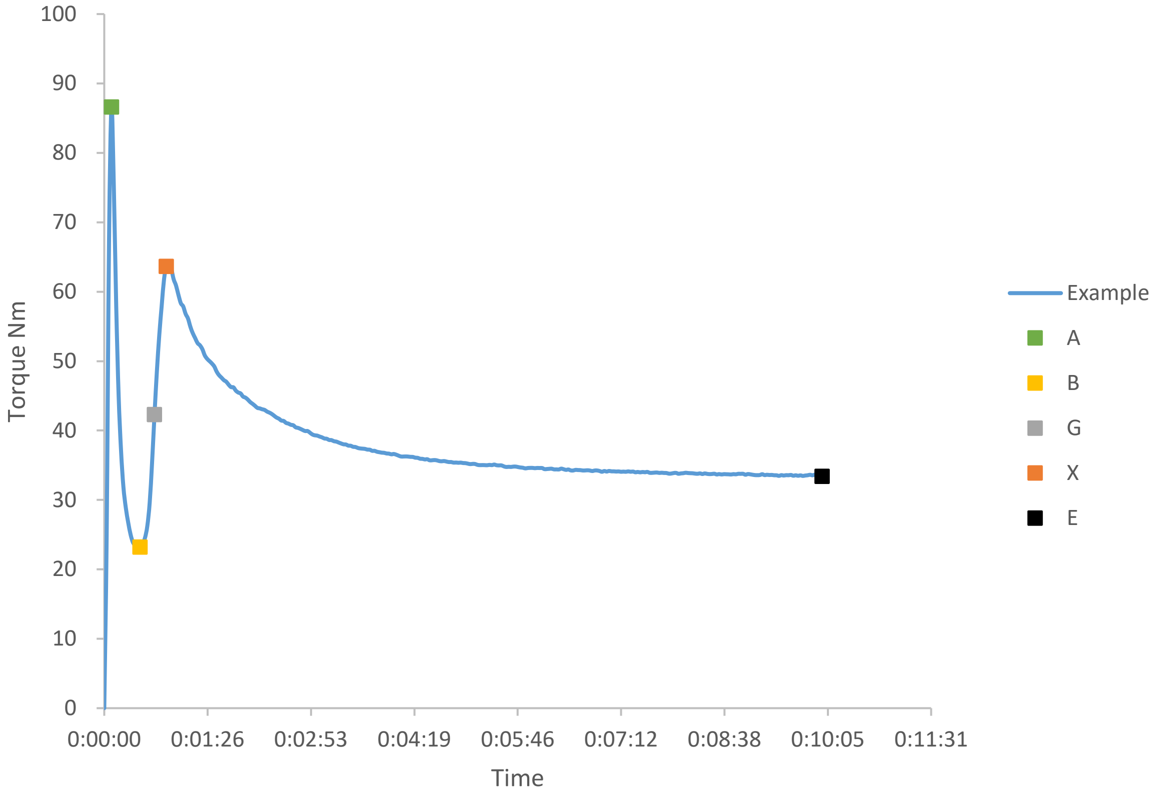


Figure 42: Example of Brabender gelation test with torque (Nm) as function of time

3.2.5.4 Colour

The colour of the processing aid is tested with the CIE-lab system. This system represents a colour space defined by the International Commission on Illumination. The dimensions of this space are represented by a, b and L. Here, +a = red, -a = green, +b = yellow and -b = blue. L ranges from black (L=0) to white (L=100) where L =50 is considered grey.

Values of L, a and b allow to characterise and compare discolouring between different processing aids. The yellow colour is expressed more specific as Yi and an additional Haze test provides extra information about the appearance of the powder [33]. The processing aid powder is added (3 phr) to a PVC compound (NWGII) and tested with a Hunterlab Colorquest XE.

3.2.5.5 Heat stability

The heat stability is tested by producing narrow sheets of product (NWGII & PA) and placing them in a Mathis thermotester oven. The NWGII formulation is shown in table. 3 phr of processing aid is added to the NWG II formulation.

Table 17: NWG II formulation

Compound	Function	Amount (PHR)
PVC Solvin 257RF	PVC	100
L1	Internal lubricant	1.0
L2	External lubricant	0.5
R	Stabilizer	1.5
E	Stabilizer	1.5

The oven is set at a temperature of 185°C. The sheets are inserted into the oven for 20 minutes. Every 900 seconds 20 mm of the sheet is pulled out of the oven in order to cause a gradient in residence time. The parts that are exposed to the heat for a longer period of time undergo thermal degradation. This test allows to compare heat stability between samples.

3.2.5.6 Funnel test

Two funnels with different diameters (10 mm and 20 mm) are used for the funnel test. The powder. When the powder stops flowing the funnel is hit to aid flow. The funnel test expresses it values in hits/sec needed to pass the powder.

3.2.5.7 Apparent specific gravity ASG

The apparent specific gravity is measured and expressed in g/cc. This property is important for selling products. The price is fixed per mass unit. A low ASG means more packaging requirements for the same price.

4 RESULTS AND DISCUSSION

4.1 OPTIMIZATION OF AN EXISTING PROCESSING AID X

The recipe of processing aid X was systematically altered in order to improve its production process. An emulsifier change was implemented, to use smaller storage tanks, with the desire to maintain the same properties such as particle size and molecular weight. The solid content is increased, in which viscosity limitations are taken in account. Different polymerization setups were evaluated on the influence on the latex properties. An attempt to decrease the polymerization time is performed with the intention of maintaining the monomer conversion and molecular weight. The influence of post initiation strategies is tested to decrease residual monomers while maintaining the molecular weight. The parameters η_{Sp}, PS and polymerization time are coded such that comparisons can be made in relation within the test without revealing sensitive information. Specific values are chosen to represent and $\eta_{Sp}ref$, PS_{ref} and $time_{poly}$.

4.1.1 Influence of emulsifier type: test X1

The function of the emulsifier is to stabilize the growing polymer particles. Depending on the type of emulsifier, fewer or more molecules are needed in order to stabilize the polymer particles. A lack of emulsifier molecules may lead to coagulation of these particles. The current emulsifier results in homogeneous nucleation instead of micellar nucleation as mentioned in chapter 2.2. The critical micellar concentration for the current and new emulsifier differ and could possibly influences the nucleation occurring. If the new emulsifier produces similar particle size products, the presence of homogeneous nucleation is confirmed.

Test X1 consists of three polymerization reactions. The first polymerization (X1-1) contained the original processing aid recipe, which uses EM15 as emulsifier. The second polymerization (X1-2) uses EM30 instead of EM15. The new emulsifier is diluted to obtain the same latex viscosity as in the original recipe. The third polymerization (X1-3) used also the EM30 emulsifier, in this test the dosage time was reduced from 20 min to 10 min. This could affect oxygen concentration in the system, which possibly influences the polymerization reaction and hence molecular weight.

Solid content SC, molecular weight M_w and particle size PS are evaluated and shown in Table 18. The η_{Sp} represents the molecular weight of the polymer as discussed in chapter 3.2.4.3.

Table 18: Influence of emulsifier type and dosage rate on PS, M_w and SC for test X1

Parameters	**Test X1-1**	**Test X1-2**	**Test X1-3**
Emulsifier	EM15	EM30	EM30 reduced dosage time
PS (Å)	$3.246 \cdot PS_{ref}$	$3.206 \cdot PS_{ref}$	$3.276 \cdot PS_{ref}$
η_{Sp} (-)	$12.316 \cdot \eta_{Sp}ref$	$11.994 \cdot \eta_{Sp}ref$	$12.216 \cdot \eta_{Sp}ref$
SC (%)	42.71	43.59	43.55

The emulsifier change has no significant influence on the PS, M_w and SC. The increased dosage rate did not seem to have an influence on latex quality. Thus, the new emulsifier did not influence nucleation or stabilization of the polymer particles. In addition latex viscosity is measured and compared with an in house reference sample. Figure 43 shows the result for the latex viscosity test concerning test X1. The viscosity of test X1 is much lower than the reference sample. The emulsifier change and dosage time reduction did not influence the latex viscosity.

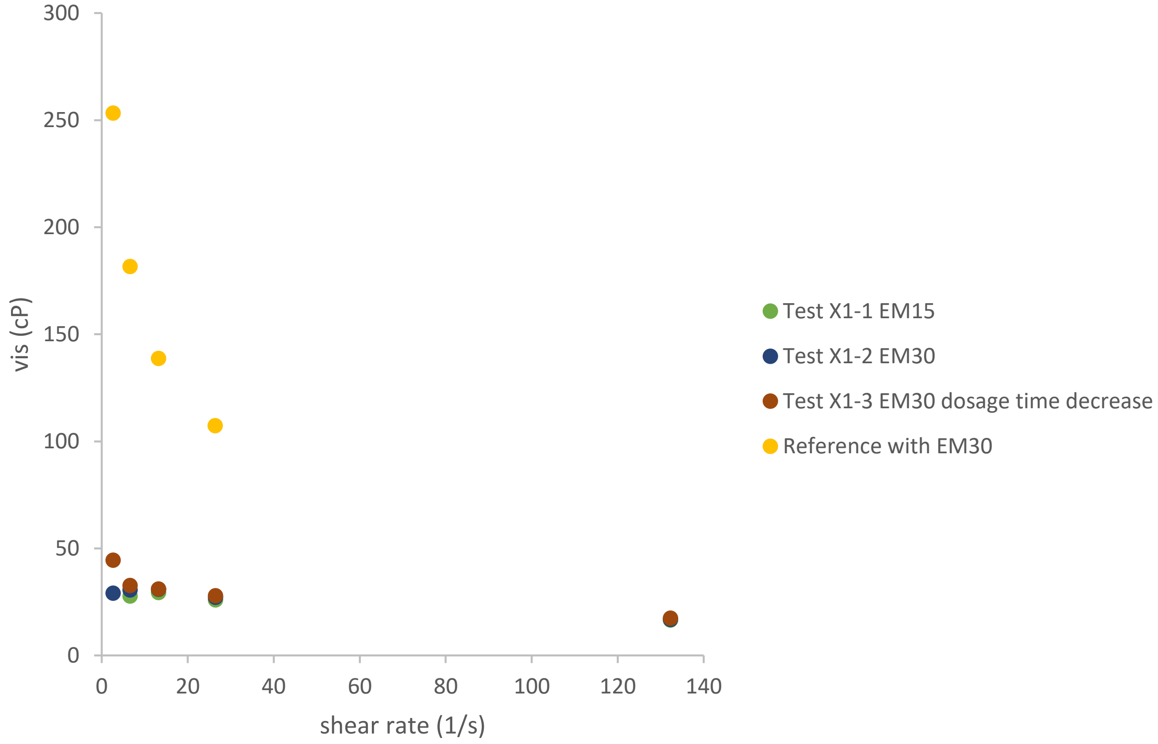


Figure 43: Latex viscosity (Cp) as function of shear rate (1/s) test for test X1

The properties of the processing aid were successfully maintained. The new emulsifier is used in all further tests. For test X1 no scales formation was evaluated.

4.1.2 Solid content: test X2

The increase in solid content enables an increase in product per batch ratio. Increasing the solid content is limited by an increasing latex viscosity. This may lead to poor heat removal and product properties. Test X2 uses the new emulsifier EM30 for all its tests. The original recipe had a solid content of 44 % and is increased to 46 %, 48 % and 50 %. The amount of process water was reduced to raise the solid content. The polymerization was closely monitored in order to intervene if mixing problems would occur. The test with 50 % SC was diluted to a SC of 48.9 % in order maintain control of the reaction. Notice that experimental SC values differ from the theoretical values. Particle size, molecular weight and solid content where analysed for each experiment and displayed in Table 19.

Table 19: Influence of SC on PS and Mw for test X2

Parameters	**Test X2-1**	**Test X2-2**	**Test X2-3**	**Test X2-4**
SC theoretical (%)	44	46	48	50
PS (Å)	$3.14 \cdot \mathrm{PS}_{\mathrm{ref}}$	$3.058 \cdot \mathrm{PS}_{\mathrm{ref}}$	$3.004 \cdot \mathrm{PS}_{\mathrm{ref}}$	$3.032 \cdot \mathrm{PS}_{\mathrm{ref}}$
η_{Sp} (-)	$11.744 \cdot \eta_{Sp}ref$	$11.982 \cdot \eta_{Sp}ref$	$11.96 \cdot \eta_{Sp}ref$	$11.82 \cdot \eta_{Sp}ref$
SC (%)	43.26	45.36	47.00	47.63
Scales (%)	0.23	0.22	0.48	0.51

An increase in solid content leads to a decrease in particle size. The decrease in particle size is not significant. The molecular weight expressed as η_{Sp} is constant for all experiments. An increase in scale formation is visible for test X2-3 and X2-4. During test X2-3 and X2-4 a substantial increase in viscosity was visible. Movement in proximity to the baffles was minimal. The viscosity of the latex products is evaluated in order to conclude which solid content could be used as shown in Figure 44.

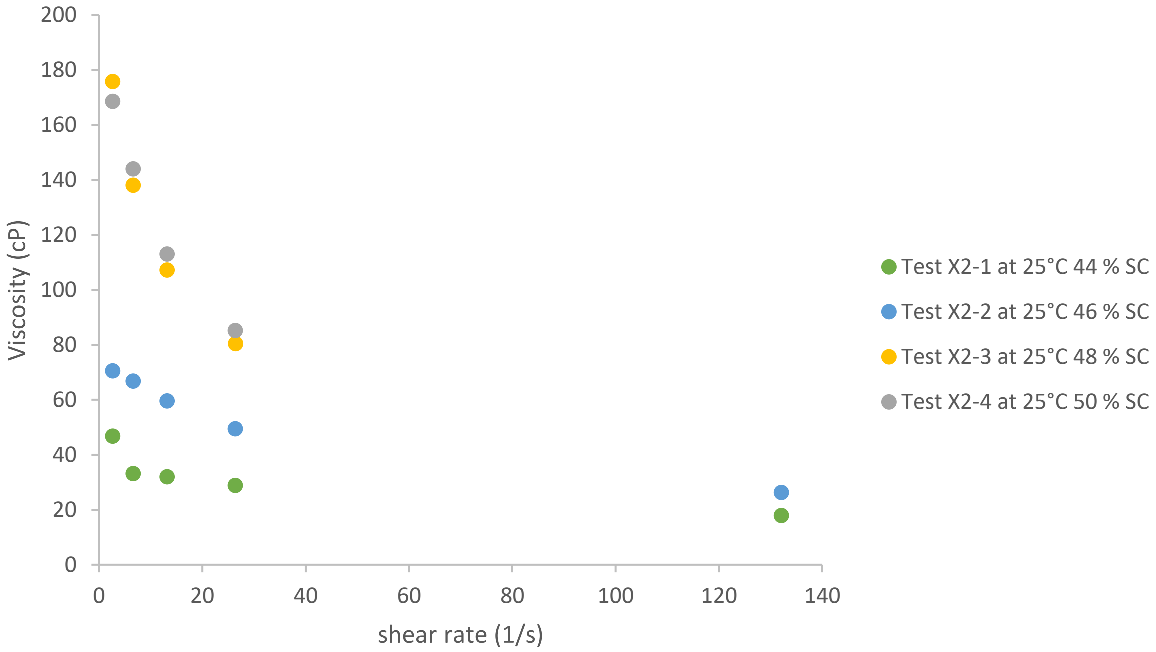


Figure 44: Latex viscosity (Cp) as function of shear rate (1/s) test for test X2

Tests X2-3 and X2-4 both show viscosity increases which are undesired. Visual monitoring during polymerization did show no movement of the latex in proximity to the baffles. Test X2-2 showed movement in proximity to the baffles and no significant increase in viscosity is visible in Figure 44. Test X2-2 was able to maintain properties such as PS and M_w. The increase of solid content was as success for test X2-2. Further tests with SC between the 46-48 % have to be conducted in order to find the optimal point.

4.1.3 Influence of polymerization setup: test X3

Changing polymerization setup results in different mixing patterns which could alter the properties of the latex. Test X3 evaluates the sensitivity of the recipe for a setup change. The recipe for test X3-1 and X3-2 are the same as for X2-1 and X2-2 respectively. Different baffles and mixer where used for test X3. Table 20 shows results of the analysis. The setup used for test X3 is known to promote more undesired scale formation. Therefore scale formation is monitored as well.

Table 20: Influence of polymerization setup on PS, Mw and scales

Parameters	**Test X2-1**	**Test X2-2**	**Test X3-1**	**Test X3-2**
Setup	Old setup	Old setup	New setup	New setup
PS (Å)	3.14 · PS$_{ref}$	3.058 · PS$_{ref}$	3.056 · PS$_{ref}$	3.066 · PS$_{ref}$
η_{Sp} (-)	11.744 · $\eta_{Sp}ref$	11.982 · $\eta_{Sp}ref$	11.792 · $\eta_{Sp}ref$	11.904 · $\eta_{Sp}ref$
SC theoretical (%)	44	46	44	46
SC experimental (%)	43.26	45.36	43.53	44.61
Scales (%)	0.23	0.22	1.96	0.78

The particle size and the M_w were not influenced by the setup change. The new setup promoted scale formation. Test X3-1 had an exceptional increase in scale formation. The different mixing pattern is able to generate enough force to coagulate latex particles which can lead to scales. The increase was not so predominantly visible in test X3-2. An overall higher scale formation is observed for test X3 with the new setup. Test X3-1 formed a lot of scales but no precautions had to be taken because the scale formation did not surpass 2 % which is the threshold set by Kaneka. Figure 45 shows the scales for each test.

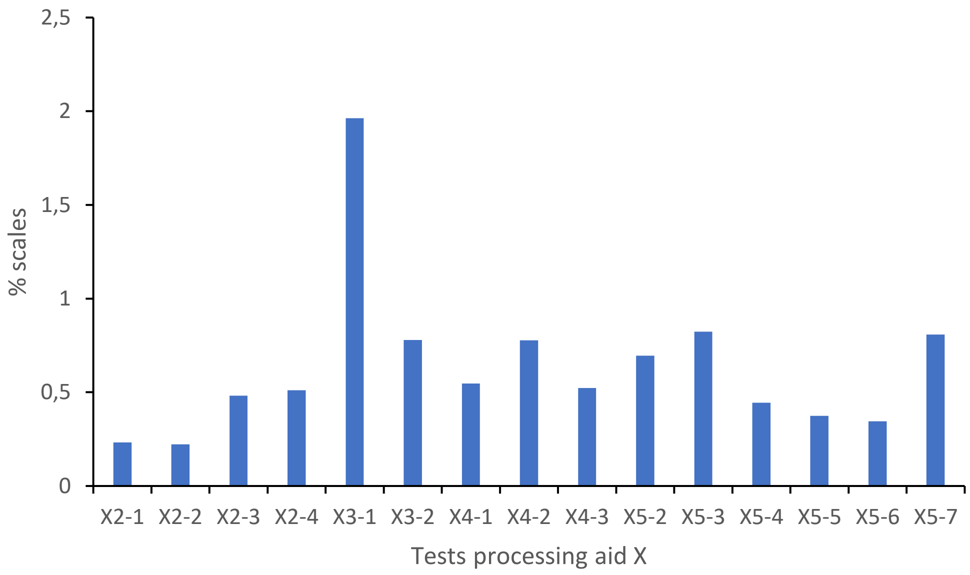


Figure 45: Scale formation for processing aids X tests

4.1.4 Polymerization time: test X4

Decreasing the polymerization time without changing latex properties is desired in order to increase the production capacity. A specific value is chosen to represent time$_{poly}$ to compare tests without revealing sensitive information. The original polymerization time was 12 · time$_{poly}$ hours and will be used as reference. Test X4-1, X4-2 and X4-3 were conducted in 12, 11 and 10 · time$_{poly}$ hours respectively. Reduction of polymerization time is restricted by monomer conversion and molecular weight. The monomer conversion was determined through solid content measurements for test X4. Table 21 shows the monomer conversion, η_{Sp} and PS values for test X4.

Table 21: Influence of polymerization time on conversion, Mw and PS

	Test X4-1	**Test X4-2**	**Test X4-3**
Polymerization time (hours)	$12 \cdot \text{time}_{poly}$	$11 \cdot \text{time}_{poly}$	$10 \cdot \text{time}_{poly}$
PS (Å)	$3.152 \cdot \text{PS}_{ref}$	$3.194 \cdot \text{PS}_{ref}$	$3.08 \cdot \text{PS}_{ref}$
η_{Sp} before post initiation (-)	$12{,}929 \cdot \eta_{Sp}ref$	$12{,}562 \cdot \eta_{Sp}ref$	$12{,}474 \cdot \eta_{Sp}ref$
η_{Sp} after post initiation (-)	$12.368 \cdot \eta_{Sp}ref$	$11.836 \cdot \eta_{Sp}ref$	$11.736 \cdot \eta_{Sp}ref$
η_{Sp} reduction (%)	4.335	5.778	5.925
Monomer conversion (%)	97.11	97.78	98.69
Scales (%)	0.55	0.78	0.52

The η_{Sp} value shows a trend in which a longer polymerization time results in a higher η_{Sp} value which signifies a higher molecular weight. These values suggest a longer polymerization time is necessary to acquire a high molecular weight. The post initiation step has a higher scission effect on the lower polymerization times. On the other hand the monomer conversion suggests that test X4-3 gives the best result. However temperature changes between the tests have to be taken in account. The temperature influences the polymerization rate which effects the conversion and molecular weight as well. Figure 46 shows the temperature plot for test X4.

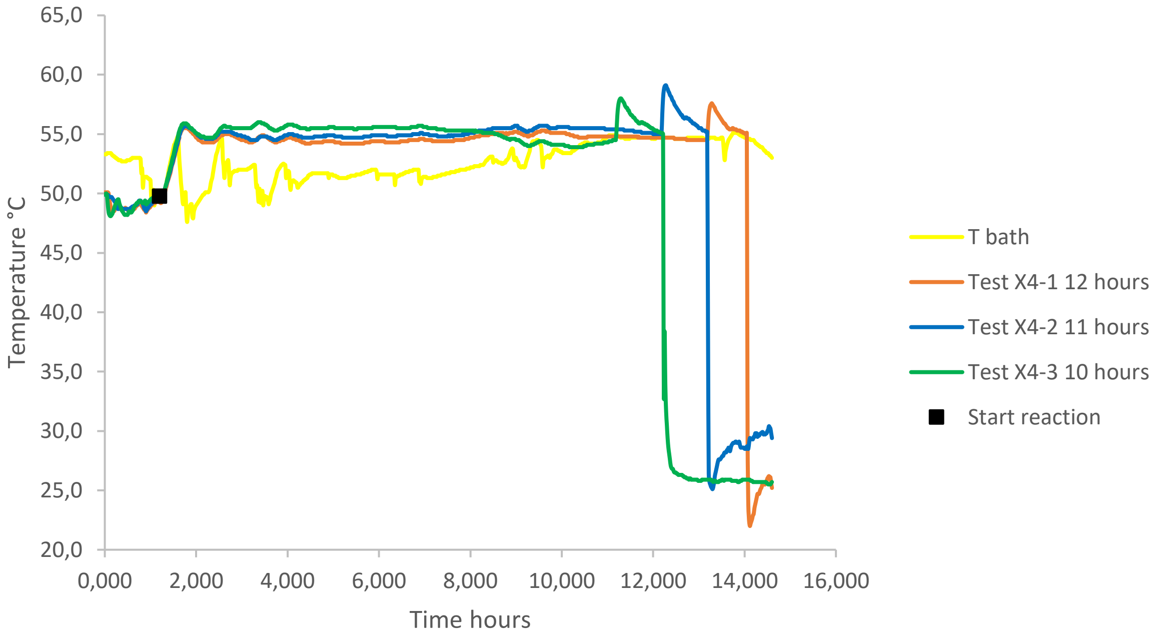


Figure 46: Temperature trend for test X4

Test X4-3 has an increased temperature for the first part of the polymerization which may explain conversion differences as well. Test X4-2 has a similar temperature trend to test X4-1. Monomer conversion between these two tests is similar. The final η_{Sp} value of test X4-2 is similar to test X2 and X3. The polymerization time of $11 \cdot \text{time}_{poly}$ hours is able to produce the desired η_{Sp} value and monomer conversion. A decrease in polymerization time is a success.

4.1.5 Post initiation: test X5

Test X5 aims to reduce residual monomer content within the latex while maintaining the molecular weight of the polymer chains. P4 and P11 are chemicals added to approximate 100

% monomer conversion as closely as possible by reacting with residual monomers. These chemicals have the ability to react with polymer chains that causes an undesired scission effect, reducing the molecular weight of the polymer chain. Test X5-1 uses the standard post initiation strategy and will be used as reference. The standard strategy uses P4 addition in two equal charges with 15 minutes reaction time after each charge. Test X5-2 alters the quantity of the first and second charge of P4. The first charge is decreased to 1/3 and the second charge is increased to 2/3 of total P4 addition. The decrease in first charge is done to evaluate the effect of smaller dosage on the η_{Sp} value and monomer conversion. The same amount of P4 is added in total to each test to evaluate the final η_{Sp} value and monomer conversion. Test X5-3 increased the pH from 7.7 to 9.16 to evaluate the effect on η_{Sp} value and monomer conversion. A. Rahman and C. W. Brown researched the effect of pH on the rate of emulsion polymerization [34]. They observed an increase in the rate of polymerization as pH increases. The ionic charge of the micelle may be influenced by addition of electrolyte. The electrolyte may change the micellar size by altering the charge density. An increase in pH decreases the micellar size and the number of micelles increase. The polymerization rate is dependent on the number of micelles. Test X5-4 uses a combination of P4 and P11. P11 could have a different affinity towards the residual monomers which may improve monomer conversion. Test X5-5, X5-6 and X5-7 are performed with a polymerization time of 11 hours. Test X5-5 is used as reference and implements the same post initiation strategy as test X5-1. Test X5-6 changed the reaction time between addition steps. The elevated reaction time could influence the ability of the P4 to react with the residual monomer content and thus increase conversion. Test X5-7 is based on test X5-2. The difference is that second charge is divided in order to have a third charge. This means no large (2/3) addition of P4 occurs. This is done to prevent a scission effect due to excess P4 reacting with the polymer chain instead of reacting with the scarce residual monomer content. An overview of the different tests is shown in Table 22.

Table 22: Overview of test X5 with all post initiation strategies

Test overview	**Strategy**	**First charge**	**Reaction time min**	**Second charge**	**Reaction time min**	**Third charge**	**Reaction time min**	**Polymerization time in hours**
Test X5-1	P4 addition	$^1/_2$	15	$^1/_2$	15	-	-	12
Test X5-2	P4 addition	$^1/_3$	15	$^2/_3$	15	-	-	12
Test X5-3	P4 addition with pH increase	$^1/_2$	15	$^1/_2$	15	-	-	12
Test X5-4	P4 addition	$^1/_2$	15	$^1/_2$	15	-	-	12
	P11 addition	$^1/_1$		-		-		
Test X5-5	P4 addition	$^1/_2$	15	$^1/_2$	15	-	-	11
Test X5-6	P4 addition	$^1/_2$	30	$^1/_2$	15	-	-	11
Test X5-7	P4 addition	$^1/_3$	15	$^1/_3$	15	$^1/_3$	15	11

Samples are taken before addition of P4 and P11. Gas chromatography will be used to evaluate the strategies ability to reduce residual monomer without decreasing η_{Sp}. A desired outcome is an increased conversion with a high final η_{Sp} value. The influence of these strategies on maintaining the η_{Sp} value is shown in Table 23.

Table 23: Influence of post initiation strategy on maintaining the η_{Sp} value for test X5

	Test X5-1	**Test X5-2**	**Test X5-3**	**Test X5-4**	**Test X5-5**	**Test X5-6**	**Test X5-7**
η_{Sp} before first charge	13.022 · $\eta_{Sp}ref$	12.46 · $\eta_{Sp}ref$	12.704 · $\eta_{Sp}ref$	12.776 · $\eta_{Sp}ref$	12.684 · $\eta_{Sp}ref$	12.706 · $\eta_{Sp}ref$	12.704 · $\eta_{Sp}ref$
η_{Sp} before second charge	12.504 · $\eta_{Sp}ref$	12.568 · $\eta_{Sp}ref$	12.12 · $\eta_{Sp}ref$	12.06 · $\eta_{Sp}ref$	12.118 · $\eta_{Sp}ref$	12.186 · $\eta_{Sp}ref$	12.348 · $\eta_{Sp}ref$
η_{Sp} before third charge	x	x	x	x	x	x	12.12 · $\eta_{Sp}ref$
η_{Sp} final	11.606 · $\eta_{Sp}ref$	11.616 · $\eta_{Sp}ref$	11.572 · $\eta_{Sp}ref$	11.31 · $\eta_{Sp}ref$	11.45 · $\eta_{Sp}ref$	11.45 · $\eta_{Sp}ref$	11.818 · $\eta_{Sp}ref$
% η_{Sp} decrease after first charge	3.99 · $\eta_{Sp}ref$	-0.86 · $\eta_{Sp}ref$	4.60 · $\eta_{Sp}ref$	5.61 · $\eta_{Sp}ref$	4.45 · $\eta_{Sp}ref$	4.09 · $\eta_{Sp}ref$	2.80 · $\eta_{Sp}ref$
% η_{Sp} decrease after second charge	7.18 · $\eta_{Sp}ref$	7.58 · $\eta_{Sp}ref$	4.52 · $\eta_{Sp}ref$	6.23 · $\eta_{Sp}ref$	5.51 · $\eta_{Sp}ref$	6.05 · $\eta_{Sp}ref$	4.29 · $\eta_{Sp}ref$
% η_{Sp} decrease after third charge	x	x	x	x	x	x	2.50 · $\eta_{Sp}ref$
% η_{Sp} decrease in total	10.88 · $\eta_{Sp}ref$	6.78 · $\eta_{Sp}ref$	8.91 · $\eta_{Sp}ref$	11.49 · $\eta_{Sp}ref$	9.72 · $\eta_{Sp}ref$	9.89 · $\eta_{Sp}ref$	6,97 · $\eta_{Sp}ref$

Comparing the % η_{Sp} decrease after the first charge for test X5-1 to X5-4 reveals that X5-2 did not provoke a scission effect. The decrease in P4 dosage prevented a drop in molecular weight of the polymer chain. The first charge of X5-4 had the largest impact on the η_{Sp} value due to the addition of P11. The pH change in test X5-3 resulted in a larger drop in η_{Sp} for the first charge compared to the reference test X5-1.

Comparing test X5-1 to X5-4 for the second charge unveils that the higher dosage of P4 for test X5-2 is detrimental for the η_{Sp}. However this scission effect is comparable to test X5-1 despite of the lower dosage of P4 added. Test X5-1 and X5-4 both induced a significant scission effect. Test X5-3 is able to have the least impact on changing the η_{Sp}value for the second charge.

Test X5-2 scored the best regarding total % η_{Sp} decrease followed up with the pH approach of test X5-3. Addition of P11(test X5-4) did not aid the post initiation strategy as it did more damage to the molecular weight than the standard test X5-1. Smaller dosages of P4 and implementation of pH increase have a positive influence on the molecular weight of the polymer.

Test X5-5 to X5-7 show that X5-7 had the best result for the first charge of P4 thanks to the lower dosage. Tests X5-5 and X5-7 showed a similar scission effect despite a difference in reaction time. This implies that 15 min reaction time is sufficient.

The smaller dosage of P4 in test X5-7 as second charge displays a lower scission effect.

Comparing the overall results for test X5-5 to-X5-7 shows no difference between test X5-5 and X5-6. The reaction time between addition steps have no influence on the scission effect. Test X5-7 scored the best thanks to smaller dosages.

Test X5-2 and X5-7 are the best strategies when preventing scission effect of the polymer chains. Their strategies are similar in which addition of P4 is dosed in small amounts.

The post initiation strategies do not only focus on maintaining the M_w but also aim to reduce the residual monomers. Figure 47 shows the monomer reduction expressed in percentage for each charge and for the total reduction of monomer.

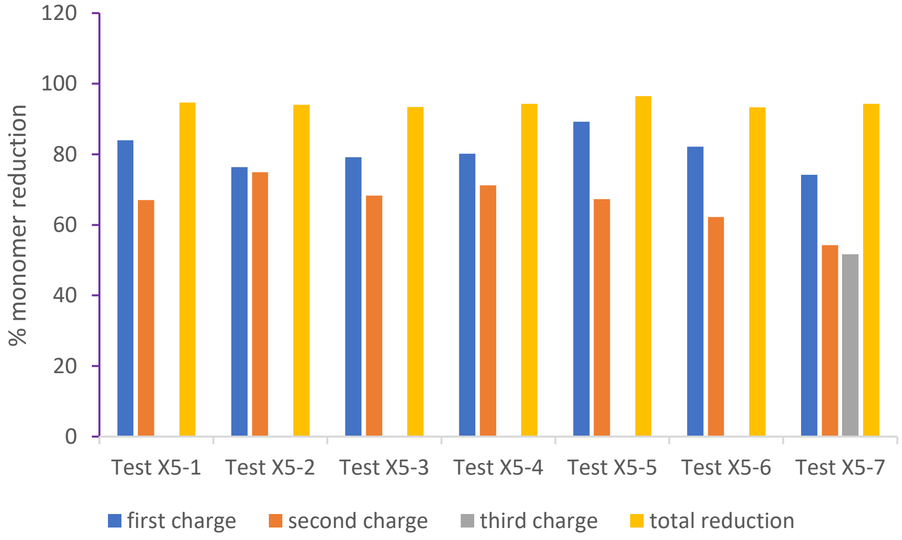


Figure 47: Comparison of monomer reduction for test X5

The first charge has the biggest impact on reducing residual monomer. This is expected because more residual monomer is available for the reaction. Test X5-2 shows a monomer conversion for the first charge that almost matches the conversion for test X5-1, X5-3 and X5-4 despite of the lower dosage of P4. Test X5-1 and X5-3 shows that the pH change did not influence monomer reduction. The addition of P11 in test X5-4 did not influence monomer conversion.

In general all test of experiment X5 did well in reducing the total residual monomer content.

Test X5-2 and X5-7 where able to obtain a good monomer reduction without negatively affecting the molecular weight of the polymer chains. Smaller dosages are effective in preventing the scission effect. Test X5-3 showed that increasing pH level has a positive effect on the molecular weight. Further experiments combining pH increase and small P4 dosages could be examined to find the optimal strategy.

4.1.6 Powder quality evaluation of processing aid X

It is possible that the processing aid with new emulsifier discolours the final product. Thus, a colour test was performed to compare the original recipe to processing aid X. The processing aid powder is added (3 phr) to a PVC formulation (NWGII) to produce a sheet. The results are shown in Table 24.

Table 24: Colour test for influence of emulsifier

	Original recipe (industrial scale)	**Test X1-2**	**Test X1-3**
L	90.92	89.66	89.60
a	-0.19	-0.12	-0.16
b	8.41	10.94	11.00
Yi	15.91	20.78	20.85
Haze	17.32	16.34	17.08

The colour test revealed that the new emulsifier had a small effect on yellowing the powder product as seen by the Yi parameter. This increase is acceptable for Kaneka's standards.

A Brabender gelation test was carried out to evaluate the influence of the emulsifier on the gelation of PVC as shown in Figure 48 and Figure 49. The emulsifier change is compared to the original recipe (lab scale and industrial scale). The loading peak differs between samples but no differences are visible for the minimum and maximum torque values. The final torque is similar as well.

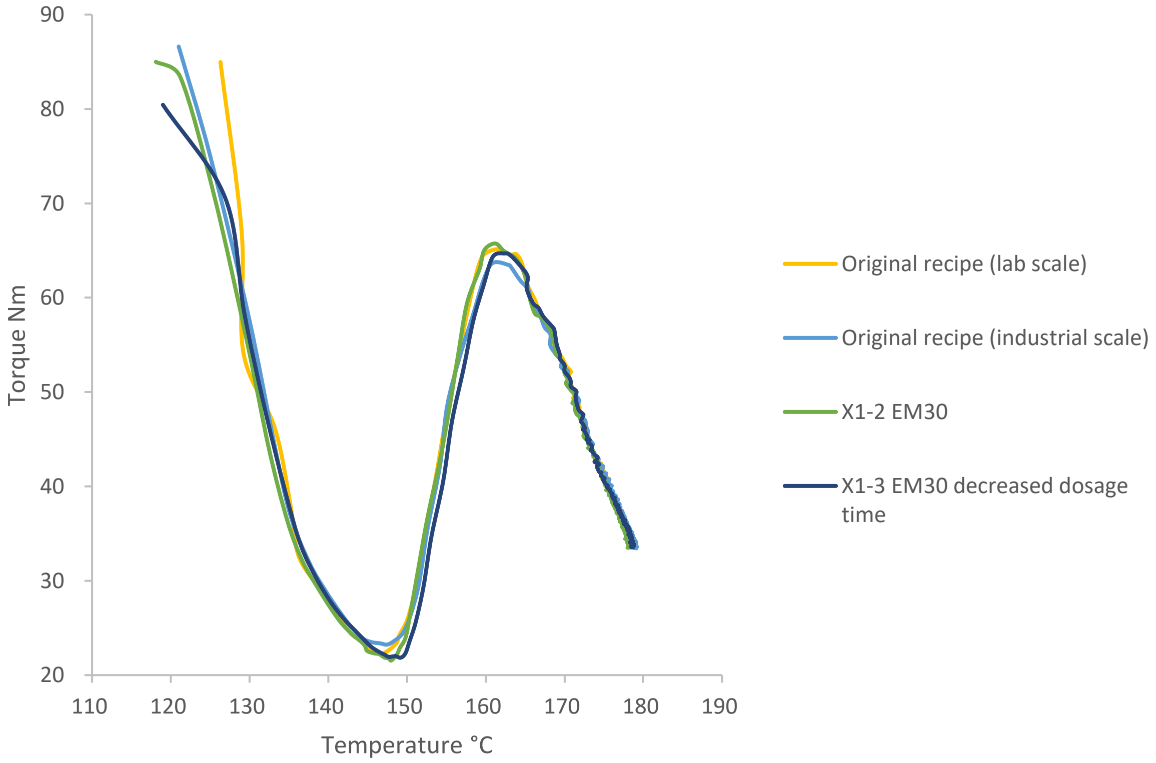


Figure 48: Brabender gelation test, torque (Nm) as function of temperature (°C), to evaluate the influence of emulsifier type

The torque versus temperature graph (Figure 48) shows as similar trend for all the tests. Figure 49 shows no difference in fusion time between the tests.

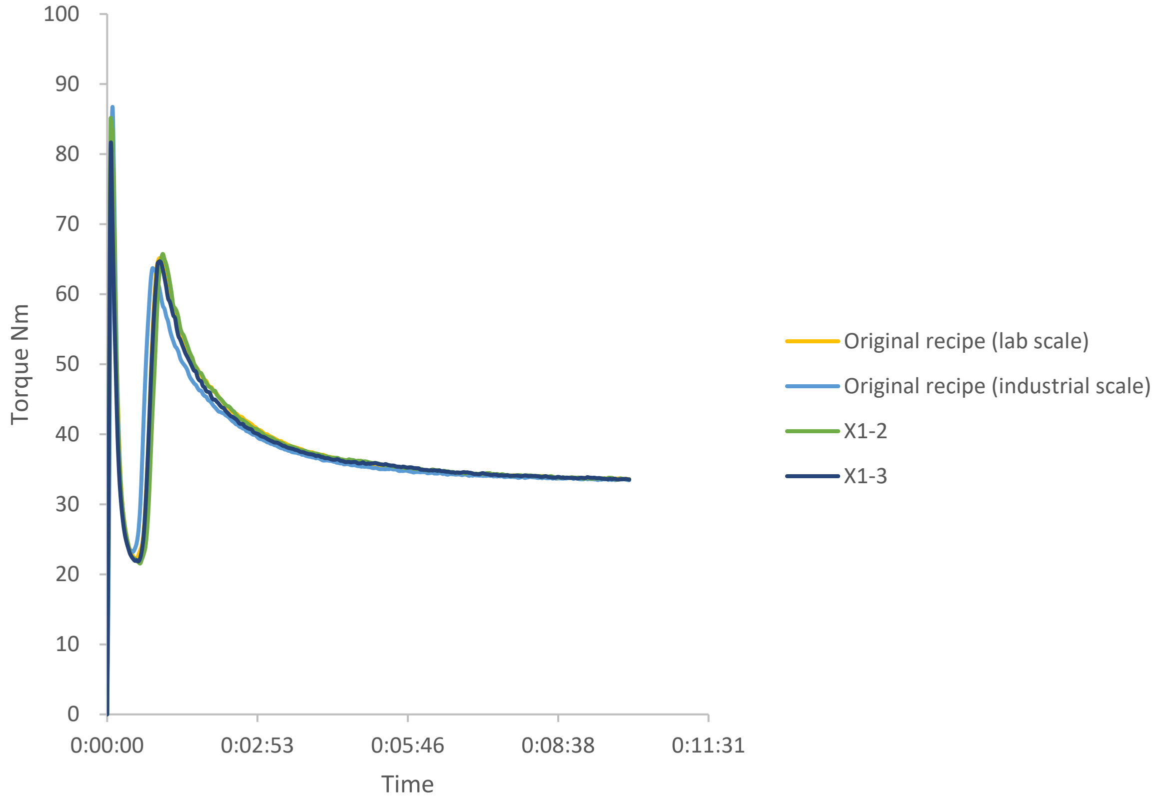


Figure 49: Brabender gelation test, torque versus time, for emulsifier influence

The new emulsifier has no influence on the gelation behaviour of PVC recipe.

A funnel test revealed that the emulsifier improved transport through funnels when compared with the industrial sample. The industrial sample is dried with a different setup resulting in different powder properties. The difference in drying setup explains the differences in funnel test. The lab scale sample could not be tested due to a lack of sample The results of the funnel test are shown in Table 25.

Table 25: Funnel test for emulsifier change

	Original recipe (lab scale)	**Original recipe (industrial scale)**	**Test X1-2**	**Test X1-3**
10mm hits/sec	Not enough powder	3/27sec	0/19sec	0/19sec
20mm hits/sec		0/7sec	0/3sec	0/3sec

The apparent specific gravimetry measurements, shown in Table 26, are comparable to the original processing aid (lab scale). The industrial sample differs due to a difference in dry setup.

Table 26: Apparent specific gravity for emulsifier change

	Original (lab scale)	**Original recipe (industrial scale)**	**Test X1-2**	**Test X1-3**
ASG g/cc	0.363	0.384	0.343	0.346

The new emulsifier has similar powder properties as the original recipe.

4.1.7 Conclusion of optimization of processing aid X

The goal of the emulsifier switch was to maintain current properties of processing aid X. Both latex and powder properties of the processing aid are maintained. The new emulsifier has a higher concentration which means less storage capacity is needed and transport costs are reduced.

An increase in solid content was tested without compromising heat removal and mixing. An increase in solid content increases the viscosity. An increase in solid content from 44 % to 46 % was performed without causing viscosity problems. Attempts to reach a solid content of 48 and 50 % was inhibited due to the undesired increase in viscosity. Further tests, between 46-48 % SC, need to be conducted to find an optimal point. The batch production rate increased with 5 % per batch.

A setup change influences mixing patterns which could affect polymerization and the properties of the processing aid. Scale formation is monitored as well. The alternative setup increases scale formation but did not disturb the other properties of the processing aid. The scales were monitored for all experiments. The scale formation did not surpass the threshold of 2 % set by Kaneka.

Reduction of polymerization time, from 12 hours to 11 hours, was achieved. 11 hours of polymerization time was able to achieve a similar molecular weight to previous tests. The monomer conversion was up to standard as well. The test for 10 hours could not be compared fairly due to temperature changes during polymerization. Extra tests could lead to an optimal polymerization time.

Different post initiation strategies were conducted. The residual monomer was measured through sampling and gas chromatography. The post initiation strategies affect not only the residual monomer content but also the molecular weight of the polymer. The chemicals P4 and P11 are able to react with the polymer chain. Test X5-2 and X5-7 both did well in reducing residual monomers without promoting the scission effect on the molecular weight of the chain. Dosing smaller amounts of P4 is the winning strategy. It gives the P4 time to react with the available residual monomers. When a large amount is dosed inefficient reactions occur such as reaction with other P4 or with the polymer chain. Increasing time in between dosing steps showed no improvements.

The final processing aid X implements the new EM30 with a solid content of 46%. The polymerization time is 11 hours. The post initiation step implements a low dosage P4 addition strategy. P4 should be added 1/3 for the first charge and 2/3 for the second charge with 15 minutes between addition steps.

4.2 DEVELOPMENT OF A NEW GENERATION PROCESSING AID Y

The new generation processing aid Y aims to improve surface finish and density of PVC applications. Different strategies are tested and evaluated using the Brabender, Rheotens and die swell tests. Test Y1 is based on the finalised recipe of processing aid X. Herein the post initiation step was removed in order to increase the molecular weight. Test Y2 blends the latex produced in test Y1 with a processing aid Z. Blending provides a combination of properties. Blending aims to combine the molecular weight of the Y1 recipe with the lower molecular weight of processing aid Z to improve the melt strength. Test Y3 implements different monomers while maintaining the same glass transition temperature as in test Y1. The addition of these monomers may differ in the length of side chains which could influence its properties. In test Y4 a different ratio of monomers is used compared to test Y1 in order to decrease the glass transition temperature. A decrease in glass transition temperature results in higher mobility of the polymer chains that may aid PVC fusion. Test Y5 adds monomer H in order to implement a functional group. The functional group could increase the compatibility with the PVC matrix through reaction. Test Y6 increases tacticity of the processing aid by increasing monomer T. The tacticity increase could influence die swell and melt strength properties. The following tests are produced in multiple reactors therefore small variations in latex properties are present for each test. Multiple reactors are needed to produce enough latex such that testing is possible. The variations between reactors were not significant so that mixing them is allowed with exception of test Y6. Test Y6 was produced in two reactors (Y6-1 and Y6-2). The mixer malfunctioned for one of the reactors which resulted in different latex properties for (Y6-2). The final Y6 product contains 20 % of Y6-2 to ensure enough product is available for the spray dry setup and evaluation tests.

4.2.1 Processing aid X with high molecular weight: test Y1

Recipe Y1 is based on the improved processing aid X. The new emulsifier and increased solid content are maintained during all the tests concerning processing aid Y. Post initiation is excluded to prevent the scission effect in order to increase the molecular weight. The high molecular weight of the processing aid Y1 should increase melt strength and die swell of the PVC formulation considerably. These properties are important for foam applications. Table 27 shows properties such as PS, M_w, η_{Sp}, SC, monomer conversion and scales to compare between test Y1 and processing aid X (X2-2).

Table 27: Comparing PS, M_w, SC, scales and monomer conversion of test Y1 to processing aid X

Parameters	Test Y1	Test X2-2
Post initiation strategy	none	½ P4 with 15 min reaction time
PS (Å)	$3.082 \cdot PS_{ref}$	$3.058 \cdot PS_{ref}$
η_{Sp} (-)	$12.63 \cdot \eta_{Sp}ref$	$11.98 \cdot \eta_{Sp}ref$
SC experimental (%)	44.03	45.36
Scales (%)	0.62	0.22
Monomer conversion (%)	96	99

A similar particle size is obtained for test Y1. The molecular weight is increased for test Y1 as expected. The lack of post initiation results in a higher molecular weight but compromises on monomer conversion. The loss in conversion is visible in the solid content. The 46% solid content was not reached due to lack of conversion. An increase in scales is noticeable but the value does not approximate the threshold value of 2%.

4.2.2 Blending High molecular weight with processing aid Z: test Y2

Processing aid Z is blended with the improved processing aid X (Y1). The blend consists of 20 m% processing aid Z which causes a decrease in η_{Sp} value of the blend.

4.2.3 Monomer composition: test Y3

Addition of monomer B2 is implemented in the recipe for test Y3. The recipe contains monomer M2, B1 and B2. The influence of the new monomer could be related to differences in side chains. The composition of monomer is chosen in such way to obtain the same glass transition temperature as test Y1. The latex properties of test Y3 are compared with test Y1 (see Table 28).

Table 28: Comparing PS, M_w, SC, scales and monomer conversion of test Y3 to test Y1

Parameters	Test Y3	Test Y1
Monomer composition	M2, B1 and B2	M2 and B1
PS (Å)	$3.115 \cdot PS_{ref}$	$3.082 \cdot PS_{ref}$
η_{Sp} (-)	$14.99 \cdot \eta_{Sp}ref$	$12.63 \cdot \eta_{Sp}ref$
SC experimental (%)	44.74	44.03
Scales (%)	0.65	0.62
Monomer conversion (%)	97	96

The change in monomer composition lead to a similar particle size compared to test Y1 but a high molecular weight polymer was obtained. The η_{Sp} value of test Y3 surpassed test Y1. The solid content increased compared to test Y1. Similar scales and monomer conversion is obtained for both tests.

4.2.4 Glass transition temperature decrease: test Y4

Test Y4 focusses on decreasing the glass transition temperature. This is accomplished by changing the ratio of B1/M2. Monomer B1 is increased with 25 % and monomer M2 is decreased with 6.25 %. A lower T_g enables an increase in mobility. This could affect the gelation behaviour. The variation in parameters between test Y4 and Y1 is represented in Table 29.

Table 29: Comparing PS, M_w, SC, scales and monomer conversion of test Y4 to test Y1

Parameters	Test Y4	Test Y1
Monomer composition	$^{B1}/_{M2}$ increase	$^{B1}/_{M2}$
Glass transition temperature	$7 \cdot T_{ref}$	$7.7 \cdot T_{ref}$
PS (Å)	$3.083 \cdot PS_{ref}$	$3.082 \cdot PS_{ref}$
η_{Sp} (-)	$12.27 \cdot \eta_{Sp}ref$	$12.63 \cdot \eta_{Sp}ref$
SC experimental (%)	44.69	44.03
Scales (%)	0.66	0.62
Monomer conversion (%)	97	96

There is no difference in particle size between test Y4 and Y1. The molecular weight of test Y4 did not reach the value for test Y1. The solid content differs but no change in scales and monomer conversion occurred.

4.2.5 Functionality implementation: test Y5

Addition of monomer H to the monomer composition aims to increase compatibility of the processing aid with the PVC matrix through reaction. The functional group of monomer H may lead to an improved gelation behaviour and melt strength. Addition of monomer H will influence latex properties, these are shown in Table 30.

Table 30: Comparing PS, M_w, SC, scales and monomer conversion of test Y5 to test Y1

Parameters	**Test Y5**	**Test Y1**
Monomer composition	B1, M2 and H	B1 and M2
PS (Å)	$3.036 \cdot PS_{ref}$	$3.082 \cdot PS_{ref}$
η_{Sp} (-)	$11.46 \cdot \eta_{Sp}ref$	$12.63 \cdot \eta_{Sp}ref$
SC experimental (%)	44.62	44.03
Scales (%)	0.55	0.62
Monomer conversion (%)	97	96

The addition of monomer H did not influence PS but did decrease its molecular weight compared to test Y1. The solid content is similar to test Y3 and Y4. Scales formation and monomer conversion are analogue to test Y1.

4.2.6 Tacticity increase: test Y6

An increase in addition of monomer T to recipe Y1 enables a tacticity increase that could affect relaxation time and die swell properties. The quantity of monomer T added is tenfold compared to test Y1. The monomers B1 and M2 are kept the same as in test Y1. Results are shown in

Table 31: Comparing PS, M_w, SC, scales and monomer conversion of test Y6 to test Y1

Parameters	**Test Y6**	**Test Y1**
Monomer composition	B1, M2 and T (increased)	B1, M2 and T
PS (Å)	$2.954 \cdot PS_{ref}$	$3.082 \cdot PS_{ref}$
η_{Sp} (-)	$11.62 \cdot \eta_{Sp}ref$	$12.63 \cdot \eta_{Sp}ref$
SC experimental (%)	44.67	44.03
Scales (%)	0.49	0.62
Monomer conversion (%)	97	96

The particle size decreased significantly for test Y6. The molecular weight is also lower in value than test Y1. The solid content is similar to test Y3, Y4 and Y5 and slightly higher than test Y1. Scale formation is decreased for test Y6. The monomer conversion is comparable between both tests.

4.2.7 Evaluation new generation processing aid

An overview of some latex properties between test Y1-Y6 are shown in following figures. There are no latex properties available for test Y2 because test Y2 is the same recipe as Y1 but is blended with processing aid Z in dried powder form. Figure 50 shows that test Y1 does not have the highest M_w value. Test Y3 was able to produce the highest M_w thanks to a composition change and addition of monomer B2. Test Y5 and Y6 have similar M_w values. The M_w will impact the performance of the processing aid on the melt strength, die swell and gelation results of the PVC formulation.

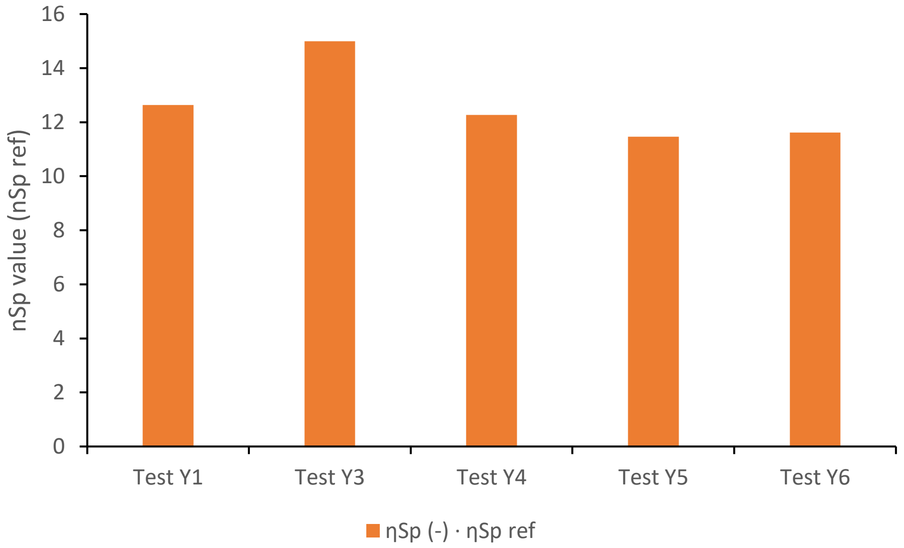


Figure 50: Comparison of η_{Sp} *values (latex) for all processing aid Y tests*

Figure 51 shows a similar trend to Figure 50 with the exception of test Y6. Despite the η_{Sp} values being similar for test Y5 and Y6 the particle size of test Y6 is much lower.

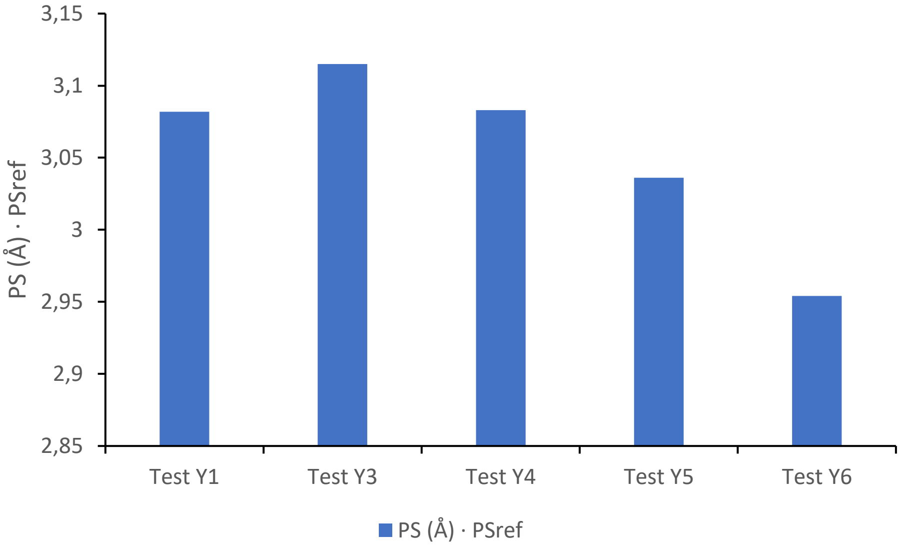


Figure 51: Comparison of PS values (latex) for all processing aid Y tests

The spray dry setup influences the properties of the processing aids. The η_{Sp} values of the dried powder are compared with the η_{Sp} values of the latex (see Figure 52). The differences are not significant with exception of test Y6. This is due to blending of test Y6-1 (80 %) with Y6-2 (20 %) with test Y6-2 having deviating properties.

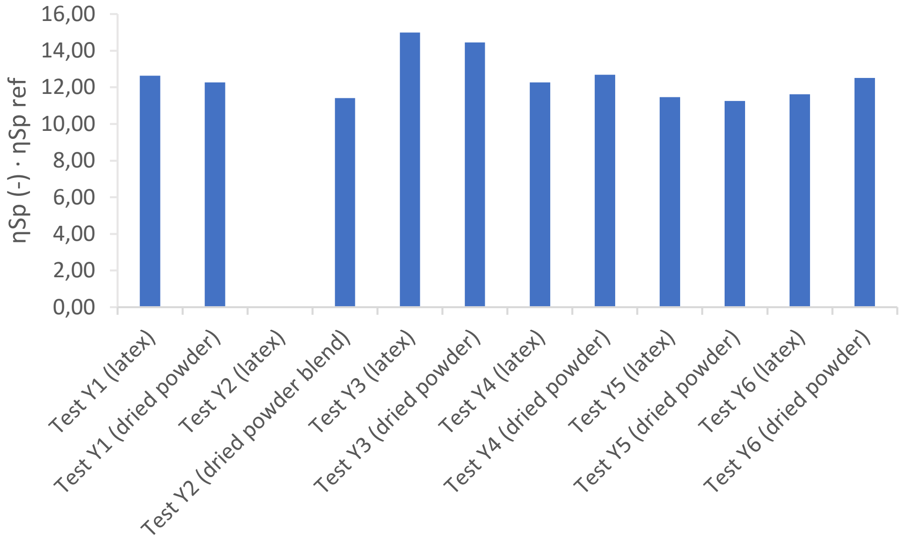


Figure 52: Comparison of η_{Sp} values for processing aid Y (dried powder and latex product)

Tests Y1 to Y6 are added to a PVC formulation to evaluate their melt strength, gelation behaviour and die swell.

4.2.7.1 Brabender gelation

The different Y-tests are tested for their ability to promote PVC fusion. The Brabender gelation test resulted in two plots, Figure 53 and Figure 54. Processing aids U and V are products with good qualities and known for their steady position in the market. These products are measured as well to have a reference point.

The torque versus temperature curve (Figure 53) firstly shows a maximum torque value that undergoes a steep decline until it reaches a minimum. The low glass transition temperature processing aid is expected to be the lowest curve in this interval due to its ease in passing on shear. Yet test Y3 is located at near the middle. The variation in T_g is not noticeable in this interval. The interval surrounding the minimum torque value should show the influence of monomer composition variations. Test Y1 and processing aid X (industrial scale) both have the same monomer composition and should be lying near to each other but Figure 53 shows otherwise. The final torque should reveal a link with the M_w of the processing aid. Even though test Y3 has a high M_w, no significant difference is observed between the tests. A repeat of the test could reveal hidden information. Alterations in dosage, temperature or rotating speed of the mixing blades could results in a Brabender gelation curve that reveals more information.

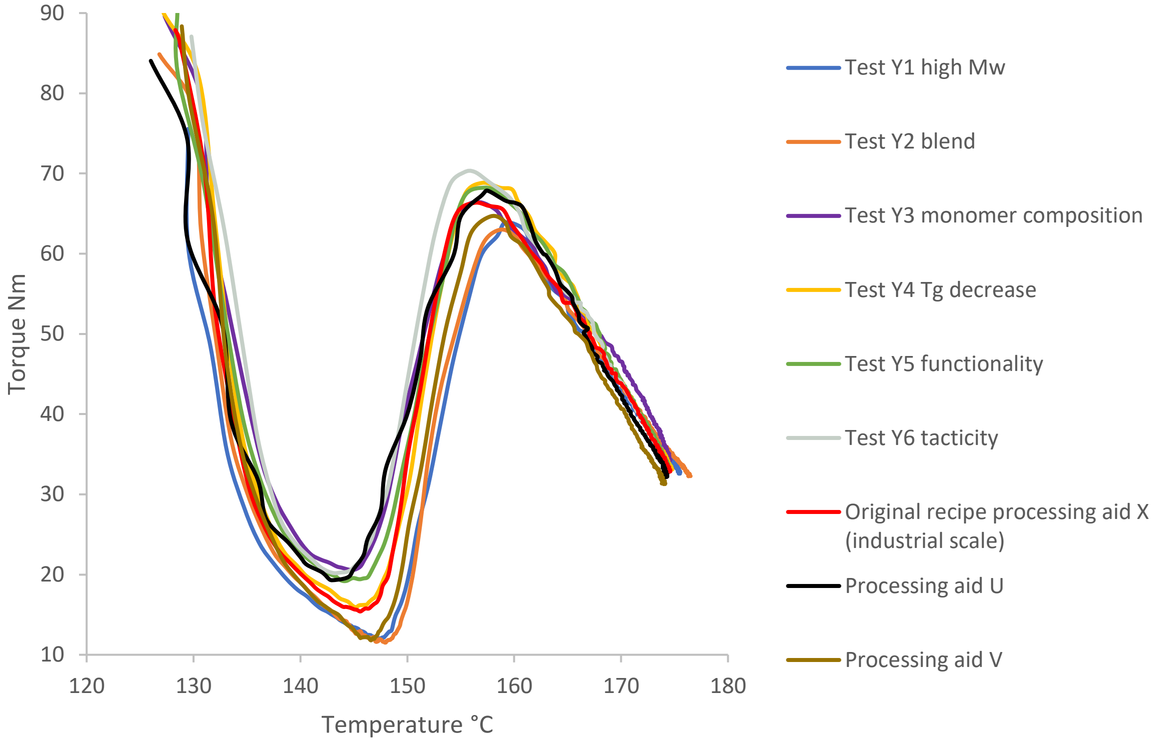


Figure 53: Brabender gelation test, torque (Nm) versus temperature (°C), for processing aid Y

Figure 54 shows a clear difference in fusion time. Tests for processing aid U, Y3, Y5 and Y6 showed the least amount of time needed to start the fusion process. Processing aid X and test Y4 have similar fusion times. The fusion times are longer for processing aid V, Y1 and Y2 increasing steps relatively. Test Y3, Y4, Y5 and Y6 show similar behaviour to the reference samples (processing aid U an V).

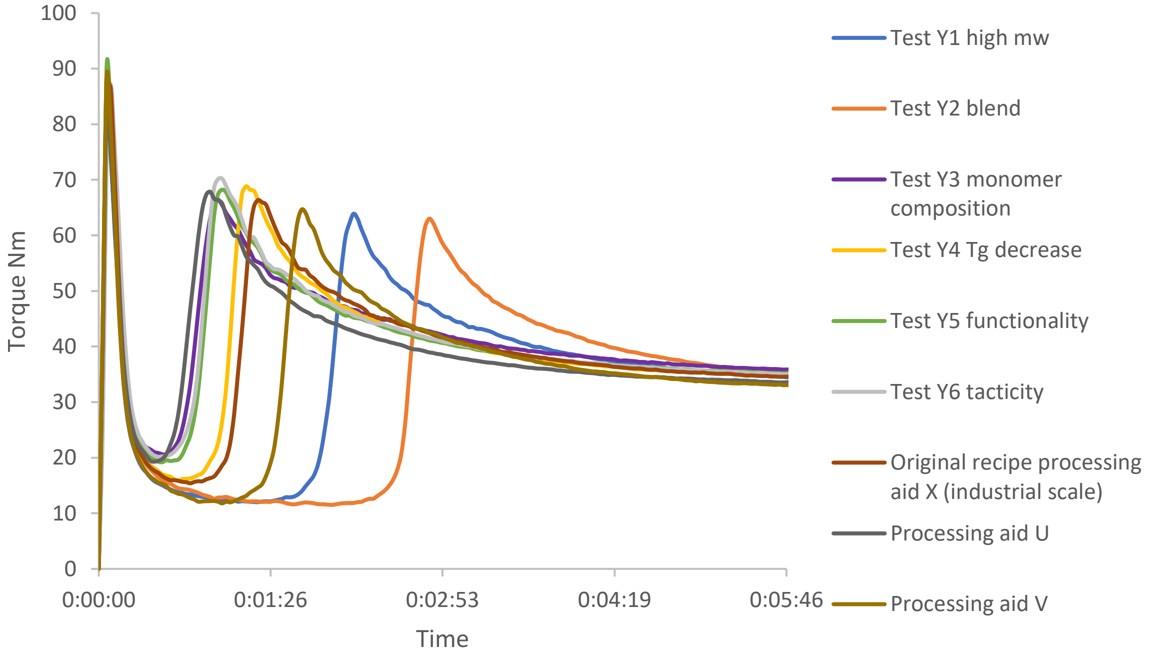


Figure 54: Brabender gelation test, torque (Nm) versus time, for processing aid Y

4.2.7.2 Die swell

The die swell tests for processing aid Y are compared to processing aid U, W and the original processing aid X (industrial scale). Processing aid V could not be compared due to an inaccurate measurement of the η_{Sp} value. The die swell ratio is plotted versus the specific viscosity. The specific viscosity represents the molecular weight of the processing aid used. Figure 55 shows the results of the die swell test.

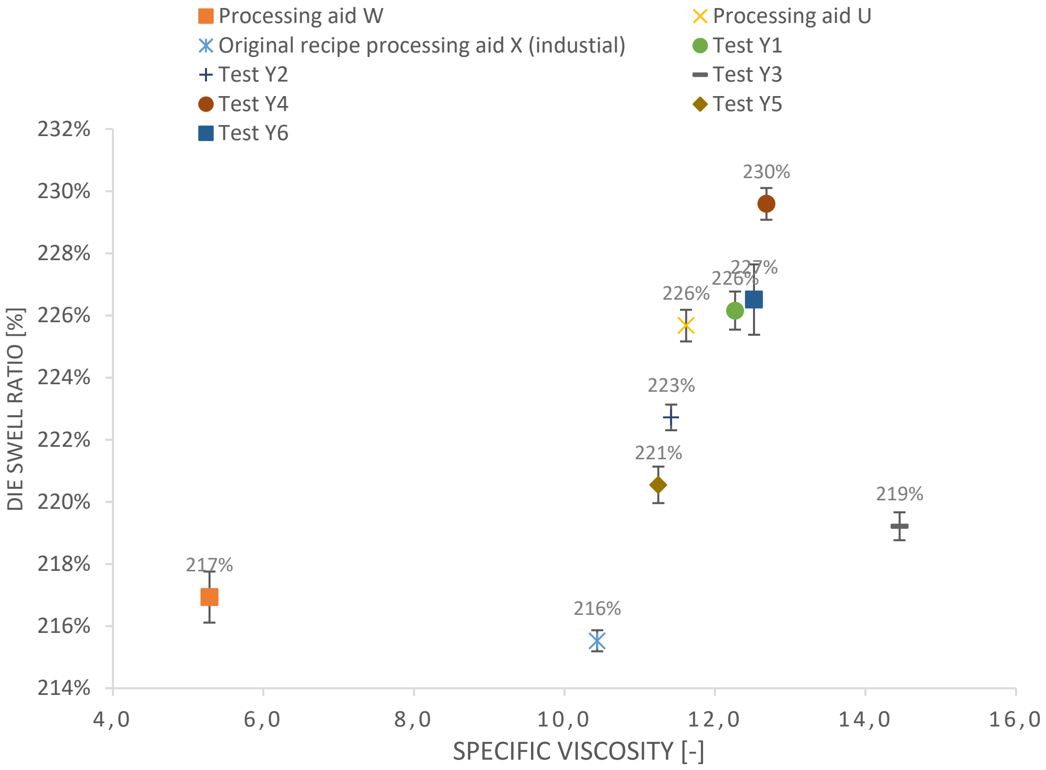


Figure 55: Die swell ratio (%) in function of η_{Sp} for processing aid Y tests

Figure 55 shows that a higher specific viscosity relates to an increase in die swell ratio. The only exception to this trend is test Y3. The differences in specific viscosity have to be taken into account in order to compare the tests. Test Y3 implemented a different monomer in the recipe. The substituent of this monomer could promote more steric hindrance between the chains. The alignment of these polymer chains would be inhibited by the substituent so a large die swell ratio would be expected. Test Y4 which implemented a different ratio of monomers, to lower the T_g, was able to obtain a high specific viscosity and die swell ratio. Test Y1 and Y6 show no significant difference in die swell ratio despite test Y6 implementing a higher tacticity. This suggest that the structure of tacticity created by monomer T does not influence the die swell ratio. Test Y5 was not able to create a high molecular weight nor a high die swell ratio in comparison to other tests of processing aid Y. Test Y2 (blend with processing aid Z) did not achieve the same specific viscosity as test Y1 did. This is due to processing aid Z having a lower M_w than Y1. A small die swell ratio is the result. Test Y1 and Y6 did manage the same die swell ratio as the reference sample processing aid U. Test Y4 managed to acquire the highest die swell ratio.

4.2.7.3 Rheotens

The rheotens test gives information about the melt strength of each formulation. In addition the elongation until rupture can be compared between tests. Figure 56 shows a plot of the pull-off force versus pull-off ratio.

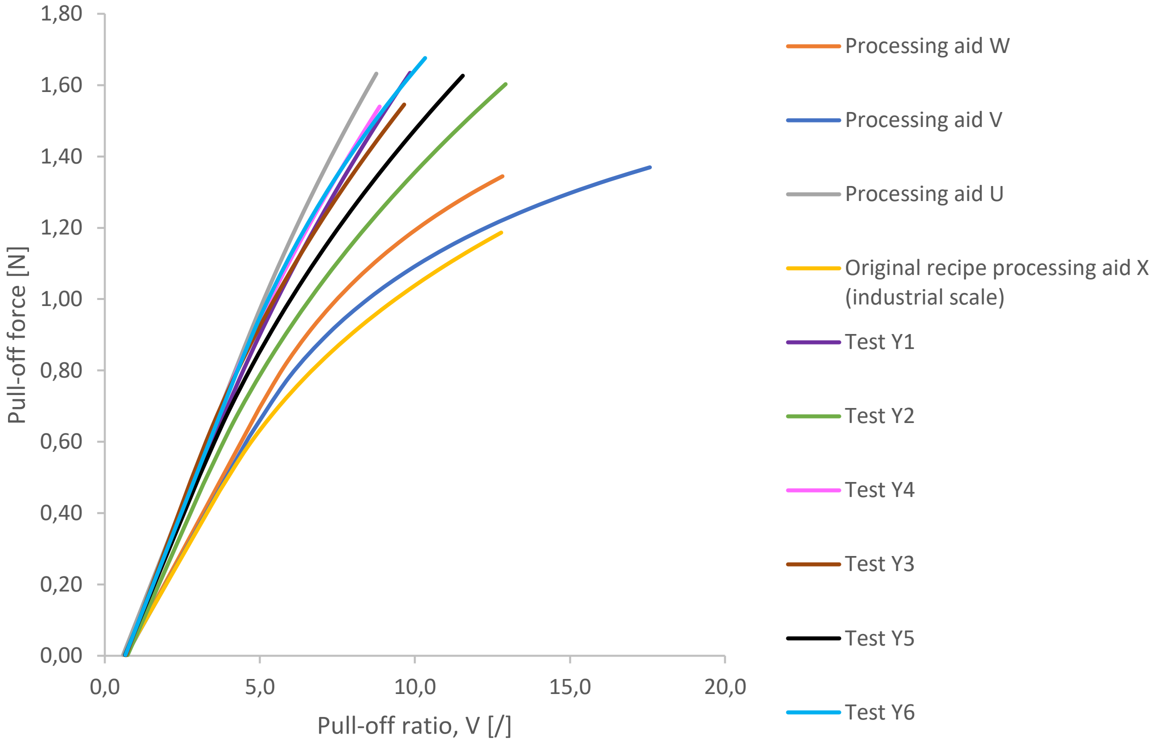


Figure 56: Rheotens test for processing aid Y: Pull-off force versus pull-off ratio

Processing aids U, V and W are used as reference samples. The reference samples succeed in producing a quality PVC foam product. Thus these samples serve as excellent reference points. Processing aid V and W have similar melt strength values. However processing aid V is able to sustain a higher elongation until rupture. Test Y1, Y3, Y4, Y6 and processing aid U have the highest molecular weight. These recipes all have a steep slope and high melt strength. Test Y5 which uses monomer H to incorporate a functional group managed to obtain a high melt strength without having a high molecular weight. The reaction with the PVC matrix ensured a high melt strength. Processing aids V, W and X have lower molecular weights which decreases the slope. The change in monomer composition enables a higher elongation value. Test Y2 has a high melt strength comparable to tests Y1, Y3, Y4, Y6 and processing aid U. The advantage of test Y2 is the higher pull-off ratio compared to previous tests. Test Y2 is blend of 80 % Y1 and 20 % processing aid Z which enables a similar melt strength as Y1 with an increased elongation.

4.2.8 Conclusion of development of new generation processing aid

Test Y1 (M_w increase) is based on the recipe of processing aid X. The post initiation step is excluded to increase the molecular weight. Test Y1 did well in the die swell test. The die swell result is comparable to processing aid U. The fusion time and elongation properties were not comparable to the reference samples.

Test Y2 (blend) has the slowest fusion time and did not excel in the die swell test. However the Rheotens test proves that blending is promising in achieving a high melt strength and pull-off ratio.

Test Y3 (monomer composition) was able to obtain the highest molecular weight. The high molecular weight enabled a high melt strength. The fusion time is similar to the reference samples. Test Y3 was not able to produce a high die swell ratio despite of the high molecular weight.

Test Y4 (T_g decrease) achieved the highest die swell ratio. The high M_w enables a high melt strength but with limiting elongation.

Test Y5 (functionality) did well in the fusion time test. A die swell of 221 % did not reach the 226 % value of the reference sample processing aid U. The rheotens test showed a good melt strength. The elongation before rupture almost matched test Y2.

Test Y6 (tacticity) was capable of achieving the same results as the reference samples for die swell and fusion time tests. A high melt strength was achieved with test Y6.

Test Y4 gave promising results but lacks in elongation capacity. The fusion time of test Y2 does not resemble the reference sample but the die swell and rheotens test are promising. The different tests does not show one clear superior strategy. Further experiments with focus on monomer composition and blending which could result in better die swell, fusion and melt strength properties.

5 CONCLUSION

Optimization of an existing processing aid X is achieved through sequential alterations to the recipe. The objective of these alterations is to obtain an improved production process for processing aid X without changing latex and powder properties.

An emulsifier change from EM15 to EM30 enables a decrease in transport costs. In addition less storage capacity is needed to store the emulsifier. The change did not influence the latex or powder properties of the processing aid.

A solid content increase from 44 % to 46 % succeeded in increasing the batch production rate with 5 % per batch. Tests with solid contents of 48-50 % showed an undesired latex viscosity increase. Further tests with solid contents ranging from 46 to 48 % should be examined in order to ensure an optimal solid content.

Changing the setup (baffles and mixer) of the reactor is done to examine the effect on the recipe. The alternative setup increases scale formation but did not disturb the other properties of the processing aid. The scale formation was monitored for every test and no test surpassed the threshold value of 2 % set by Kaneka.

Reduction of polymerization time from 12 hours to 11 hours was achieved. The M_w and monomer conversion were up to standards. Further tests should be conducted to check if an optimal polymerization time can be reached. The test for 10 hours could not be compared to the other tests due to deviations in the temperature trend of the polymerization.

Different post initiation strategies were tested in their ability to increase monomer conversion with minimal decreasing effect on the M_w. The strategy that dosed the total P4 in smaller amounts was most successful. The increase in time between steps did not impact the M_w nor the monomer conversion. Increasing the pH did reduce the scission effect but further testing should be done to verify the results. A combination of pH increase with smaller dosing amounts could be an interesting test for further research.

Optimization of the production of processing aid X was a success.

Development of a new processing aid Y was researched by producing different recipes. A recipe with increased M_w was achieved through exclusion of the post initiation step. A second recipe blends previous recipe (80 %) with processing aid Z (20 %). The blend aims to combine the properties of the two processing aids. A third recipe changed the monomer composition via addition of monomer B2. This recipe managed to obtain the highest M_w. The fourth recipe, based on the first recipe, changes the monomer ratio to decrease the T_g. The fifth recipe implemented functionality through addition of monomer H. The final recipe increased the monomer T value tenfold compared to the first recipe to increase tacticity.

Interpretation of the die swell, Brabender and Rheotens tests did not result in one optimal recipe. The fourth recipe (decreased T_g) showed promising results for die swell but lacks a high elongation until rupture point. The second recipe (blend) did well in the die swell and rheotens tests but differed in fusion time compared to the reference samples. Further experiments with focus on monomer composition and blending could result in better die swell, fusion and melt strength properties.

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