

Development/optimization of polymer additives

Lénaïc Arnold

Master of Chemical Engineering Technology

Introduction



Kaneka Belgium is a subsidiary company of Kaneka Corporation. The modifier division of Kaneka Belgium produces and develops additives for PVC. Processing aids are **polymer additives** that **strongly improve the processability** of PVC compounds. Processing aids are made via emulsion polymerization as shown in Figure 1. Addition gives control over the PVC melt flow. Acrylic copolymers are known for their excellent properties regarding compatibility with PVC and promotion of fusion as shown in Figure 2 and Figure 3. These flexible long polymers entangle with the short stiff PVC chains as shown in Figure 2. Ultra high molecular weight **acrylic polymers enhance PVC foam applications** such as lower density and improved surface finish. Molecular weights ranging from 1 – 10 million g/mol are common. The processing aids are made with **free radical emulsion polymerization** and form a latex. A schematic overview of emulsion polymerization is shown in Figure 1. **A latex is a medium dispersed with colloidal polymer particles**. The medium is often water. Processing aids provide melt strength and elasticity which are important for foam applications. The PVC formulation consists of many additives (Figure 4) and is processed via an extruder (Figure 5)

Objective



The target of this thesis is twofold. First objective is to **improve the production of an existing processing aid recipe**. Second objective is the **development of a new processing aid**. **Manufacturing improvements** of the recipe are desired **without changing properties** on foam applications. Development of a new processing aid capable of **increasing surface finish and decreasing foam density of PVC products** is the target. Properties of the final foam product are the result of **melt strength, melt viscosity, die swell and PVC fusion** induced by the chemical composition of the processing aid.

Method & Material



Emulsion polymerization experiments are performed with variations in recipe. In order to evaluate properties of the formed latex, samples are analysed for molecular weight (determined by solution viscosity), particle size distribution, solid content, viscosity, residual monomer, etc... When these properties remain constant or within the desired range, the altered recipe is tested in an end application. The PVC formulation with altered processing aid is tested on its melt rheology behaviour. Shear viscosity (Contifeed), die swell and Brabender gelation test yield information about the PVC fusion process.

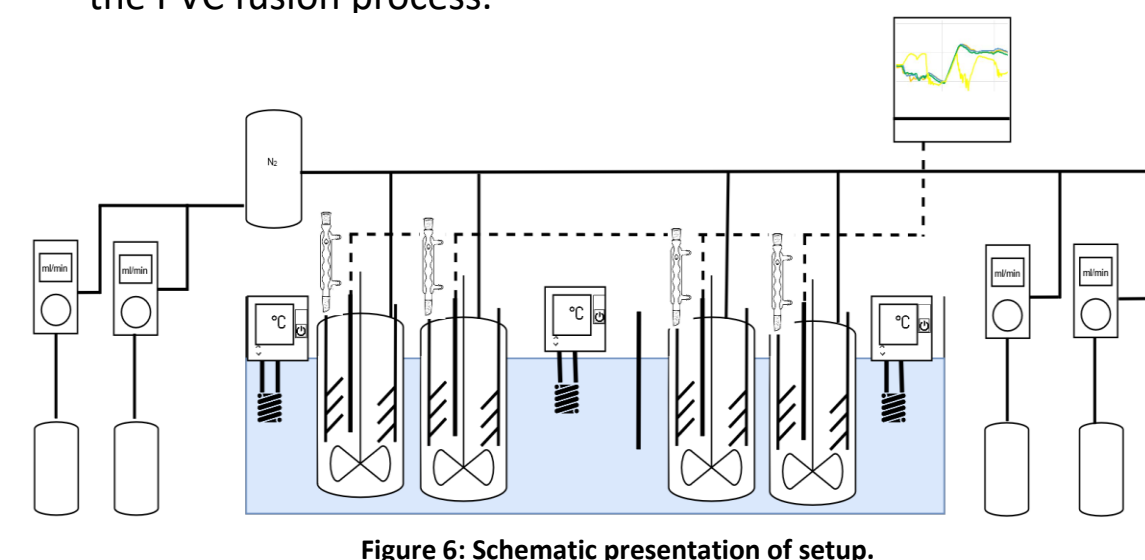


Figure 6: Schematic presentation of setup.

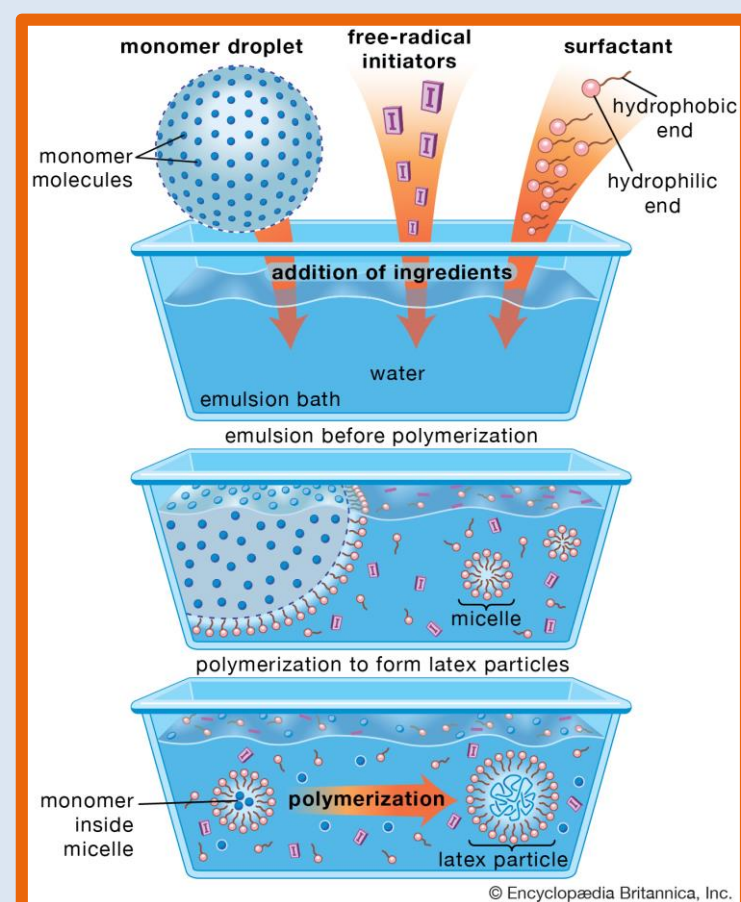


Figure 1: Schematic representation of emulsion polymerization [1].

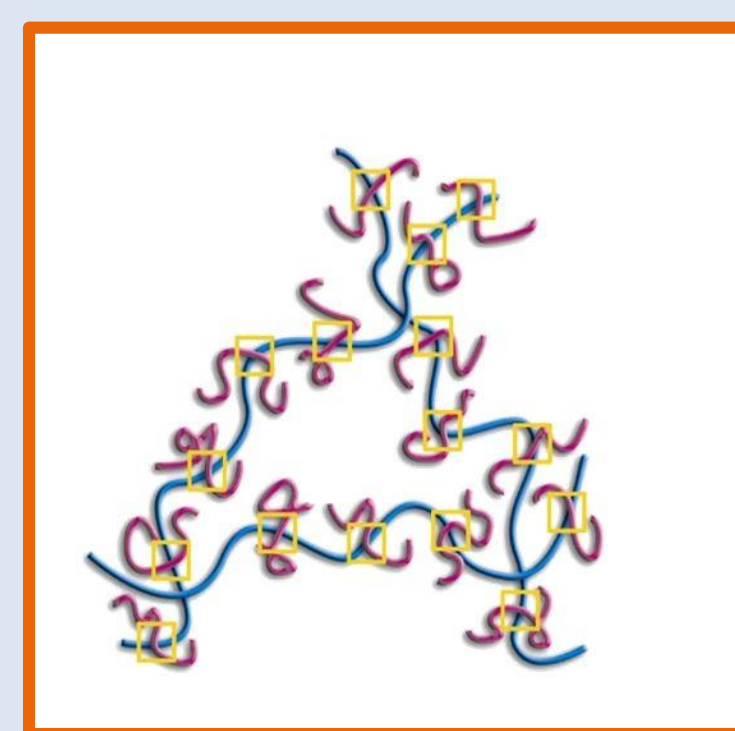


Figure 2: Processing aid (long flexible blue chains) entangled with PVC (short stiff purple chains) [2].

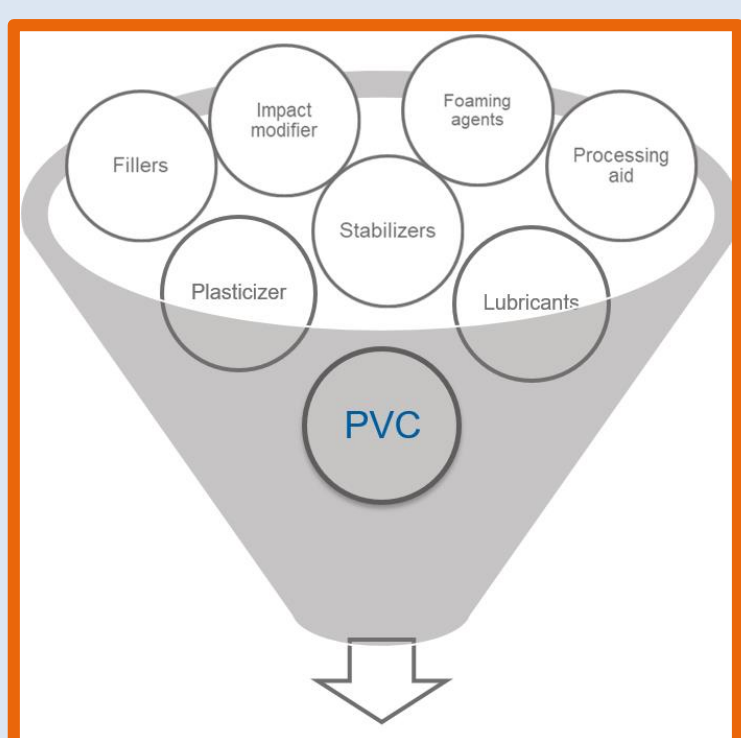


Figure 4: PVC formulation consists many additives such as fillers, impact modifiers, foaming agents, plasticizer, lubricants and processing aids.

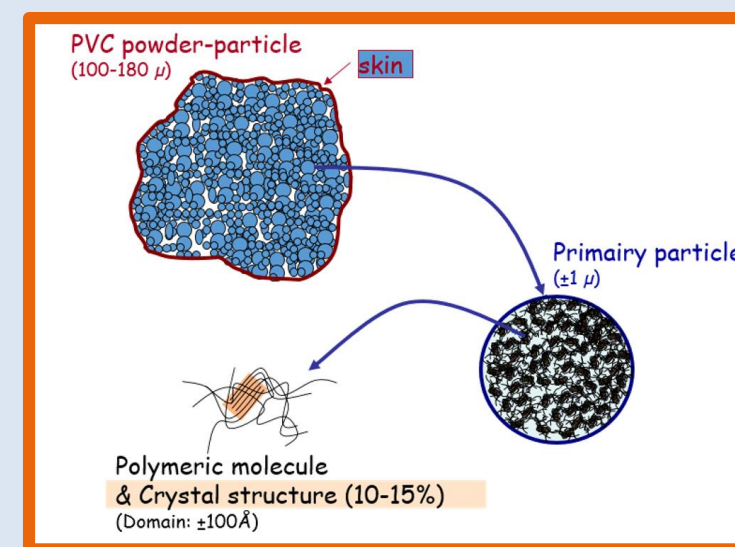


Figure 3: Processing aid promotes fusion of PVC resin. Breakdown of agglomerates into primary particles [2].

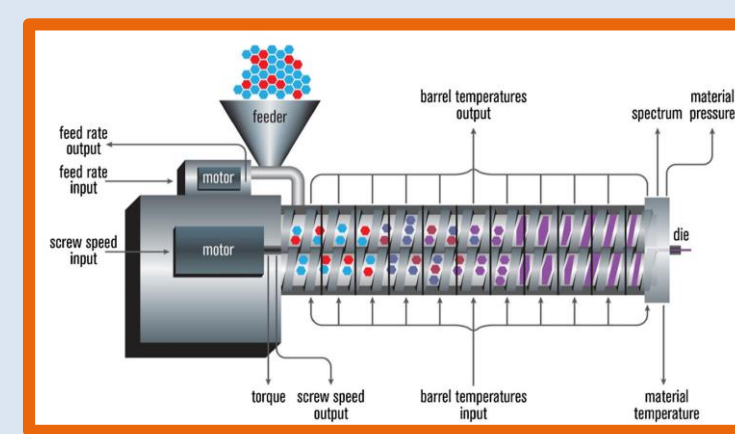
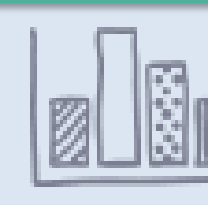


Figure 5: Overview of extrusion process [3].

Results



Processing aid X: improve production

Test X1: A change in emulsifier (EM15 → EM30) enables less storage capacity and vehicular transport.

Test X2: A solid content increase (44 % - 46 %) to increase production rate.

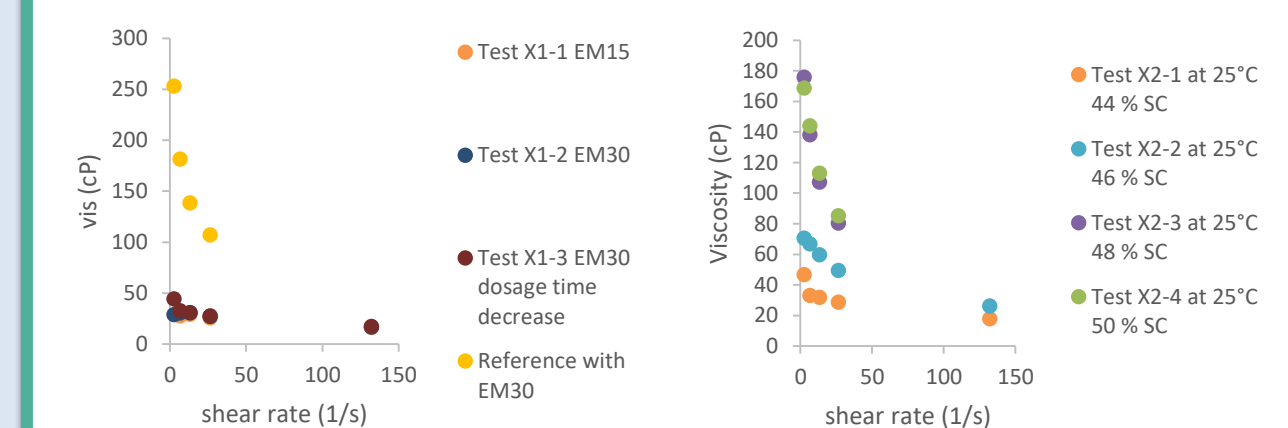


Figure 7 and 8 show latex viscosity tests, viscosity (cP) as function of shear rate (1/s) after altering the recipe.

Test X3: A setup change increased scale formation. The threshold value of 2% was not surpassed.

Test X4: Reduction of polymerization time from 12, 11 and 10 h¹ was tested while maintaining monomer conversion and Mw.

Test X5: Post initiation strategies were tested to reduce scission effect on the polymer chain while maintaining monomer conversion.

Processing aid Y: development

Strategy	Test Y1 Mw increase	Test Y2 Blend	Test Y3 Monomer composition	Test Y4 Tg decrease	Test Y5 Functionality	Test Y6 Tacticity
----------	------------------------	------------------	--------------------------------	------------------------	--------------------------	----------------------

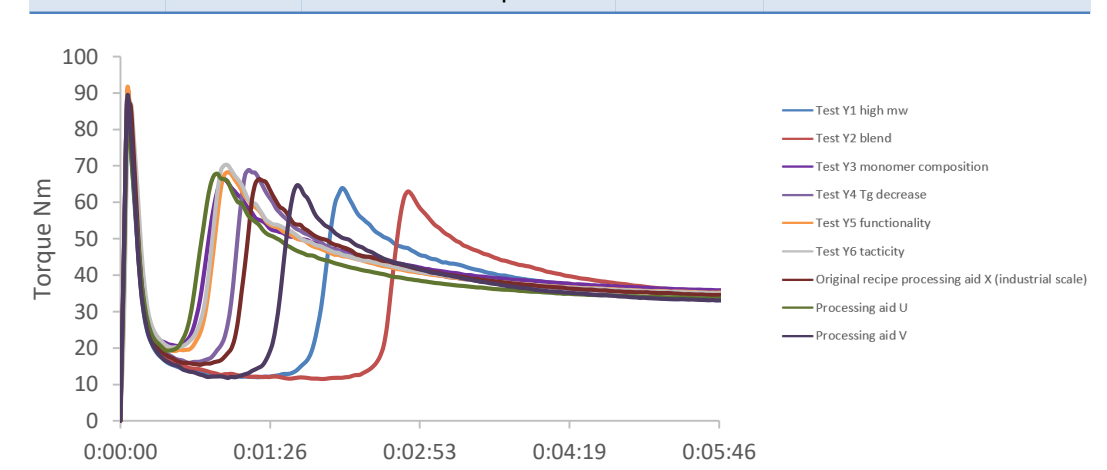


Figure 9: Brabender test: torque (Nm) as function of time

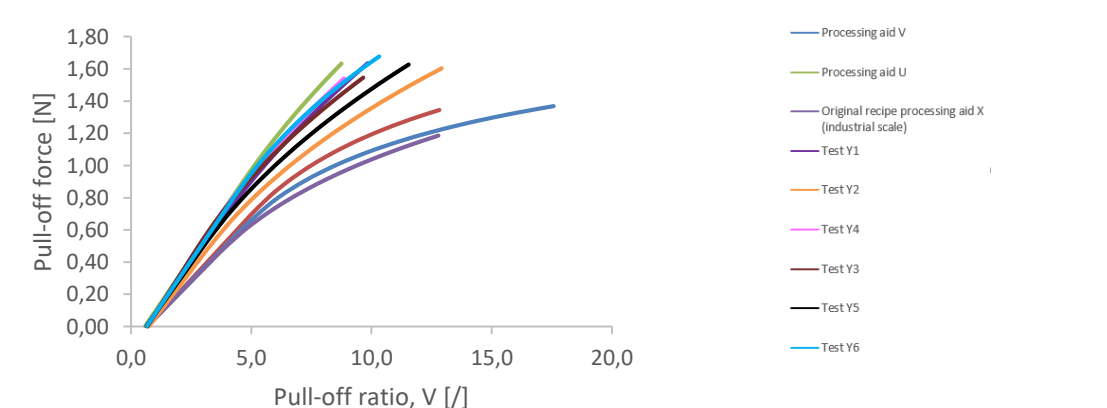


Figure 10: Rheotens test: pull-off force (N) as function of pull-off ratio (-)

Conclusion



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. The EM change leads to less storage capacity necessary and less vehicular traffic. The solid content increase leads to a 5 % increase in batch production rate. A decrease in polymerization time while still achieving the desired molecular weight and desired monomer conversion is obtained. This results in an increase in production rate. An improved post initiation method was developed to prevent scission of the polymer chains. This strategy lead to a high molecular weight product while still reaching desired monomer conversion.

Development of processing aid Y implemented a wide range of variations to the recipe of the improved processing aid X. Test Y2 is a blend of processing aid Y1 (80 %) and processing aid Z (20 %). Test Y2 achieved a desired melt strength and pull-off ratio. Test Y4 (Tg decrease) obtained a die swell ratio of 230 % thanks to its high melt strength. Test Y4 did not achieve the same pull-off ratio as test Y2. The optimal processing aid induces a high melt strength, high pull-off ratio and die swell ratio in order to produce low density PVC applications. Further research can be carried out with focus on blending and monomer composition changes.

¹ The polymerization time differs from depicted values in order to protect sensitive information

Supervisors / Cosupervisors: Dr. ir. Sofie Sannen and Prof. dr. ir. Jozefien De Keyzer