Operational Safety of the Polymerization Reactors

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Abstract

At SGL Composites, S.A., the formation and constant safety awareness aims to make known the right procedures, as well as to develop and adjust the employees' behavior. However, it is also necessary to conduct a detailed risk analysis to implement the right specific control instrumentation, in order to correct all the possible perturbations so the stationary state can be achieved as soon as possible. In the scope of *FM Global*, it was found necessary to evaluate the polymerization reactors' zone to comprehend if there is any possibility/probability, even slightly, of explosion or *runaway,* despite the existing control instrumentation. Therefore, after studying the polymerization area and the chemical reactivity of the polymerization system – reaction kinetics and an adiabatic system simulation –, it was determined and analyzed the worst-case scenarios that are possible to occur in the polymerization process, using the software *Aspen Plus* and the Pilot Unit of the firm. Hereupon, a critical review of the control instrumentation was proceeded and it was proposed to be considered the installation of some devices, such as a level sensor, a bubble separator, a filter, among others. Lastly, it was possible to verify that SGL Composites, S.A. respects all the Process Safety Management umbrella relevant aspects, always considering the safety, the quality and the environment.

Keywords: acrylonitrile, vinyl acetate, polyacrylonitrile, acrylic fibers, acrylonitrile free-radical copolymerization

Introduction

ACRYLONITRILE

Acrylonitrile was first synthetized in 1893 by the French Chemist Ch. Moureau, although it had at the time no significant technical or commercial applications until the late 1930s. Just before the second world war, IG Farben industry [1] introduced a synthetic rubber based on a copolymer of butadiene and acrylonitrile and, during the same period, in USA, projects related to nitrile rubber received special support due to their strategic importance. This way, acrylonitrile became recognized as a monomer of commercial importance and, in 1950, the acrylonitrile demand began to increase due to the acrylic fibers. [2, page 3]

Nowadays, all acrylonitrile is produced by direct catalytic conversion of propene, oxygen (as air) and ammonia, and its world production is approximately 5 million tons per year. In addition, acrylonitrile is, today,

1

an industrial intermediate used predominantly in the production of polymeric materials: acrylic fibers accounts for 60%, while the plastics accounts for 25% of world consumption. [2, page 3]

POLYACRYLONITRILE

Polyacrylonitrile (PAN) was first synthetized by Dr. º Hans Fikentscher and Dr. º Claus Heuck, in 1930, in the laboratories of IG Farben, in Ludwigshafen, a German company that patented its polymerization method. However, since the polymer was insoluble in most common solvents, the substance was considered to be unusable. Even so, the investigations continued and, in 1931, Dr. º Herbert Rein, also from IG Farben but in Bitterfeld, discovered that PAN, obtained from a sample when visiting the Ludwigshafen plant, could be dissolved in the ionic liquid 1-Benzylpyridinium chloride and converted into fibers. Later in 1942, the same chemist discovered a better solvent for the polymer – dimethylformamide, a discovery that allowed to develop the spinning process to produce fibers and films. Due to the second world war, the investigations were interrupted and the polymerization process was not used in an industrial scale. [3]

Despite the interruption, when the war time was over, in 1946, DuPont introduced the large-scale production of PAN to produce the Orlon fibers and patented the wet-spinning process. Later, the Dormagen Bayer company introduced the production of Dralon fibers and patented the dry-spinning process. [3]

Throughout the production of PAN, it was realized that among its main features is the versatility of being able to be chemically modified and thus to produce a wide variety of materials: [3]

- Fibers;
- Carbon Fibers;
- Adhesives;
- Engineering plastics;
- Superabsorbent polymers.

This polymer is essential for textile and high technology applications due to its special properties, such as thermal stability, high strength and modulus of elasticity, UV degradation stability, non-fusible and chemical resistance. Therefore, the main application is in textile industry, while the second one is related to the production of carbon fibers. However, there are other minor applications which use is growing, such as: [3]

- Fibers for cement reinforcement;
- Filtration membranes;
- Awning fabrics and outdoor applications;
- Oxidized PAN fibers for thermal and acoustic insulation;
- Anti-flame fibers;
- Felts' manufacture for hot air filtration.

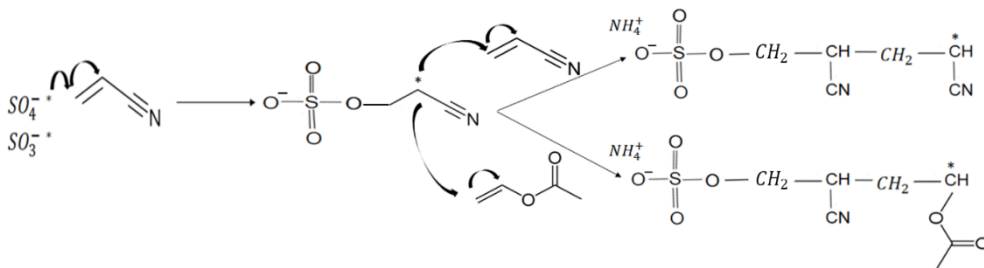## Acrylonitrile Polymerization at SGL Composites, S.A.

The acrylonitrile polymerization at SGL Composites, S.A. is based on a free-radical reaction of the acrylonitrile and vinyl acetate. [4] This exothermic reaction takes place in an aqueous medium and occurs continuously under quasi steady state conditions with an 88% conversion. The feeding aqueous

solutions are previously prepared and the redox system consists of ferrous sulfate (catalyst), ammonium persulfate (main initiator) and sodium bisulfite (chain-transfer agent that regenerates the oxidized form of the ferrous ion and, hence, acts simultaneously as an initiator). To keep a constant pH, a sulfur acid filtered solution is used. [5, page 1] The polymerization reactional mechanism is as follows: [6, page 12]
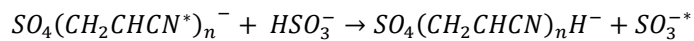
Initiation

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-*} + Fe^{3+}$$

$$HSO_3^- + Fe^{3+} \rightarrow SO_3^{-*} + Fe^{2+} + H^+$$
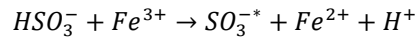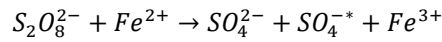
Propagation [1]

Concerning the termination step, free-radical polymer chains can terminate by three mechanisms:

Chain Transfer (more likely to happen) [6, page 11]

$$SO_4(CH_2CHCN^*)_n^{\ -} + HSO_3^- \rightarrow SO_4(CH_2CHCN)_nH^- + SO_3^{-*}$$

Radical Recombination [1]

$$SO_4CH_2CHCN^{*-} + SO_4(CH_2CHCN^*)_{n-1}^{\ -} \rightarrow SO_4(CH_2CHCN)_nSO_4^{\ 2-}$$

Disproportionation [1]

$$SO_4CH_2CHCN^{*-} + SO_4CH_2CHCN^{*-} \rightarrow SO_4CH = CHCN^- + SO_4CH_2CH_2CN^{\ -}$$

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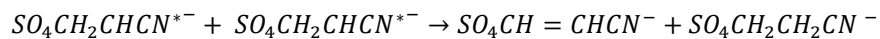
[1] Mechanisms shown and explained in a presentation at SGL Composites, S.A. on 04/2018

Moreover, the reactional mixture is continuously agitated by a propeller-type stirrer, describing an axial movement. While the reaction occurs, the polymer suspension is expelled out of the respective reactor by overflow. In the reactors discharge tube is added the inhibitor solution to prevent the reaction to last. [5, pages 1 and 2] The reactional temperature is controlled by the cooling water that circulates in the cooling jackets of the reactors, in a closed circuit and with a high flow.

In addition, after the reaction step, the slurry proceeds to a column so the unreacted monomers can be separated. This is followed by filtration and washing steps and, after that, the polymer is pelletized, dried, ground and finally stored for later spinning. [7, page 836] To produce PAN fibers after obtaining the polymer, there are those who apply the dry-spinning process, but SGL Composites, S.A. follows the Mitsubishi Rayon example and applies the wet-spinning process using dimethylacetamide as solvent.

Experimental Section

To diagnose the probability of runaway or explosion at the polymerization reactor, the worst-case scenarios were analyzed. To do so, the software *Aspen Plus* was used to understand the behavior of the reactional mixture towards the flow variation of the feeding solutions, while in the Pilot Unit it was studied the behavior of the reactional mixture towards the cooling and agitation loss, the lack of inert media, the pH variation and the unexpected introduction of unreacted MB. These deviations were evaluated through the reactional mixture temperature.

ASPEN PLUS

After establishing the stationary state, the worst-case scenarios were simulated as sensibility analysis and it was possible to understand how a manipulated variable impacts the variable to be studied. The reactor here simulated was a 12 m^3 one and, after running the known stationary state, it was obtained an overflow temperature of 62,0°C. The reactional mixture temperature was measured at the overflow.

PILOT UNIT

While in *Aspen Plus* a 12 m^3 reactor could be defined, in the Pilot Unit the experiments were carried out in a 5,7 L reactor (consequently, the industrial conditions had to be adjusted to this volume). To do so, the following experimental setup was prepared:
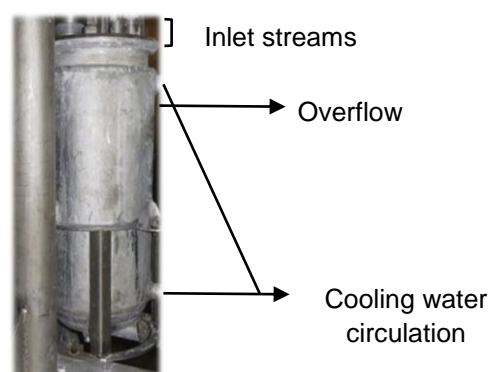

Figure 1. Experimental setup

and a check-list was completed. Besides, the materials were yet prepared, bearing in mind the following information:

Table 1. Necessary quantities to prepare the solutions

	m_{solid} (g)	Total (g)
CD	1592	80000
CE	404	80000
CB	1800	80000
HS	200	19000
AN+AV	11383 (AN)	14376
	1013 (AV)	

Besides the preparations above, it was also necessary to weight the following quantities from the previous preparations, during the reactor's pre-start:

Table 2. Required quantities of CB and HS solutions for the reactor's pre-start

	m_{liquid} (g)
CB (1:1000)	103
HS	26
DIW2	3975

Results and Discussion

Concerning *Aspen* simulations, from all the variations of the feeding flows, the variation of the MB feeding flow is the one that impacts the reactional mixture temperature the most (Figure 2) – the temperature of the reactional mixture decreases with the MB feeding flow increasing and vice-versa. In fact, if there are more monomers reacting, there are more monomer radicals forming, which means that more chains are growing at the same time. However, the residence time remains, so each chain does not grow as much and, thus, the final polymer chains are smaller. This results in polymeric chains with lower molecular weight. The energy released is lower than the usual and, consequently, the temperature decreases.

Regarding Pilot Unit experiments, the worst-case scenarios with more impact on the reactional mixture temperature were the agitation loss, the cooling loss and the unexpected introduction of unreacted MB – when each condition was tested, the reactor inner's temperature increased infinitely and uncontrollably and the reactional mass even solidified. In case any of these worst-case scenarios happens industrially, all the control loops of the reactors zone actuate automatically and have the right indicators and alarms to warn the operators of what is happening at the time. Besides, all the operators well know the right procedures in case an intervention is needed.

The figures Figure 2 and Figure 3, presented below, are an illustration of one of the four simulations completed in Aspen and one of the 6 experiments done in the Pilot Unit, respectively.
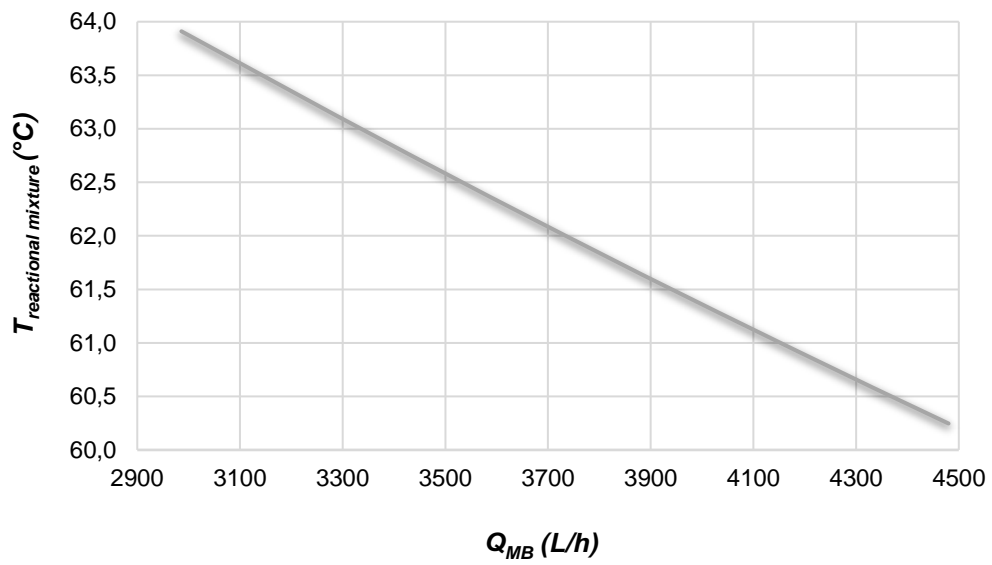
Figure 2. Reactional mixture temperature dependence on MB feeding flow
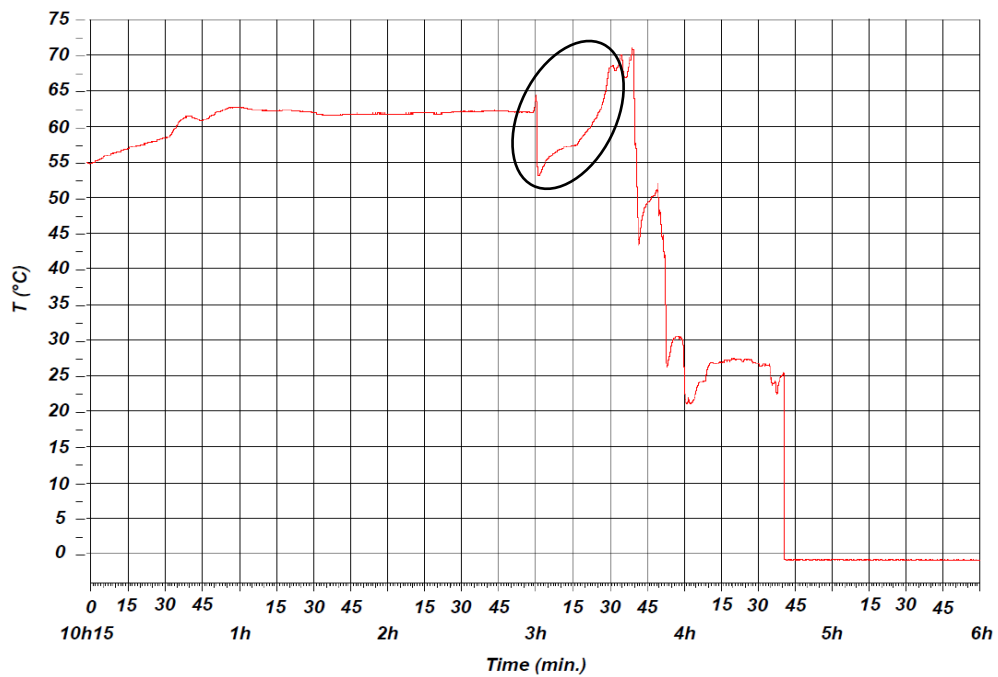

Figure 3. Impact of the unexpected introduction of MB on the reactional mixture's temperature

After testing all the worst-case scenarios to understand the reactor's behavior, the most common anomalies and the existing control instrumentation were analyzed so some improvements could be proposed. Briefly, and knowing the improvements made over time, the implementations proposed were:

- a rupture disk in the polymerization reactors; [8, page 2]
- a manual self-cleaning filter connected to the overflow; [9, page 2]
- an obstruction detector in the overflow;
- a level sensor near to the DSF entrance; [10, page 3]
- a bubble separator before the flowmeters of the reactors' feeds;
- a second measurement system.

Conclusions

In the scope of FM Global, this dissertation was directed to the polymerization reactors in order to study the occurrence probability of explosion or runaway. This part of the thesis was based on computational simulations and experimental work.

Regarding the computational simulations, the software used was *Aspen Plus*, *Polymers* template, and the deviations triggered were just related to the variation of the reagents feeding flow. By these results, it was witnessed the temperature varies with the variation of any reagent feeding flow, but CB. However, the variation of MB feeding flow has a different impact on the reactional mixture temperature than the variation of CD and CE feeding flows: in MB case the temperature variation is linear, while in CD and CE cases the temperature does not change with any flow variation. This impact difference might be related to the fact that CD and CE are present in faster reactions (initiation and/or termination), while MB is the principal reagent during propagation (a reaction that takes up almost all the free-radical reaction time). Nonetheless, it cannot be forgotten that, although in reality the adjustment of the manipulated variables is automatic, the possible controller lag and the possibility of an operator intervention are not considered, so the differences between the results returned by the software and the real-life results are to be expected. Even though it was confirmed that, so far, the existing control loops and the used controllers, as well as the room operators' training and experience, have proved to be able to prevent a nefarious occurrence, such as a runaway, the controller response can be improved to avoid the "human error". Returning to the results, despite changing, almost all temperature variations are within the alert limits – bigger MB feeding flow variations might result in unacceptable temperatures; however, those MB feeding flow values are unlikely. Summarizing the computational simulations, there is no reason to be threaten by any variation of reagents feeding flow. There is no probability of explosion or runaway: no result was alarming and it was confirmed that SGL Composites, S.A. has the necessary control instrumentation to a correct automatic adjustment and the required equipment to alert the operators of the anomalies that are occurring at the time.

Concerning the experimental work, it could be concluded that the pH increasing, pH decreasing and the lack of inert media do not affect the reactor safety. But, the pH variation scenarios affect the product specification. Actually, during the pH increasing experiment, the NSP was sent to measure: 0,164, while the central value is 0,175. Concerning the agitation loss, cooling loss, adiabatic system and the unexpected introduction of unreacted MB scenarios, these affect the reactor safety and are hard to control since the reactional mixture solidifies in minutes and its temperature increases infinitely. Even so, accidents are avoided because, meanwhile, the reactor is immediately stopped and cleaned out – no one lets the reactor to reach its maximum. Additionally, and regarding the existing instrumentation, it was once more confirmed that SGL Composites, S.A. has the necessary equipment to alert the operators of the anomalies that are occurring at the time. Summarizing the experimental work, it is necessary to be vigilant of any system alteration but still, nefarious occurrences are prevented, at least any one triggered by the scenarios here simulated.

The process instrumentation was critically reviewed and some proposals were made to contribute to the overall process safety and to increase the "intrinsically safe" components.

Summing all up, there is no need to be threaten about a possible explosion or runaway, at least considering the operating procedures, the operators' training and experience and the existing control instrumentation. However, a progress that can be made gradually over time is the improvement of the controllers' response, decreasing its slowness that sometimes may require the intervention of an operator.

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