

Increasing Safety by Shifting Semi-Batch Polymerizations into Semi-Continuous Production

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Shifting from discontinuous to continuous (BtoC) processes is one of the most studied topics in the current chemical engineering research mainly because it implies a huge impact on safety due to the strong reduction of the reactor size (which leads to intrinsically safe processes).

The aim of this work is to carry out a high viscosity, high monomer content (70% w/w) emulsion tetrapolymerization reaction in a series of Continuously Stirred Tank Reactors (CSTRs).

Emulsion polymerizations are usually carried out in semi-batch (SB) reactors, by dosing a mix of micelles swollen with unreacted monomer (which can be called “premix”) on a water-based buffered solution. The reaction is highly exothermic thus a good temperature control can be maintained in an industrial reactor using long dosing times.

The proposed BtoC procedure is quite simple, and it is based on the total accomplishment of three main constraints: 1) process productivity must be increased with respect to the SB recipe; 2) reactors workup must be reduced; 3) no loss of product during the start-up phase of the continuous system (this constraint also includes avoiding runaway reactions triggering). The approach suggests to: 1) divide the SB recipe in two main phases; 2) start-up the series of CSTRs following the first part of the SB recipe; 3) go to continuous by activating a pump to transfer the content of the first reactor in the second one; 4) fill the second reactor of the series following the second part of the SB recipe; 5) go to continuous by unloading the content of the second reactor in the final workup reactor. Such an approach was tested with a recipe of industrial interest, based on butyl acrylate. The experimental setup was carried out with a battery of 2 CSTRs, 5 pumps, and a tank for the final product. Multiple samples were collected overtime and analyzed, tracking free monomer content and particle size. From this study, we found that the process started up using the proposed BtoC procedure reached a steady state which was not acceptable from a product quality point of view. Anyway, the continuous process could be carried out for a limited amount of time (this means that it was possible to run a semi-continuous process) by optimizing dosing times and reactors volume. Under such conditions, it was possible to run a semi-continuous synthesis without loss of product due to the start-up phase, in smaller and easier to control reactors than the semi-batch ones.

Keywords: high viscosity; emulsion polymerizations; industrial scale optimization; runaway reactions; batch to continuous procedure.

1. Introduction

Polymerizations are still today reactions of great interest, considering their importance in both industrial and research sectors. Since decades, these two environments have shared a common target: developing continuous processes for polymerizations (Alarcia et al., 2004). The advantages brought by a continuous process over a batch or semi-batch option are several: increase of productivity, higher products quality, reduction of reactors volume, enhanced process safety and so on. Nevertheless, shifting a polymerization process in such a way is not a simple task: these reactions are characterized by high exothermicities, fouling issues, phase inversions and industrial recipes composed by several steps, depending on the specific process considered. Particularly, this work focused on emulsion polymerizations. Several studies have been carried

out on this specific topic, proposing a series of continuous reactors setup concepts and case studies (Alarcia et al., 2004; Goikoetxea et al., 2011; Pauer, 2018). Recently, also studies on mini-reactors manufactured with a 3D-printer have been done (Bettermann et al., 2018), highlighting the advantages of working with very small reactors.

In this framework, one of the most challenging aspects of synthesizing an industrial latex via emulsion polymerization in a continuous system is the monomer content: the high viscosity related to a high monomer content leads to several complications. Indeed, most of the current literature works have showed applications of continuous reactors for latexes with monomer content well below 50% w/w.

In this work, a simple batch to continuous (BtoC) procedure (where “continuous” means “in a series of Continuously Stirred Tank Reactors, CSTRs”) suitable to synthesize a high viscosity, high monomer content (70% w/w) emulsion tetrapolymer was proposed and tested at lab-scale.

The validation of the proposed approach was carried out in an experimental workstation composed of 2 CSTRs that worked under transient state. We called this specific setup as pseudo-continuous process. This choice is related to the fact that the final latex must respect narrow quality standards to accomplish the market requirements. In this sense, the most crucial property was the particle size: for this reason, the proposed system could work under a limited amount of time.

2. Industrial Case Study: Semi-batch Recipe

The object of this work was to propose a procedure to perform an emulsion polymerization process in a continuous operating mode. We referred to a target product named Acr910, which can be obtained by an emulsion polymerization of acrylate monomers, such as butyl-acrylate (BA), methyl-methacrylate (MMA), pure acrylic acid (AA) and 2-Hydroxyethyl acrylate (HEA). This reaction has been already deeply studied and analyzed in a previous work by Copelli et al. (2019). Table 1 reported all the substances involved in the recipe.

Table 1: Components of Acr910 latex (amounts referred to a desired laboratory scale productivity of 2.4 kg).

Substance	Initial Load (RO) [g]	Monomer Mixture (MO) [g]	Initiator 1 Solution (CO) [g]	Initiator 2 Solution (CR) [g]
Water	260.3	274.8	108.5	54.2
Buffer	1.1			
Emulsifier		50.6		
Initiator WP			28.9	
BA		1482.4		
MMA		90.4		
AA		10.8		
HEA		36.2		
Initiator PP				1.8

The standard synthesis required four different mixtures to be prepared: RO (initial reactor load), MO (stable emulsion of water, emulsifier and the four monomers involved in the recipe), CO (solution of water and principal initiator acting in the continuous phase – WP) and CR (solution of the secondary initiator acting inside the growing polymer particles, PP) (Copelli et al., 2019).

Such mixtures are involved into the Acr910 synthesis according to the following procedure: 1) loading of the reactor with the RO solution; 2) reactor thermal conditioning until an operating temperature of about 80-82 °C is reached; 3) one shot dosing of about 1/2 of the total CO solution; 4) starting of the dosing of both MO and the remaining amount of CO under an isothermal temperature control mode (end of phase 1 of the SB recipe); 5) when the dosing of both MO and CO is finished, activation of a waiting time of about 1 h (batch time); 6) starting of the dosing of the CR solution (duration about 15-30 min, end of phase 2 of the SB recipe); 7) waiting time of about 1 h and final treatments (conventionally considered out of the recipe phases).

3. Batch to Continuous Procedure

We chose to fulfil the following constraints to design an effective batch to continuous (BtoC) procedure (the manufacturing of a good with the same market quality requirements of the standard semi-batch option is tacit):

- increasing productivity with respect to the SB recipe;
- reducing reactors volume with respect to the SB recipe;
- eliminating whatever loss of product during the start-up procedure (without undergoing thermal loss of control).

Before proposing a BtoC procedure, several design factors must be solved: 1) Identification of the number of required continuous reactors; 2) Identification of a control loop strategy for the liquid level inside the reactors;

3) Identification of a temperature control strategy (that is, isothermal or isoperibolic) where the Proportional-Integral parameters should be dynamically adapted to address for the best control strategy in the different phases of the process.

In this work, we proposed an experimental setup based on 2 Continuously Stirred Tank Reactors (CSTRs), installed in series. The choice of this strategy perfectly fitted the proposed SB recipe (ideally constituted by two separated phases), and it was realistic for an eventual full-scale configuration. As reactors, two small-scale options were investigated:

- Synthesis workstation Easymax™ (Mettler Toledo), 400 mL of maximum volume capacity;
- Synthesis workstation Optimax™ (Mettler Toledo), 1000 mL of maximum volume capacity.

Concerning the level control, we used the observed virtual volume (the visible reacting mixture level indicated into the reactor) to calibrate the peristaltic pumps dedicated to ensure the continuous operating mode. To handle the several feeds required, 3 volumetric pumps were used for MO, CO and CR injections, and 2 peristaltic pumps were operated to either move the reaction mixture from R1 to R2 or empty R2 in the final workup vessel. The choice of peristaltic pumps is due to the fact that the reaction mixture is sensible to mechanical stresses. Hence, a peristaltic pump is capable of moving such substances without compromising their stability and properties.

Regarding the temperature control in the synthesis workstations, the system is provided with a dynamically adaptable PI controller, allowing for a versatile and automatic temperature control and monitoring.

After being solved all the design issues, the following BtoC procedure was proposed:

- 1) SB recipe, detailed in paragraph 2, was divided in two main phases (that is, Phase 1 – P1: steps from 1 to 4; and, Phase 2 – P2: steps from 5 to 6);
- 2) the series of CSTRs was started up according to the steps detailed in P1;
- 3) the first reactor started to operate under a continuous mode when the chosen setpoint level was reached and the first peristaltic pump was activated to transfer the content of the first reactor in the second one (from this time onward, in the first reactor there was a continuous dosing of MO and CO according to required amounts to fulfil the productivity requirements);
- 4) the second reactor of the series was started up following the steps detailed in P2;
- 5) the second reactor started to operate continuously when the setpoint level was reached and the second peristaltic pump started to unload the content of the second reactor in the final workup reactor (from this time onward, in the second reactor there was a continuous dosing of reacting mixture coming from reactor 1 and CR).

In order to verify the applicability of such BtoC procedure, the latex exiting from either reactor 1 or 2 was tested by determining the following properties: Brookfield viscosity (25 °C), final Butyl Acrylate content, particle size (average diameter), Peel Adhesion (Steel 20 min), Quick Stick (Steel), Shear (Steel) (15x20 mm) (these tests were carried out according to the corresponding ASTM standards: D 3330/D 3330M; D6195 – 03; D 3654/D 3654M – 02).

4. Results and Discussion

As previously reported, two different synthesis workstations were used to validate the proposed BtoC procedure:

- Easymax 402 (400 mL maximum capacity);
- Optimax (1000 mL maximum capacity).

Referring to constraints a) and b) reported in paragraph 3, we decided to introduce two different dimensionless intensification factors: the Productivity Intensification Factor (*PIF*) and the Workup Reduction Factor (*WRF*), whose definitions were reported in Eq(1) and Eq(2), respectively.

$$PIF = \frac{F_{out,1}}{V_{prod,SB}/t_{proc,SB}} \quad (1)$$

$$WRF = \frac{V_{prod,SB}}{V_1} \quad (2)$$

Particularly, $F_{out,1}$ was the volumetric flowrate exiting from the first reactor of the CSTRs series, [mL/min]; $V_{prod,SB}$ was the total latex volume produced using the SB recipe, [mL]; $t_{proc,SB}$ was the total time required for the SB synthesis, [min]; and, V_1 was the setpoint volume in the first reactor of the CSTRs series, [mL].

The syntheses conducted within the EasyMax 402 workstation were carried out by testing very strict operating conditions, that is, high *PIF* and *WRF*.

The first test performed (Test 1) had PIF=5.3 and WRF=12; that is, a MO and CO dosing rate equal to about 25 [mL/min] was used. The contact time within the first reactor (when the filling transient was expired) was around 8 [min]. The main aim of this test was to understand whether this contact time was sufficient to make the reaction possible without triggering runaway phenomena. Whereas this solution had been found to be investigable, this would have led to a very strong process intensification.

Figure 1 reported both reactor (blue line) and jacket (red line) temperature within the first EasyMax 402 reactor. The tracks of the second reactor were not present as the test was interrupted before the transfer.

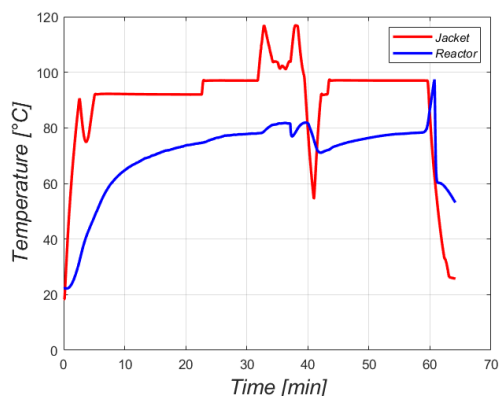


Figure 1: Test 1. Temperatures profiles in the first reactor.

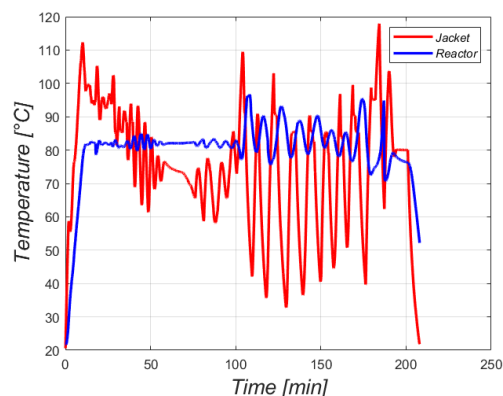


Figure 2: Test 2: Temperatures profiles in the first reactor.

By observing Figure 1, it is possible to note that after about 36 [min] the initial CO load was introduced into the reactor; while, at about 40 [min], the dosage of both MO and CO was started. At the very beginning of this dosage, there was a sharp drop in the reactor temperature compared to the set point value (which was 82 [°C]). This drop in temperature continued until 42-43 [min], then the temperature in the reactor began to rise slowly; until, at 59 [min], a strong thermal runaway was triggered with a temperature rise above 96 [°C], uncontrolled boiling and foaming followed by a leakage of the reactant mass from the reactor head. The reaction was stopped by inserting a quenching solution of water and inhibitor. This experimentation highlighted a very important aspect of the process under analysis: too short contact times led to strong accumulation within the system and cannot be used (for obvious safety reasons).

After such results, it was decided to relax the hypothesis of process intensification planning a second test (Test 2) with PIF=2.6 and WRF=12; that is, a MO and CO dosing rate equal to around 12-13 [mL/min]. The contact time within the first reactor of the series was 16 [min].

Figure 2 showed the thermal trace within the first reactor of the series. After about 27 [min] the dosing of MO and CO began. From that moment on, strong disturbances were observed in the reactor temperature trace (blue curve): medium intensity oscillations persisted and gradually tended to increase in amplitude. On several occasions it was necessary to intervene in the temperature control action manually bypassing the control parameters initially entered ($K_p = 10$, $K_i = 150$ [s], standard parameters for organic mixtures) to maintain the set point value (82 [°C]). After about 40 [min] pumps were activated, emptying the first reactor and filling the second one. The temperature fluctuations continued to increase in amplitude up to values such that incipient boiling of the mixture made impossible to continue the experimentation. The reactor was therefore quenched by injection of water and inhibitor.

At the conclusion of these two experimental tests, the following points of attention emerged: 1) the peristaltic pumps used for transferring the reacting mixture from the first to the second reactor and, then, the final workup vessel were not adequate as the flow / level control was extremely poor; 2) the temperature control parameters needed a tuning able to manage the strong variations in heat capacity / global heat transfer coefficient that occurred during the syntheses (see fluctuations in the temperature).

To address the first criticality, it was decided to increase the effective reaction volume up to 500-600 mL of reacting mixture: in this way the unavoidable level fluctuations experienced during the first two syntheses could be contained. As regards the second criticality, it was decided, using the information provided by the calibrations carried out on the initial load and the final reacting mixture, to change the parameters of the temperature controller whenever there was a significant change in the heat capacity of the mixture: in particular, at the start-up of the first reactor one works with the optimal parameters for aqueous systems ($K_p = 22$, $K_i = 150$ s), then one passes to the parameters for organic mixtures ($K_p = 10$, $K_i = 150$ s).

In the second series of tests, the configuration used to study the continuous process consisted of:

- 2 Optimax 1001 synthesis stations, with 1 L maximum capacity reactors;

- 1 5 L finished product collection flask equipped with a cooling system;
- 2 peristaltic pumps for transferring the latex from the first to the second reactor and from the second reactor to the third collection flask;
- 3 volumetric pumps for loading MO, CO and CR solutions within reactors 1 and 2.

The recipe used is the same of the Easymax 402 workstation, with a level per reactor maintained around 500 mL in the third test (Test 3) and 600 mL in the fourth (Test 4). This choice aimed to achieve an adequate mixing efficiency. Higher volumes would have led to potential stagnant phases within the reactive environment. This setting, however, introduced the need for a precaution on the stirring system of the first reactor (in the second, given the low conversions, no precautions were taken): the anchor selected to ensure good mixing during the continuous phase, did not allow a good temperature control during the start-up. The reason is linked to its geometry which, given its thickness, did not allow the thermocouple of the synthesis station to contact with the mixture that constituted the initial load. The temperature control during the start-up phase is an essential element for the success of the reaction, for this reason the stirring of the reaction mixture was started using a propeller and, then, we carried out a change of stirrer (to anchor) once the start-up phase was over. This operation, which took times between 60 and 80 [s], required an opening of the reactor head, with loss of information on the temperature. For this reason, a fictitious temperature drop, linked to this operation, appeared in the thermal traces. However, the timing of this operation was fast enough to avoid remarkable changes in the outcome of the synthesis.

Using the above formulation, two experimental tests were carried out: Test 3 (PIF=1.8 and WRF=4.8) and Test 4 (PIF=1.8 and WRF=4). The required volumetric productivity was 2400 [mL], with an active volume for each reactor equal to 500 [mL] and 600 [mL] respectively. Figure 3 reported the thermal traces of Test 3 for the first reactor of the series.

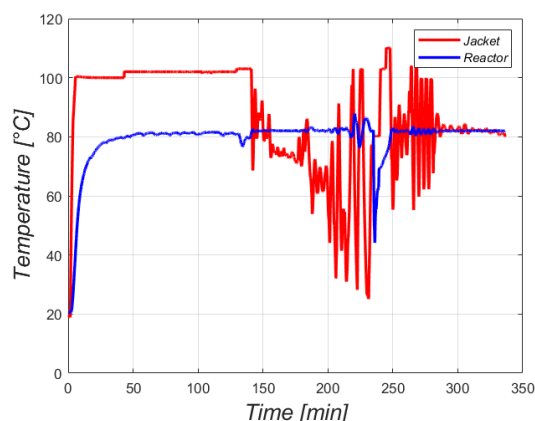


Figure 3: Test 3. Temperatures profiles in the first reactor.

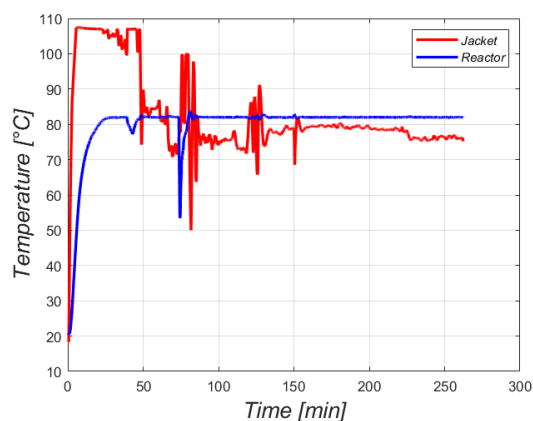


Figure 4: Test 4: Temperatures profiles in the first reactor.

It is possible to note that using this formulation the reactor temperature control was good. There were only some disturbances (oscillations) after the introduction of MO and CO (at about 2 [h] and 18 [min], with medium intensity fluctuations on the jacket temperature) and around the time at which the agitator change occurred (at 3 [h] and 27 [min], approximately, high intensity oscillations on the jacket temperature due to a momentary blockage of the peristaltic pump). Figure 4 reported the thermal traces of Test 4 within the first reactor of the series (reactor 2 has no data of particular interest). As already explained above, a temperature drop due to the change of the stirrer (at about 1 [h] and 14 [min]) can be noted. However, it can be seen how the system quickly re-stabilized itself at the process temperature, without observing excessive oscillations on the cooling jacket; this suggested the relatively low impact that this operation had on the reaction itself. After the filling phase of the first reactor, the process continued with an excellent control of the thermal profile. However, towards the end of the process (precisely at 225 [min]), a constant lowering of the jacket temperature could be observed. Considering that no other parameter was changed after the first reactor was filled, the most plausible cause was an increase in the viscosity of the mixture (also confirmed by the increase in the power absorbed by the stirring motor), which worsened the heat exchange. The hypothesis proposed to justify this effect was a surfactant starving phenomenon. In fact, micelles were mainly formed in the initial reaction load; after about 4 hours of feeding, the loss of this initial effect caused a rearrangement of the polymer particles, which involved coalescence in the areas close to the agitator, on the walls and on the surface (dead zones), generating a local increasing in the system viscosity. Table 2 reports a quick summary of the results achieved by the experimental tests.

Table 2: Summary of the tests results.

#Test	PIF	WRF	Runaway?	Product Quality
1	5.3	12	Yes	Not tested because batch loss
2	2.6	12	Yes	Not tested because batch loss
3	1.8	4.8	No	Good
4	1.8	4.0	No	Good

As it is possible to notice from Table 2, Test 1 and Test 2 led to runaway operating conditions not suitable for process intensification. Test 3 and Test 4 did not involve runaway phenomena; therefore samples were taken from the second reactor outlet to verify the conversion and the particle diameter. Results are reported in Table 3 for Test 4 (as the sake of example).

Table 3: Mean particle size and free BA content at the second reactor outlet (progressive times).

#Sample	0 [min]	5 [min]	15 [min]	30 [min]	50 [min]	75 [min]	Final
Particle Diameter [nm]	367	240	273	295	284	293	384
Free BA content [ppm]	7100	8500	7950	8300	8400	7400	5300

Concerning the particle diameter, good results were obtained: all samples perfectly met the expected standards. With regards to the amount of free BA, conversions between 99% and 99.5%, which were very close to the target (99.85%), could be observed.

5. Conclusions

From all the tests carried out, it is possible to draw the following conclusions relating to the best conditions in correspondence of which it is possible to operate the semicontinuous system: 1) it is possible to maintain a good temperature control within the first reactor (the most critical from the point of view of thermal stability) only when an optimal control of the liquid levels is maintained within both reactors of the series; 2) the maximum dosing rate tolerated by the system at the laboratory scale is 8.5 [mL/ min], corresponding to a PIF equal to 1.8; 3) the minimum working volume at which is possible to operate the recipe is approximately 500/600 [mL], corresponding to WRF equal to around 4.8/4, with a contact time in the first reactor of the series equal to 59/70 [min]. Summing up: i) the possibility of operating a high dry content latex production process in a semi-continuous manner by serialization of 2 CSTRs was demonstrated; ii) it was demonstrated that it is possible to start the CSTRs series without any product losses (as happens for all processes based on continuously stirred reactors); iii) productivity: 1.8x with current product quality maintained; iv) the increase in productivity was accompanied by a drastic reduction in volumes compared to the current state: from 2400 [mL] to 500/600 [mL]. This implies greater safety in the thermal control of the process given the favored ratio between volume and surface available for heat exchange.

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