Example 8: Styrene Butadiene Emulsion Copolymerization Process

Ref: Aspen Polymers: Examples & Applications, 2013, Aspen Technology, Inc.

The styrene butadiene emulsion copolymerization process model illustrates the use of Aspen Polymers to model the free-radical emulsion polymerization of styrene and butadiene in a semi-batch reactor. The model is used to examine several process parameters as a function of time: average number of radicals per particle, monomer concentration in the various phases, and monomer conversion.

About This Process

In this process, the emulsion copolymerization of styrene and butadiene is carried out in a batch reactor using ammonium persulfate (APS) as the initiator, sodium lauryl sulfate (SLS) as the emulsifier and tertiary dodecyl mercaptan (TDM) as a chain transfer agent. Functionalized styrene-butadiene emulsions are used in a variety of applications such as paper coatings, carpet backings, non-wovens, etc. In addition, emulsion polymerization is the major route for the production of synthetic rubber used in the tire industries. Most styrene-butadiene rubber (SBR) latexes are manufactured in semi-batch reactors. SBR production technology is detailed by Blackley (Blackley, 1983).

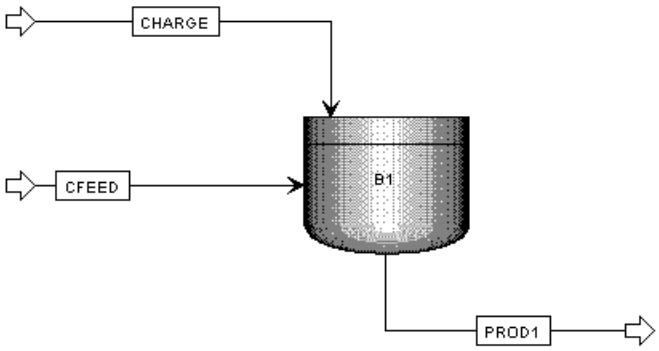
In a typical semi-batch process employing in-situ seeding, the initial charge is used for the production of seed particles, with the desired particle size and particle size distribution. Usually, anionic emulsifiers and water-soluble persulfate initiators are used for particle nucleation by the micellar mechanism.

When the initial mixture is heated, the radicals generated from the initiator become surface active and enter micelles to form particles. Once the particle specifications are met, monomers and other ingredients, such as chain transfer agent, stabilizers, initiators, are continuously added to the reactor, and the particles are grown to the desired final particle size.

The latter stage of the reaction is also known as the growth stage of the reaction, and is responsible for the development of the properties of the emulsion polymer: molecular weight, composition, micro structure, etc. The growth stage is the better understood stage of the process. Therefore, this stage provides more opportunities to control the emulsion process. The adjustable process parameters include temperature and feeding strategy of monomer and other ingredients. Control of polymer composition is very often achieved by feeding the monomers in a manner such that there is no separate monomer droplet present in the reactor. Very often the productivity of the reactor is limited by its cooling capacity. Chain transfer agents are usually added to control molecular weight, and degree of branching.

Process Definition

The process flowsheet consists of the batch reactor with an initial batch charge and a continuous feed for the addition of monomers and other ingredients:



This model provides the base case, which can be used to study various process variables: effect of initiator and emulsifier levels, temperature, kinetics, etc.

Process Conditions

The process conditions are:

- ✓ Components:

ID	Type	Component Name	Description
H2O	Conventional	WATER	Dispersant
STY	Conventional	STYRENE	Monomer
BD	Conventional	1,3-BUTADIENE	Monomer
POLYMER	Polymer	GENERIC-POLYMER-COMPONENT	Polymer
STY-SEG	Segment	STYRENE-R	Repeat Segment
BD-SEG	Segment	BUTADIENE-R-1	Repeat Segment
APS	Conventional	WATER	Initiator (Mw=228.2) Select H2O
SLS	Conventional	WATER	Emulsifier (Mw=288.4) Select H2O
TDM	Conventional	STYRENE	Chain transfer agent (MW= 202.4, select C8H8)

- ✓ Polymer characterization and distribution:

Item	Value
Built-in attribute group	Emulsion selection
Attribute list	SFRAC, SFLOW, DPN, DPW, PDI, MWN, MWW, ZMOM, FMOM, SMOM, PSDZMOM, PSDFMOM, DIAV
Distribution	Number of points = 100, Upper limit = 100000, GPC = No

- ✓ Physical Properties: POLYNRTL property method with supplied binary interaction parameters.

✓ The NRTL binary interaction parameters are:

Component i	Component j	Temperature units	AIJ	AJI	BIJ	BJI	CIJ
H2O	STY-SEG	K	10	10	0	0	0.3
H2O	STY	K	3.626	-4.436	1513.5	2869.7	0.36
H2O	BD	K	3.589	-0.852	862.82	702.17	0.3
STY-SEG	STY	K	0	0	411.838	-16	0.167
APS	STY	K	20	20	0	0	0.1
APS	BD	K	20	20	0	0	0.1

✓ Pure component data:

Property	APS	SLS	TDM	STY-SEG	BD-SEG
MW	228.2	288.4	202.4		
TGVK, ^{o}C				100	-54

✓ Streams:

Parameter	CHARGE	CFEED
Temperature, ^{o}C	20	20
Pressure, bar	10	10
STY, kg/hr	300	700
BD, kg/hr	300	700
SLS, kg/hr	30	100
APS, kg/hr	7	3
TDM, kg/hr	30	0
H2O, kg/hr	1000	1000

✓ Reactor: RBatch

Specifications		Temperature Profile		Continuous Feed Profile	
		Time, hr	T, ^{o}C	Time, hr	Flow, kg/hr
Pressure, bar	10	0	65	0	0
Reaction Time, hr	10	0.5	65	1	0
Total Cycle Time, hr	1	0.5	70	1	1200
Report Time Step, hr	0.2	1	70	2	1200
Flash Option	Liquid Only	1	75	2	0
Stop Criteria: Time	10 , hr	2	75		

✓ Kinetics: EMULSION

The rate constants for the kinetic scheme are obtained from Broadhead and are summarized here (Broadhead, 1984; Ponnuswamy & Hamielec, 1997):

Type	Phase	Comp 1	Comp 2	Pre-Exp (k_{ref}) 1/sec	Act-Energy (E_a) J/kmol	Efficiency
INIT-DEC	DISPERSANT	APS	-----	1e16	140200000	0.8
PROPAGATION	POLYMER	STY	STY	22000000	32000000	
PROPAGATION	POLYMER	STY	BD	44000000	32000000	
PROPAGATION	POLYMER	BD	STY	85000000	38800000	
PROPAGATION	POLYMER	BD	BD	120000000	38800000	
CHAT-MON	POLYMER	STY	STY	2200	32000000	
CHAT-MON	POLYMER	STY	BD	4400	32000000	
CHAT-MON	POLYMER	BD	STY	8500	38800000	
CHAT-MON	POLYMER	BD	BD	12000	38800000	
CHAT-AGENT	POLYMER	STY	TDM	283000	26800000	
CHAT-AGENT	POLYMER	BD	TDM	850000	38800000	
TERM-COMB	POLYMER	STY	STY	1300000000	9900000	
TERM-COMB	POLYMER	STY	BD	1300000	9900000	
TERM-COMB	POLYMER	BD	STY	1300000	9900000	
TERM-COMB	POLYMER	BD	BD	1300000	9900000	

- ✓ Partition coefficients for phase equilibria:

  Phase basis = Monomer, $K_{STY} = 0.7$, $K_{BD} = 0.5$, $K_{TDM} = 0.8$

- ✓ Particles specifications:

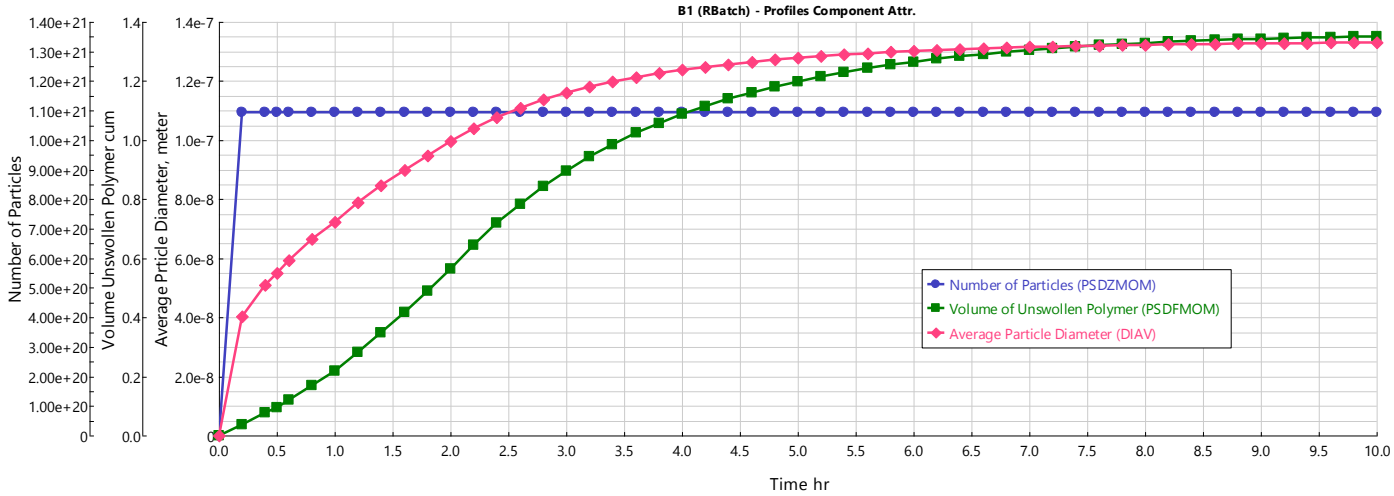
  Micellar nucleation parameters: Emulsifier = SLS, CMC (kmol/m^3) = 0.009, Area (m^2/kmol) = 5e6

  Radical adsorption by particles: k_o = 1e-7 (1/sec), Radical adsorption by micelles: k_o = 1e-7 (1/sec)

Results

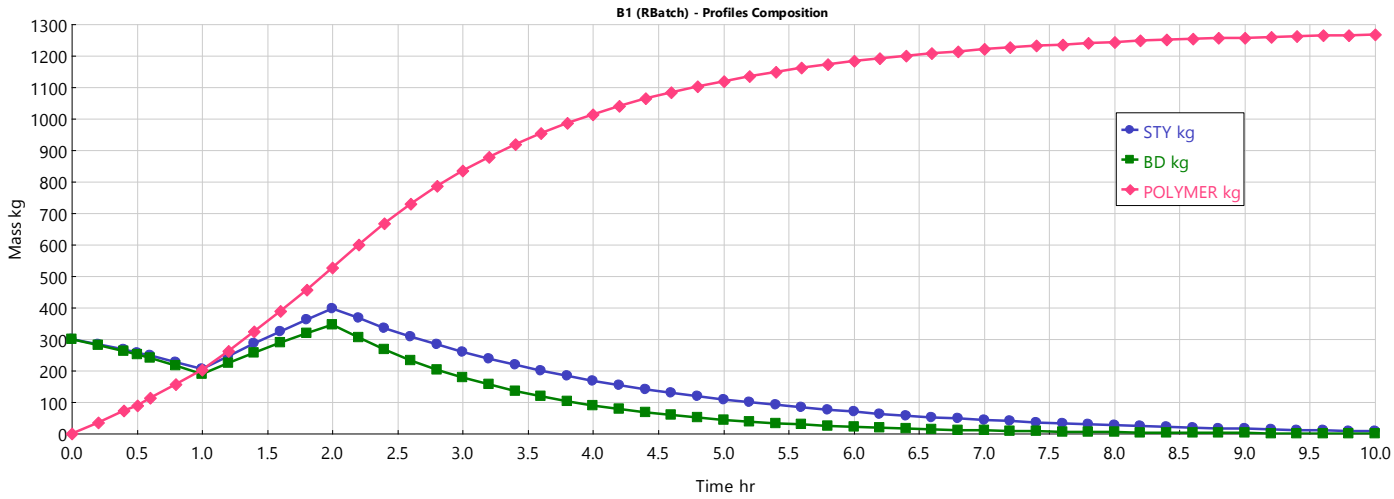
The simulation results are shown in the following figures.

- ✓ The nucleation and growth of emulsion polymer particles in the reactor



As shown, the number of particles formed early remains constant throughout the reaction. In this figure, first moment, which is the total volume of the unswollen polymer particles, increases throughout the polymerization as expected. The figure also shows that the average diameter of the unswollen particle increases as expected.

✓ The mass of monomers and polymer in the reactor



Although the flow rates of styrene and butadiene are equal, the figure shows that butadiene reacts faster than styrene due to its higher reactivity.

✓ The number average and weight average degree of polymerization and the polydispersity