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School of Chemical and Biomolecular Engineering

**ADVANCED MODELLING OF EMULSION
TERPOLYMERISATION FOR ONLINE
OPTIMISATION AND CONTROL**

By

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DECLARATION

I declare that the entire contents of this thesis are, to the best of my knowledge and belief, original, unless otherwise acknowledged in the text. I have not submitted this material, in whole or part, for another degree at this or any other institution.

Mourtada Hussein Srou

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TO whom will save humanity

TO whom will light darkness

TO the waited leader of humanity

AL-IMAM ALMEHDI

ABSTRACT

Polymer manufacturing is a major worldwide industry, attracting the attention of numerous industrial units and research institutes. Increasing demands on polymer quality, process safety and cost reduction are the main reasons for growing interest in the design and control of emulsion polymerisation. Emulsion polymerisation process implemented with free radical polymerisation has significant advantages over other processes, such as the production of polymer of higher molecular weights at high conversion rates, easier temperature control due to the low viscosity of the reaction media, high degree of selectivity and more friendly to environment due to the use of an aqueous medium. It allows for the production of particles with specially-tailored properties, including size, composition, morphology, and molecular weights. Introducing two or more different monomers to the polymerisation process (named multi-polymerisation) can lead to the synthesis of an almost unlimited number of new polymers types.

Emulsion polymers are products by process, meaning that the manner in which the polymerisation is carried out is perhaps more important than the raw materials in determining the form of the final product. This highlights the significance of the systematic approach in online process control which requires thorough understanding of the process phenomena as a prerequisite for development of a mathematical description of the process as the model. It is thus evident and based on research observations that process control for emulsion terpolymerisation is a particularly difficult task because of the lack of validated models and the lack of online measurements of most of polymer properties of interest. Therefore, a well validated model is crucial for optimising and controlling the emulsion terpolymerisation operations allowing for design of the polymer product properties.

In this study, a framework for process design and control of emulsion terpolymerisation reactors was developed. This framework consisted of three consecutive stages, dynamic modelling of the process, optimising the process for

finding the optimal operating strategies and final online controlling the obtained optimal trajectories through multivariable constrained model predictive control.

Within this framework, a comprehensive dynamic model was developed. Then a test case of emulsion terpolymerisation of styrene, methyl methacrylate and methyl acrylate was investigated on state of the art facilities for predicting, optimising and control end-use product properties including global and individual conversions, terpolymer composition, the average particle diameter and concentration, glass transition temperature, molecular weight distribution, the number- and weight-average molecular weights and particle size distribution. The resulting model was then exploited to understand emulsion terpolymerisation behavior and to undertake model-based optimization to readily develop optimal feeding recipes. The model equations include diffusion-controlled kinetics at high monomer conversions, where transition from a ‘zero-one’ to a ‘pseudo-bulk’ regime occurs. Transport equations are used to describe the system transients for batch and semi-batch processes. The particle evolution is described by population balance equations which comprise of a set of integro-partial differential and nonlinear algebraic equations. Backward finite difference approximation method is used to discretise the population equation and convert them from partial differential equations to ordinary differential equations. The model equations were solved using the advanced simulation environment of the gPROMS package.

The dynamic model was then used to determine optimal control policies for emulsion terpolymerisation in a semi-batch reactor using the multiobjective dynamic optimisation method. The approach used allows the implementation of constrained optimisation procedures for systems described by complex mathematical models describing the operation of emulsion terpolymerisation reactors. The control vector parameterisation approach was adopted in this work. Styrene monomer feed rate, MMA monomer feed rate, MA monomer feed rate, surfactant feed rate, initiator feed rate and the temperature of reactor were used as the manipulating variables to produce terpolymers of desired composition, molecular weight distribution (MWD) and particle size distribution (PSD). The particle size polydispersity index (PSPI), molecular weight polydispersity index (MWPI) and the overall terpolymer composition ratios were incorporated as the objective functions to optimise the PSD,

MWD and terpolymer composition, respectively. The optimised operational policies were successively validated with experiments via one stirred tank polymerisation reactor.

Due to the lack of online measurements of key process product attributes for emulsion terpolymerisation, an inferential calorimetric soft sensor was developed based on temperature measurements. The calorimetric soft sensor obtains online measurements of reactor temperature, jacket inlet and outlet temperatures helped estimate the rate of polymerisation. The model includes the mass and energy balance equations over the reactor and its peripherals. Energy balance equations include the heat of reaction, internal and external heat transfer effects, as well as external heat losses.

An online multivariable constrained model predictive control was formulated and implemented for online control of the emulsion terpolymerisation process. To achieve this implementation, a novel generic multilayer control architecture for real-time implementation of optimal control policies for particulate processes was developed. This strategy implements the dynamic model for the emulsion terpolymerisation as a real-time soft sensor which is incorporated within the implemented MPC. The methodology was successively validated using six case studies within the on-line control of terpolymerisation reactors. The cases were online controlled the composition of terpolymers, PSD and Mn with specific constraints for the operation conversion and particle average radius.

An advanced Supervisory Control Architecture named ROBAS was used in this work. It provides a completely automated architecture allowing for the real time advanced supervisory monitoring and control of complex systems. The real time control application strategy was developed within MATLAB, Simulink, gPROMS and Excel Microsoft softwares and implemented on line through ROBAS Architecture.

The manipulated variables are measured using on-line measurements connected to the DCS system through Honeywell. These measurements were sent to MATLAB and then to the dynamic model in gPROMS through an excel spread-sheet interface. Then the dynamic model used them to estimate the controlled variables of the MPC. The estimated values of the controlled variables obtained from the dynamic model, were

then sent to the Simulink and fed through the DCS system to the MPC developed in MATLAB. The MPC would then calculate optimal trajectories, which are then sent as set point signals through the DCS system to the regulatory controller.

The MPC formulation was found to be robust and handles disturbances to the process. The result showed that the online multivariable constrained MPC controller was able to control the desired composition and Mn as specified set points with great accuracy. The MPC algorithm succeeded under constrained conditions, in driving the PSD to the desired target. Although some offset was observed with a certain degree of model mismatch, the experimental results agreed well with predictions.

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NOMENCLATURE

A	Heat transfer area (m^2)
a_g	Empirical constant for glass transition temperature.
a_s	Polymer particle area occupied by an adsorbed surfactant molecule, dm^2
$C_{i,l}^{sat}$	Saturated concentration of monomer l in i phase, $\text{mol}\cdot\text{L}^{-1}$
C_p	Concentration of monomers in polymer particle phase, $\text{mol}\cdot\text{L}^{-1}$
C_w	Concentration of monomers in aqueous phase, $\text{mol}\cdot\text{L}^{-1}$
C_w^{sat}	Saturated concentration of monomers in aqueous phase, $\text{mol}\cdot\text{L}^{-1}$
$C_{d,l}$	Concentration of monomer l in droplet phase, $\text{mol}\cdot\text{L}^{-1}$
$C_{P,l}$	Concentration of monomer l in the latex particles, $\text{mol}\cdot\text{L}^{-1}$
C_{pi}	Heat capacity of reactor content i ($\text{J/g}\cdot\text{K}$)
$C_{w,l}$	Concentration of monomer l in the water phase, $\text{mol}\cdot\text{L}^{-1}$
$C_{micelle}$	Concentration of micelles, mol L^{-1}
[cmc]	Critical micelle concentration, mol L^{-1}
D	Reactor diameter (m)
$D_{mon,l}$	Diffusion coefficient of monomer l in particle phase, dm^2
$D_{w,l}$	Diffusion coefficient of monomer l in water phase, dm^2
$D_{rd,l}$	Diffusion coefficient arising from reaction-diffusion, dm^2
d	Impeller diameter (m)
$d_{p,l}$	Density of polymer l , kg L^{-1}
$d_{m,l}$	Density of monomer l , kg L^{-1}
ΔH_i	Enthalpy of monomer i homopolymerisation (J/mol)
[$E\cdot$]	Aqueous phase concentration of desorbed radicals, $\text{mol}\cdot\text{L}^{-1}$
e_e	Entry efficiency coefficient
f	Efficiency dissociation constant
$F_{comp,l}$	Mole fraction of monomer l in the polymer
F_I	Flow rate of initiator, $\text{mol}\cdot\text{s}^{-1}$

f_l	Mole fraction of monomer l in the system
$F_{m,l}$	Flow rate of monomer l , g.s ⁻¹
F_s	Flow rate of surfactant, mol.s ⁻¹
F_w	Flow rate of monomer , L.s ⁻¹
G	The number of radius increments to be integrated
h_r	Transfer coefficient between the reaction mixture and the internal wall(W/m ² K)
[I]	Initiator concentration in the reactor, mol.L ⁻¹
[IM _i [*]]	Aqueous phase concentration of oligomeric radicals of degree ‘i’, mol.L ⁻¹
j _{crit}	Critical degree of polymerisation for homogeneous nucleation
K_{st}	Stirrer constant
K	Rate of propagation volume growth per particle, L s ⁻¹
$K_{i,j}^l$	Partition coefficient of monomer l between i and j phases
k_d	Rate coefficient for initiator decomposition, s ⁻¹
k_{dm}	Rate coefficient for desorption of monomeric radicals from particles, s ⁻¹
$k_{dm,l}^j$	Rate coefficient for desorption of monomeric radicals l from particles of radius j, s ⁻¹
$k_{diff,l}$	Diffusion-controlled rate coefficient of monomeric radicals l , s ⁻¹
$k_{e,l}^{i,j}$	Rate coefficient for entry of an oligomeric radical l of degree ‘i’ into an existing particle of radius j, L.mol ⁻¹ .s ⁻¹
$k_e^{i,j}$	Overall rate coefficient for entry of oligomeric radical of degree ‘i’ into an existing particle of radius j, L.mol ⁻¹ .s ⁻¹
k_{eE}	Overall rate coefficient for re-entry of desorbed monomeric radicals l , L.mol ⁻¹ .s ⁻¹
$k_{eE,l}^j$	Overall rate coefficient for re-entry of desorbed monomeric radicals l into an existing particle of radius j, L.mol ⁻¹ .s ⁻¹
$k_{e,micelle}^i$	Rate coefficient for entry of an oligomeric radical of degree ‘i’ into a micelle, L.mol ⁻¹ .s ⁻¹
K_i	Volume growth rate coefficient for free monomeric radical l existing in a particle, L.mol ⁻¹ .s ⁻¹

k_p	General propagation rate coefficient in polymer particle, $L.mol^{-1}.s^{-1}$
k_{po}	Propagation rate coefficient at low conversion in polymer particle, $L.mol^{-1}.s^{-1}$
$k_{p,ij}$	Propagation rate coefficient of polymeric radical i with monomer j , $L.mol^{-1}.s^{-1}$
$k_{p,aa}^i$	Aqueous phase propagation rate coefficient for oligomeric radicals of degree 'i', $L.mol^{-1}.s^{-1}$
k_p^{aa}	Overall aqueous phase propagation rate, $L.mol^{-1}.s^{-1}$
$k_{t,ij}^l$	termination rate coefficient between oligomeric radicals of degree 'i' and 'j' in phase l , $L.mol^{-1}.s^{-1}$
k_{to}^p	Termination rate coefficient between oligomeric radicals in particle phase at low conversion, $L.mol^{-1}.s^{-1}$
$k_{t,aa}$	Overall termination rate coefficient in the aqueous phase, $L.mol^{-1}.s^{-1}$
$k_{t,ij}^{aa}$	Termination rate coefficient between oligomeric radicals of degree 'i' and 'j' in the aqueous phase, $L.mol^{-1}.s^{-1}$
k_{tr}	Rate coefficient for radical transfer to monomer, $L.mol^{-1}.s^{-1}$
M	Molecular weight of polymer chain, $kg..mol^{-1}$
M_{avg}	Average molecular weight of the different monomers, $kg..mol^{-1}$
M_l	Molecular weight of monomer l , $kg..mol^{-1}$
M_n	Number average molecular weight, $kg.mol^{-1}$
M_w	Weight average molecular weight of polymer, $kg.mol^{-1}$
N	Agitation speed (rev/s)
N_A	Avogadro's constant, mol^{-1}
N_l	Total number of moles of monomer l in the system, mol
$N_{m,l}^{fed}$	Total number of moles of monomer l added to the system, mol
N_t	Total number of moles of all monomers in the system, mol
$N_{terp,l}$	Number of moles of monomer l in the polymer, mol
N_p	Total number of polymer particles in the reactor, particles
n_{agg}	Micelle aggregation number ,i.e. the average number of surfactant molecules in a micelle
$n(v)$	Molar concentration density of particles of unswollen volume v , $mol.L^{-1}.dm^{-1}$

$n_0(v)$	Molar concentration density of particles of unswollen volume v containing no radicals, $\text{Mol.L}^{-1}.\text{dm}^{-1}$
$n_1^m(v)$	Molar concentration density of particles of unswollen volume v containing monomeric radicals, $\text{mol.L}^{-1}.\text{dm}^{-1}$
$n(G)$	Molar concentration density of particles of radius increments G , $\text{mol.L}^{-1}.\text{dm}^{-1}$
$n_0(G)$	Molar concentration density of particles of radius increments G containing no radicals, $\text{mol.L}^{-1}.\text{dm}^{-1}$
$n_1^m(G)$	Molar concentration density of particles of radius increments G containing monomeric radicals, $\text{mol.L}^{-1}.\text{dm}^{-1}$
$n_1^p(G)$	Molar concentration density of particles of radius increments G , containing polymeric radicals, $\text{mol.L}^{-1}.\text{dm}^{-1}$
$P(M)$	Instantaneous molecular weight distribution
$\bar{P}(M)$	Cumulative molecular weight distribution
$PSPI$	Particle size polydispersity index
Q_f	Heat flux across the reactor wall (W)
Q_l	Heat losses (W)
Q_r	Heat-generation rate due to the chemical reaction (W)
Q_{st}	Heating due to stirrer (W)
Q_{feed}	Heat flow due to the reactor feed (W)
R_p	Polymerisation reaction rate, $\text{mol. L}^{-1}.\text{s}^{-1}$
$R_{i,l}$	Rate of polymerisation of monomer l in phase i , $\text{mol. L}^{-1}.\text{s}^{-1}$
r_s	Swollen radius of latex particle, dm
r_u	Unswollen radius of latex particle, dm
$[S]$	Concentration of added surfactant per unit volume of the aqueous phase, mol L^{-1}
$[S_{ads}]$	Concentration of adsorbed surfactant on the polymer particles surface, mol L^{-1}
T	Temperature of the reaction, K
T_{amb}	Ambient temperature ($^{\circ}\text{C}$)
T_r	Reactor temperature ($^{\circ}\text{C}$)
$T_{j,out}$	Outlet jacket temperature ($^{\circ}\text{C}$)

$T_{j,in}$	Inlet jacket temperature (°C)
T_w	Reactor wall temperature (°C)
T_g	Glass transition of polymer, K
$T_{g,l}$	Glass transition of polymer formed from monomer l , K
$[T^\bullet]$	Total oligomers concentration in the aqueous phase, mol.L ⁻¹
U	Heat transfer coefficient (W/m ² K)
V	Total volume of polymerisation reaction, m ³
V_d	Total volume of monomer droplets in the system, dm ³
V_p	Total volume of polymer in the system, dm ³
V_s	Volume of swollen polymer particle, dm ³
V_u	Volume of unswollen polymer particle, dm ³
V_w	Volume of aqueous phase in the system, L
V_{wo}	Volume of water in the system, L
V_{wm}	Volume of dissolved monomers in water, L
X	Total instantaneous monomers weight conversion
X_l	Instantaneous molar conversion monomer l
z	Critical degree of polymerisation for entry

Greek letters

ρ	Pseudo rate coefficient for all entry events (oligomeric radicals and exited radicals) into existing particles, s ⁻¹
ρ_{init}	Pseudo rate coefficient for entry of an oligomeric radical into an existing particle, s ⁻¹
α	Coefficient for heat losses (W ^o C ^β)
β	Power coefficient for heat losses
ρ_l	Density of latex (Kg/m ³)
ρ_m	Density of monomer (Kg/m ³)
ρ_p	Density of polymer (Kg/m ³)
ρ_w	Density of water (Kg/m ³)