Optimal Control of Particle Size Distribution in Semi-Batch Emulsion Polymerisation

by

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Abstract

Emulsion polymerisation is a widely used polymerisation technique employed in industry to produce adhesives, paints, coatings, drug delivery systems and many other products. The particle size distribution (PSD) of the latex produced strongly influences some important properties of the final products. Hence, the control of the PSD is very important in producing polymers with defined characteristics. The idea is to control the full PSD, and not just a few moments of the distribution, the latter approach not being capable to accurately define the final properties of the polymers. Due to the need of accounting for the interactions between the different phenomena that drive the PSD evolution, to have a description of the process as a whole and to produce distribution profiles often complex and multi-modal, a model-based control strategy appears to be the most suitable. A detailed first principles model based on population balance equations was used, which also simplifies model update and feed-back corrections. The use of a model introduces the need of accounting for possible model mismatches and required the introduction of a parameter identification procedure. An optimisation routine capable of producing operating policies that attain target PSD was identified. It showed the ability of gradient-based routine to solve this family of non-convex optimisation problems characterised by discontinuities. Different open-loop control strategies, from single-objective to multi-objective, were implemented following both a direct and hierarchical approach. The effect of measurement limitations and process constraints on the attainability of defined PSD profiles was also studied. Difficulties in the implementation of in-batch feedback can be encountered, making the batch-to-batch control strategy a viable and necessary alternative. As a sample demonstration, an inferential control of the rheology of the latex via PSD was developed.

In memoria di nonno Nicola,
per i bei momenti trascorsi insieme

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Nomenclature

Roman symbols

A	Hamaker constant
A_L	matrix of linear constraint functions
c	vector of nonlinear constraint functions
c_1	additive factor for repulsive potential
c_2	multiplicative factor for repulsive potential
c_3	multiplicative factor for coagulation kernel
cmc	critical micelle concentration
$C_{micelle}$	micelle concentration
D	distance between particle centres
D_0	diffusion coefficient
dry	weight of the polymer particles in each sample
D_{wi}	parameter in entry rate coefficient
e_i^l	entry rate constant into particles
$e_{i,micelle}^l$	entry rate constant into micelles
F	particle density function
f	objective function
$F_{corrected}$	updated particle density function (coarser to finer level)
F_j	particle density function in bin j
F_{new}	updated particle density function (finer to coarser level)
F^c	particle density function at the coarser level
F^f	particle density function at the finer level

$factor_i$	multiplicative correction factor
$Growth_i$	growth contribution to the population distribution
$Growth_{N_{FE}}$	integrated growth rate for the coarser bin 1
$Growth_{jN_{FE}}$	integrated growth rate for the coarser bin j
H	Heaviside function
j_{cr}	critical chain length
k	Boltzmann constant
k_i	particle-particle interaction parameter
k_{dMj}	rate constant for desorption of monomeric radicals
k^w_{pav}	pseudo-homopolymer rate constant for propagation in aqueous phase
k_{pij}	rate constant for propagation in particle phase
k^w_{pij}	rate constant for propagation in aqueous phase
k_{tav}	pseudo-homopolymer rate constant for termination
k_{trij}	rate constant for chain transfer to monomer in particle phase
k^w_{trij}	rate constant for chain transfer to monomer in aqueous phase
L	extensional length of surfactant chain into the aqueous phase
L	distance between particle surfaces (equation 2.26)
l	chain length (equation 2.13)
l	lower bound vector
l_j	lower bound j
$\left[M_j\right]$	molar concentration of monomers of type j
MW_j	molecular weight of monomer j
N	normalised weighted PSD
n	number of decision variables (section 3.1.4)
n	number of radicals per particle
$\bar{n}$	average number of radicals per particle
n_1	number of radicals of type 1 per particle
n_2	number of radicals of type 2 per particle
N_A	Avogadro number

N_{exp}	number of experimental values
N_{bin}	number of finite elements of the particle size domain
N_{FE}	number of finer grids per coarser grid
Np	number of particles
$\left[P_w^l\right]$	molar concentration of oligomers of length l in the aqueous phase
p_i	probability that a radical is of type i in the particles
p_{w_i}	probability that a radical is of type i in the aqueous phase
$\Re$	process rate
$\Re^{'}$	process rate for a single particle
r	particle radius
$\bar{r}$	average particle radius
$r^{'}, r^{''}$	radii of two coagulating particles
rb_i	upper boundary of finite element i
r_{co}	cross-over radius
$r_{cut-off}$	cut-off radius for coagulation
ri_i	representative size for finite element i
r_{max}	maximum radius for coagulation
$r_{micelle}$	micelle radius
r_{nuc}	radius of the particle nuclei
r_s	swollen radius of particles
r_{upper}	upper radius for coagulation
S_w	free surfactant concentration
sc	solids content
T	temperature
t	time
t_f	duration of the batch
u	upper bound vector
u_j	upper bound j
V_{aq}	volume of the aqueous phase

V_p	unswollen particle volume
W	Fuch's stability ratio
W	weight-averaged PSD (chapters 3, 4 and 5)
w	objective function weight
w_i	objective function weight for the intermediate time t_i
w_2	weight for objective function θ_2
w_3	weight for objective function θ_3
wet	weight of the sample
W_{max}	highest value of the actual weight-averaged PSD
x	particle size (section 2.2.2)
x	decision variables vector
x_i	decision variable i

Greek symbols

$\alpha_{m,s}$	area occupied by one surfactant molecule
β	coagulation kernel
β	model parameter (equation 4.1)
Γ	surface coverage of the particles with surfactants
γ	shear stress
δ	Dirac delta function
ΔR_i	width of finite element (bin) i
Δt	time step
ΔV_i	width of finite element i on volume basis
$\Delta V_{N_{FE}}$	integrated volume for the coarser bin 1
$\Delta V_{jN_{FE}}$	integrated volume for the coarser bin j
ϵ	tolerance
ϵ	permittivity of water (equation 2.26)
ϵ_i	penalty on the objective function i
ζ	zeta potential of particles

$[\eta]$	intrinsic viscosity
η_r	relative viscosity
θ_1	error between the end-point and target weight-averaged PSD
θ_2	error between simulated and target solids content profile
θ_3	error between simulated and target number of particles profile
Ψ	net interaction potential
Ψ_R	repulsive potential
Ψ_A	attractive potential
ρ_p	density of polymer
σ	particle-particle interaction
ϕ	solids content
ϕ_n	maximum packing factor

Subscripts

bin	finite element of the particle size domain
co	cross-over
coag	particle coagulation
corrected	updated/corrected
cr	critical
$cut-off$	cut-off size for coagulation
depletion	depletion of particles by coagulation
desorption	desorption of radicals from particle
dM	desorption of monomeric radicals
entry	entry of radicals into particle
exp	experimental value
f	final time/end of the batch
formation	formation of particles by coagulation
FE	finite element
growth	particle growth

homogeneous	homogeneous nucleation
i	intermediate time (equation 3.3)
j_{cr}	critical chain lenght
max	maximum
m, s	molecule of surfactant
micellar	micellar nucleation
micelle	micelle
meas	experimentally measured
model	model simulation
n	number of radicals per particle
$\bar{n}$	average number of radicals per particle
n_1	number of radicals of type 1 per particle
n_2	number of radicals of type 2 per particle
new	updated/new
N_{FE}	number of finer bins per coarser bin
nuc	particle nucleation
p	particle phase
p	polymer chain propagation (in k_p)
recipe	recipe optimisation
ref	reference (target)
tav	termination average
pav	propagation average
termination	termination of radicals within particle
tr	polymer chain transfer (to monomer)
update	model update parameters optimisation
upper	upper size for coagulation
w	aqueous phase

Superscripts

c	coarser level
f	finer level
l	chain length
j_{cr}	critical chain length
n	model parameter (equal to 1 or 2)
N_{FE}	number of finer bins per coarser bin
w	aqueous phase

Abbreviations

BuA	Butyl Acrylate
CCD	copolymer composition distribution
cmc	critical micelle concentration
CHDF	capillary hydrodynamic fractionator
CSTR	continuous stirred tank reactor
CTA	chain transfer agent
DAE	differential algebraic equation
DI	deionised
DLVO	Derjaguin, Landau, Verwey and Overbeek theory
E04JYF	NAG Fortran library routine
E04UCF	NAG Fortran library routine
FD	finite difference
FE	finite element
FORTRAN	mathematical formula translating system - programming language
FV	finite volume
GA	genetic algorithm
GB	gigabyte
GHz	gigahertz
MHz	megahertz
MPC	model predictive control

MWD	molecular weight distribution
MWR	method of weighted residuals
NAG	numerical algorithms group
NLP	nonlinear programming
Np	number of particles
OCFE	orthogonal collocation on finite elements
ODE	ordinary differential equation
PBE	population balance equation
PDE	partial differential equation
PFR	plug flow reactor
PI	proportional-integral control scheme
PID	proportional-integral-derivative control scheme
PLS	partial least square
PSD	particle size distribution
QDMC	quadratic dynamic matrix control
QP	quadratic programming
rpm	revolutions per minute
sc	solids content
SCOPE	simulation and control of polymer emulsions model
SDS	sodium dodecyl sulphate
SFS	Sodium Formaldehyde Sulphoxylate
SQP	sequential quadratic programming
t-BHP	*t*-Butyl Hydrogen Peroxide
VAc	Vinyl Acetate

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Chapter 1

Introduction to the Process, Motivations and Objectives

In this chapter a brief overview of the emulsion polymerisation process and its control will be introduced. The need for controlling the particle size distribution (PSD) will be explained, along with the specific objectives of this thesis. The logic behind the different strategies and approaches implemented in the different stages of the project will be clarified. A short introduction to the other chapters will be also presented.

1.1 Introduction to emulsion polymerisation

Emulsion polymerisation is a widely used polymerisation technique that allows production of industrially relevant products such as paints, coatings, adhesives, foams, cosmetics, synthetic rubber, inks, and many other products. Million of tons of synthetic polymer latexes are produced via emulsion polymerisation.

Emulsion polymerisation is a free-radical heterogeneous polymerisation in which polymeric chains grow inside colloidal particles ($\sim$ 2 nm - 1 μm) dispersed in an aqueous phase. These particles are stabilised by surfactant (also referred as emulsifier) molecules, which limit particle coagulation.

Polymer particles are formed by homogeneous or micellar nucleation. In the first case,

oligomer chains precipitate in the aqueous phase, are stabilised by surfactant molecules and surrounded by other monomer molecules that promote the polymer growth by chain reaction. Alternatively to this mechanism, micellar nucleation occurs when monomer swollen micelles are formed and an initiator radical or molecule, or a still water soluble active oligomer, enters a micelle and generates a polymer radical. Polymers grow into particles by continuous addition of monomer molecules to the active sites. The rate of polymerisation in these loci is much higher that the one in the aqueous phase, where the monomers are dispersed and not directly available for addition to the growing chains.

Monomer droplets are formed in the aqueous phase via agglomeration of monomer molecules. They aggregate in a locus because of their hydrophobic nature in an attempt of the system to reach a more stable state. Monomer droplets act as monomer reservoirs for the polymer particles. Monomers diffuse from the monomer droplets into the swollen polymer particles through the water phase. Their existence in the reaction bulk guarantees monomer saturation into the polymer particles. Monomer droplets are also usually stabilised by emulsifier molecules. The presence of droplets in the system can promote a third form of nucleation known as droplet nucleation. This phenomenon is considered to be predominant in miniemulsion and microemulsion polymerisation, but can be neglected when referring to emulsion polymerisation.

Initiators can be water or oil soluble, determining the phase where the initiator radicals are formed in the emulsion. Initiation can be triggered by thermal decomposition of the initiator molecules, by a redox reaction or by γ-radiation. Surfactant has a major role in defining the size and size distribution of the polymer particles. Surfactants can be divided into four main classes: anionic, cationic, non-ionic and zwitterionic (amphoteric) (Swarup and Schoff, 1993). Substances that are not miscible with each other are, for the second law of thermodynamics, inherently unstable. Hence, the need to use surfactants in emulsion polymerisation, which are used to create locus for compartmentalisation to stabilise the system.

Important features of emulsion polymerisations are the effective solution of the gelation problem that occurs in bulk polymerisations, the possibility to produce higher molecular weight polymers compared to those that can be produced by other polymerisation techniques,

the high heat transfer capacity ensured by the aqueous phase and the environmentally safe trait of this process that, unlike solution polymerisations, do not use organic solvents, but only water as reaction media.

Emulsion polymerisation latexes can be characterised through different molecular and particle-size scale qualities such as copolymer composition, molecular weight distribution (MWD), branching, particle morphology and particle size distribution (PSD). All these characteristics of the polymer latex define major properties of the final products, including their mechanical, rheological, optical and thermal properties. In particular PSD has been found to have an important role in defining the mechanical strength, rheological, adhesion, film forming and optical properties of the latex (Parkinson et al., 1970; Keddie et al., 1996; Luckham and Ukeje, 1999; Peters et al., 2000; Tzitzinou et al., 2000; do Amaral et al., 2005). These and more information on emulsion polymerisation processes and emulsion polymers can be found in the book by Lovell and El-Aasser (1997).

1.2 Emulsion polymerisation modelling and control

1.2.1 Process modelling

Smith and Ewart (Smith, 1948; Smith and Ewart, 1949; Smith, 1949), based on the mechanistic understanding of the process by Harkins (Harkins, 1945, 1946, 1947) developed the earliest model for emulsion polymerisation. Different approaches can be followed in the modelling of the process. Richards et al. (1989) used a particle number model to describe it. This approach considers the system as constituted by particles of the same average dimension and with the same characteristics as sites for polymerisation reaction (Lovell and El-Aasser, 1997).

But, often required properties of the latex are driven by complex and multi-modal PSD. These brought other scientists to build models focusing on the PSD evolution (Min and Ray, 1974; Coen et al., 1998; Immanuel et al., 2003; Park et al., 2005; Vale and McKenna, 2007; Sood, 2008). These approaches produce what are known as PSD models. The material balances in these models are written over the particle population of a given dimension at

a given time. The phenomena driving the PSD evolution, namely nucleation, growth and coagulation of the particles, are accounted through kinetic equations. The nature of the process leads to population balance structures for the PSD models and justifies the wide use of populations balance equations (PBE) in the PSD modelling of emulsion polymerisation (Saldívar et al., 1998; Ramkrishna, 2000; Immanuel et al., 2002; Vale and McKenna, 2005a; Park et al., 2005; Sood, 2008). The number of radicals per particle can also be modelled in a population balance framework to account for the number of radicals per particle for any particle size, at a given time.

A different category of models used to describe the evolution of the PSD are the age distribution models. In this case, the age of each particle, rather than its size, is predicted by the model. The SCOPE (Simulation and Control of Polymer Emulsions) model by Dougherty (Dougherty, 1986b,a) is an example of an age distribution model applied to emulsion polymerisation. Good reviews on emulsion polymerisation modelling are available in literature (Min and Ray, 1974; Penlidis et al., 1985; Lovell and El-Aasser, 1997; Saldívar et al., 1998; Vale and McKenna, 2005a).

The above mentioned papers focus on batch and semi-batch processes. Advancements have also been made in the field of continuous reactors. These are often built as series of continuous stirred-tank reactors (CSTRs), plug-flow reactor (PFR) or a combination of the two. Different approaches to the modelling of continuous emulsion polymerisation processes have been proposed (Rawlings and Ray, 1988a,b; Paquet, Jr. and Ray, 1994a,b; Ohmura et al., 1998; Sayer et al., 2002).

1.2.2 Process tracking and control

An emulsion polymerisation reactor can be run isothermally or non-isothermally, depending on the use of a controlled cooling flow in the jacket or a fixed cooling. Also, with the aim of controlling the copolymer composition of the polymer produced, a controlled addition of the more water-soluble or more reactive monomers at a defined time of the batch in a semi-batch mode can be implemented. The polymer branching can be reduced through an early interruption of the process, before completion of the monomers reaction, with the residual

reactants that can be recovered. These are some of the possible approaches for the run of an emulsion polymerisation reactor. The use of multiple initiators and surfactants can also be used for the control of specific colloidal and molecular properties.

On-line and off-line measurements of the different properties are needed for control purposes. On-line sensors for the measure of the monomer conversion have been developed based on densitometry measurements, while the free surfactant concentration can be measured using techniques for the evaluation of the surface tension. For the on-line control of PSD, techniques such as turbidity spectra measurements, size exclusion chromatography (e.g. capillary hydrodynamic fractionation) and dynamic light scattering can be used. The characteristics of gel permeation chromatography can be exploited for on-line measurements of MWD (Lovell and El-Aasser, 1997). A much more complete and wide review on recent advancements in on-line sensors for the monitoring of polymerisation rectors is given by Kammona et al. (1999). Time constraints can often make these measurements not available. They can still be inferred from states of the system through the implementation of specific state estimation strategies (e.g. Kalman filter) if a reasonably accurate model is available. Observers and state estimators can be used, other than for the estimation of unmeasured states, also for noise filtering purposes and prediction of future values of the states.

Inputs to the reactor can be classified as manipulated variables and disturbances. The manipulated (or decision) variables are adjusted to maintain the controlled variables to their desired values. Coolant or heating flow rates, feed rates of monomers, surfactant and initiator, and agitator speed are common decision variables in emulsion polymerisation. Disturbances are external inputs interfering with the normal operation of the reactor. Disturbances can be stochastic or deterministic. Stochastic disturbances are random modifications to the process usually deriving from its natural variability. Deterministic disturbances arise from known causes and are usually more spaced in time. In a control system, manipulated variables are adjusted to compensate for effect of disturbances on the controlled variables. Controlled variables are those defining our control objectives. We control their values to a certain set point we want or need to achieve.

Output variables can be divided into end use properties, usually not measurable online

and, therefore not directly controllable, but also into specific variables affecting directly the product qualities. These include MWD, monomer conversion, copolymer composition and PSD and should be controlled whenever possible. Controlled variables specifying operating conditions, such as temperature, pressure and flow rates, are a third category of outputs, usually easy to measure online and used as control variables, but with only an indirect effect on the product quality.

A process can be carried in batch, semi-batch and continuous mode. In batch processes all of the reactants are added at the beginning and no further additions are made throughout the process. This does not give much flexibility in terms of choice of the manipulated variables and limits them to such variables as reaction temperature, reactor design and speed of agitation. Semi-batch processes are more versatile and, because of that, widely used in industry and academic laboratories. In semi-batch processes only part of the total reaction formulation is introduced in the reactor at the beginning and the rest of it is added during the course of the polymerisation. This broadens enormously the variety of possible control strategies. All possible combination of reaction components (i.e. monomers, surfactants, initiators, water, chain transfer agents, etc) can be added following a predetermined schedule. Semi-batch processes facilitate the use of a single reactor, as opposed to continuous processes, and are so versatile that they can be used basically for all the possible applications of emulsion polymerisation. The only limitations of semi-batch processes could be in the reactant feed streams to the rector and the type and power of the agitator that can be implemented. The same degree of control on latex properties is not possible with continuous processes. These processes become attractive only when a large tonnage of a single latex needs to be produced. Batch-to-batch variation of the product quality is also avoided and a uniform product quality is guaranteed. But, with continuous processes important product characteristics such as specific PSD may be difficult to obtain. Continuous reactors are usually composed of a single or series of CSTRs reactors, or by a tubular (plug-flow) reactor. Various combinations of these designs can be found in the literature. For example, tubular reactors can be combined with CSTRs for improved reactor design, for example to avoid the oscillation caused by repeated periods of particle nucleation. During start-up or product change-overs, off-specification latex

is likely to be produced, leading to possible waste of products (Lovell and El-Aasser, 1997).

1.3 Control of PSD: motivations and objectives

1.3.1 The importance of latex PSD control

The PSD is strongly correlated to important end-use properties of emulsion polymers. It influences rheological, adhesion, film-forming and optical properties of the final product, their mechanical strength, and other properties. In combination with other variables such as the molecular weight distribution (MWD) and the copolymer composition, PSD is a key determining factor in defining also many other qualities of the final product. Emulsion polymerisation products include adhesives, coatings, paints, cosmetics and synthetic rubbers. Thus, the importance of PSD is easily evinced.

Often distributions that are relevant in industrial applications are complex and multi-modal. It was also observed that latexes with approximately the same average dimension of the particles, but different distributions, can give different performances. Hence, the importance of controlling not just few moments of the distribution, but the full PSD. Different studies on the rheological properties of emulsion polymerisation latexes have been conducted for mono-disperse systems (Krieger, 1972; Choi and Krieger, 1986), bi-disperse systems (Chang and Powell, 1994) and poly-disperse systems (Luckham and Ukeje, 1999) showing the influence of the dispersity on the final properties of emulsion polymers. Arevalillo et al. (2006) have recently reported a quantitative relation between PSD and rheology, in the framework of previous models (Mooney, 1951; Krieger and Dougherty, 19592; Sudduth, 1993a,b; Luckham and Ukeje, 1999). Parkinson et al. (1970) studied the effect of multi-modal PSD on the relative viscosity of non-newtonian dispersed systems. It was also observed that, for concentrated emulsions, after the volume fraction of particles, the PSD is probably the major characteristic influencing their viscosity (Guyot et al., 2002). A quantitative relation between the PSD of high-solid-content latexes and their low shear viscosity was developed by do Amaral et al. (2004). From the same research group another study, accounting this time for the influence of the PSD on the adhesive properties of the latex, was developed. It showed how marked

differences in adhesive properties may be related to particle size and particle size distribution of the latex (do Amaral et al., 2005). The influence of PSD on the film-forming properties of emulsion polymers was discussed in different papers (Jensen and Morgan, 1991; Keddie et al., 1996; Geurts et al., 1996; Zou et al., 2005). The PSD defines properties of the emulsion latex such as minimum film forming temperature, drying time, shrinkage on drying, tensile strength and water uptake, all important properties in coating applications (Peters et al., 1996). The void volume in the packing of the polymer particles is a major player in determining the effect of the PSD on the different latex properties. The presence of voids and the uniformity of their packing in the latex can influence the refractive index of the product (Tzitzinou et al., 2000) and consequently optical properties such as film transparency (Feng et al., 1995; Zou et al., 2005), having the voids a different composition than polymers. Reversibility, drying behaviour, rheological and film forming properties were related to the different blend ratios of polymer particles of different dimensions in the characterisation of printing inks by Peters et al. (2000). These and other examples of the strong correlation between latex PSD and end-use properties are available in literature. Other evidences of the different behaviour of emulsion polymers due to dissimilar PSD derive from industrial practice and are based essentially on empirical observations.

The evolution of the PSD is driven by three major phenomena. These are the nucleation, growth and coagulation of the particles. These phenomena present irreversible traits and are related in a complex way. They are characterised by different time constants and are sensitive to decision variables with different, and sometimes contrasting, effects on their dynamics. A size dependent growth rate adds up in making the process difficult to control. The aim of the proposed research is to build a control system able to handle all these aspects and drive the process towards specified PSDs. The complex way in which the available inputs influence nucleation, growth and coagulation of the particles and the strong interaction between these phenomena calls for a model-based control able to cope with process disturbances, measurement delay and model uncertainties.

1.3.2 Objectives and control strategy

Different studies (Geurts et al., 1996; Luckham and Ukeje, 1999; Tzitzinou et al., 2000; do Amaral et al., 2005; Arevalillo et al., 2006) proved that the final product properties of emulsion polymers depend upon the entire PSD and cannot be entirely captured with a small number of moments of the distribution. Hence, the focus of this project is the control of the full PSD rather than the control of specific moments of the distribution.

The large variety of emulsion polymerisation processes that can be implemented, the vast number of possible PSD profiles that can be produced and the complexity of the process, makes an empirical model for the process difficult to build and eventually not sufficiently robust. This is why a first principles model was chosen to carry out the current control studies.

The model used in these studies was built for the copolymerisation of VAc and BuA in a semi-batch reactor (Immanuel et al., 2002, 2003), but can also be implemented to other emulsion polymerisation systems. The cases where ionic and non-ionic surfactants are employed were considered. Also the use of redox and thermal initiators were both accounted for (Sweetman et al., 2006). The model is based on population balance equations (PBEs). A PBE is used to simulate the evolution in time t of the particle density function $F(r,t)$ for different values of the particle size and give us the PSD evolution:

$$\frac{\partial}{\partial t}F(r,t) + \frac{\partial}{\partial r}\left[F(r,t)\Re_{growth}(r,t)\right] = \Re_{nuc}(r,t) + \Re_{coag}(r,t) \tag{1.1}$$

The internal coordinate in equation 1.1 is the particle radius r. The three major phenomena that drive the evolution of the PSD are all embedded in this equation through the rates $\Re_{growth}(r,t)$, $\Re_{nuc}(r,t)$ and $\Re_{coag}(r,t)$.

The solution technique used to solve the model is based on a method for the solution of population balance models known as hierarchical two-tier algorithm (Immanuel and Doyle III, 2003a). As the name suggests, the numerical solution is based on two tiers. During the first tier the rate of nucleation, growth and coagulation in equation 1.1 are calculated and used to update the PSD in the second tier. The PSD is updated at each time step till the end of the batch. At each iteration the particle density function $F(r,t)$ is computed in each

of the 250 bins of 2 nm used to discretise the particle size domain in the range 0-500 nm. The structure of this algorithm constitutes also a natural framework for the implementation of the so-called multi-level discretisation technique (Sun, 2004; Sun and Immanuel, 2005), which was implemented to further reduce the computation time.

In this thesis, a model-based control strategy was developed starting from the PSD model and solution technique introduced above with the aim of controlling the full particle size distribution. Optimisation-based control strategies to produce optimal feed profile to match target PSDs were developed. Surfactant, initiator and monomers feed policies were used as manipulated inputs. First, an optimisation strategy for the computation of the optimal recipes was chosen. It was selected between different gradient-based optimisation strategies, which showed to be able to solve the family of non-convex problems generated by the system. This was followed by a series of open-loop control studies aimed at tuning the optimisation routine. Direct and hierarchical control of the PSD were both carried out. The hierarchical strategy is based on the underlying correlation between PSD, solids content and total number of particles of the latex. This allows control of the PSD through the inferential control of the other two variables. The use of the hierarchical control framework required the implementation of a multi-objective optimisation strategy.

Controllability analysis was done through feedback schemes on different PSD profiles. Measurement limitations and process constraints may prevent the implementation of in-batch feedback corrections and make the batch-to-batch strategy a necessary and valuable alternative. Batch-to-batch feedback control loops were tested on the system. The inferential control of the rheology was also considered as a case study to demonstrate the applicability of the optimal control developed for the direct control of a latex property. For the inferential control, a two-loop control, one for the computation of the PSD producing the desired end-product property and one for the computation of the optimal recipe to produce the required PSD, needs to be implemented.

Sensitivity studies were also carried out on the model to determine key parameters and possible model uncertainties. An optimisation-based parameter estimation routine was implemented following the experimental validation of one of the optimisation results. A gradient-

based optimisation technique was again tested and showed good capability in handling the complex non-convex problems associated with the emulsion polymerisation process.

1.4 Thesis structure

In this section a brief introduction to the other chapters composing this thesis is supplied to guide the reader through them:

Chapter 2: This chapter will contain most of the background information and literature review needed to follow the progress of the research project presented in this thesis. A limited, but in the attempt thorough, overview of the emulsion polymerisation processes will be supplied. Process modelling and model solution techniques for systems described by population balance equations will be analysed. The model and the solution technique specifically used in this work will be presented more in detail. Considerations on optimisation strategies, state/parameter estimation approaches and control techniques, applied to emulsion polymerisation and related processes, will be presented. They will be used as an introduction to the control strategies and optimisation results contained in chapters 3, 4 and 5.

Chapter 3: The process of selection of the optimisation routines employed in the open-loop control of the process, alongside a description of the hierarchical strategy implemented, will be presented in this chapter. A description of the single-objective and multi-objective pareto optimisation frameworks employed will be followed by the presentation of the open-loop optimal recipes produced and corresponding match with PSD, solids content and number of particles targets. The efficiency of the different decision variable and objective function combinations when applied to the control of the process will be analysed. The different strategies are applied to the semi-batch emulsion copolymerisation of Vinyl Acetate (VAc) and Butyl Acrylate (BuA). The use of different combinations of non-ionic/ionic surfactant and redox/thermal initiator is accounted for. The same system was also used in the studies presented in chapters 4 and 5 (Bianco and Immanuel, 2006a,b).

Chapter 4: In-batch feedback controllability issues due to process constraints, such as irreversibilities and measurement limitations, will be discussed in this chapter. These process limitations make the batch-to-batch strategy a valuable alternative to in-batch feedback control in those cases when in-batch corrections are not feasible. The implementation of the batch-to-batch strategy for model parameter update purposes will be presented. The suitability of PSD control for the inferential control of the rheology of emulsion latexes will also be demonstrated (Immanuel, Wang and Bianco, 2008).

Chapter 5: Starting from experimental results a sensitivity analysis approach and an optimal parameter identification strategy for model update will be formulated. In the attempt to reduce model uncertainties and account for process disturbances, experimental PSD profiles will be used as target for parameter estimation. A description of the experimental facilities and operating procedures implemented will be supplied.

Chapter 6: In this final chapter the outcomes of this research project will be summarised and the major contributions outlined. Starting from them, a path for future work will be drawn, so that further advancements can be achieved in this area.

1.5 Claims and novel findings

Optimisation formulations for the computation of input trajectories towards target PSDs were identified in this thesis for the emulsion polymerisation process and sets of optimal decision variables were selected and successfully implemented to achieve the desired distributions. A wide range of results showing the efficacy of both direct optimisation strategies and hierarchical approaches were presented in two publications (Bianco and Immanuel, 2006a,b), with more results presented in this thesis. The optimisation routines were validated for a range of different operating conditions and emulsion polymerisation systems. Gradient-based routines were implemented successfully for the solution of the highly nonlinear problems, characterised by discontinuities, typical of PSD optimisation and control problems in particulate processes.

A novel inferential strategy based on the individual control of number, size and magnitude

of the PSD modes was developed for the control of the latex rheology and proposed for the first time in (Immanuel, Wang and Bianco, 2008). A quantitative relation between PSD, solids content and viscosity of the polymer was integrated into the existing model and the rheology of the polymer latex was controlled via regulation of the nucleation events and initial growth rates, based on a hierarchical approach.

Limitations in the in-batch feedback controllability of specific PSDs were identified in the form of process irreversibilities, measurement delays and input constraints. A batch-to-batch control routine based on a dynamic recipe optimisation followed by model update through parameter identification was successfully implemented in cases where the in-batch strategy was not applicable. The results of these controllability studies and of the batch-to-batch control strategy implementation were first presented in the paper (Immanuel, Wang and Bianco, 2008).

An optimal recipe was implemented experimentally, and the results presented in this thesis. The ability to match the simulated profile with the experimental PSD proved the efficacy of the parameter identification strategy for model update proposed in (Immanuel, Wang and Bianco, 2008), when a detailed mechanistic model is used for the feedback control of the process.

Chapter 2

Background to the Project: the Underlying Blocks

In this chapter, an overview on emulsion polymerisation is initially provided, followed by background information on emulsion polymerisation modelling and population balance equation solution techniques. The PSD model implemented in the current control studies and its solution technique will be analysed and explained more in detail. A brief summary on optimisation and control of PSD in particulate processes, and their implementation in emulsion polymerisation, will also be presented.

2.1 The emulsion polymerisation process

2.1.1 Introduction

A number of synthetic polymer latexes are prepared through emulsion polymerisation processes such as synthetic rubber, foams, paints, adhesives, additives for construction materials, sealants, only to mention some of them. Emulsion polymerisation is a free-radical chain polymerisation. It is a non-homogeneous polymerisation technique where an organic phase is dispersed in an aqueous solution to form a colloidal system. The colloidal particles dispersed in the aqueous phase are the main locus for the polymerisation reaction.

In emulsion polymerisation processes both the polymerisation rate and molar mass of the

polymer can be simultaneously increased unlike in bulk, solution or suspension polymerisation, in which an attempt to increase the polymerisation rate generally leads to a reduction in the molar mass. This is a consequence of the compartmentalised nature of the process, where polymerisation loci are isolated through the aqueous medium. Water also acts to maintain a low viscosity of the reaction bulk and has good heat transfer capacity, which is advantageous in particular for highly exothermic polymerisation reactions. Emulsion polymerisation produces water-borne latexes, which are an ideal alternative to solvent-borne polymer products, which production has generated growing environmental concerns. The Tronmsdorff gel effect, common in bulk polymerisation processes, is reduced in emulsion polymerisation. This effect results in a large increase in the polymerisation rate due to the reduced viscosity of the reaction bulk, which prevents the active sites of the growing polymer chains from coming close to each other and terminate. It may result in a run-away process, with consequent difficulties in the removal of the generated heat of reaction and control of the product properties.

All the reactions, namely initiation, propagation, termination and chain transfer, that characterise free-radical polymerisations take place in emulsion polymerisation and need to be accounted for. The compartmentalisation typical of emulsion polymerisation processes constitutes the major difference compared to other polymerisation techniques. This heterogeneity causes the partitioning of the different components between four major phases. These are the particle phase, the aqueous phase, the monomer droplets and the micellar phase. Eventually, in the final stage of the process, when micelles that did not generate particles and monomer droplets have disappeared, only two phases are left.

To understand the process, we need to understand how the different variables that can influence the evolution of the system, such as, initiator, surfactant and monomer type and concentration, mode and rate of addition of the reactants, temperature, mixing rate, relates to the mechanisms and kinetics of emulsion polymerisation. The latter include phenomena such as formation, growth and coagulation of the polymer particles, evolution of particle size and number, change in molar mass and mass distribution of the polymer and polymerisation rate profile (Lovell and El-Aasser, 1997).

2.1.2 Formulation components

The main formulation components in a typical emulsion polymerisation are:

- polymer particles (2 nm - 1 μm), which are the primary locus for polymerisation reaction
- live polymer chains, which grow by free-radical chain polymerisation by adding monomer molecules to their active reaction sites
- monomer droplets (1-10 μm), *i.e.* aggregates of monomer molecules that constitute the reservoir for polymer particles (monomer diffuses from the droplets to the polymer particles through the aqueous phase)
- surfactant, which stabilises polymer particles and monomer droplets through adsorption at the particle-water interface
- micelles, which are aggregates of surfactant molecules that swell with monomer and can provide a site for particle nucleation

Water constitutes the continuous phase. It maintains a low viscosity and provides a medium for good heat transfer. Besides monomers, water and surfactants, other fundamental ingredients are initiators and chain transfer agents (CTA). Chain transfer agents are used primarily to control the molar mass of the polymer. Initiators are used to produce the free-radicals that start the polymer chain reaction.

Surfactant (also called emulsifier) can either be used for the creation of the reaction locus, in the form of monomer swollen micelles, or be used to stabilise existing polymer particles and monomer droplets. Usually, during the process of evolution of the particle size distribution, surfactant redistributes in the system. It is released from disappearing droplets and micelles that have not been initiated and used to stabilise growing polymer particles. The most commonly used surfactant is anionic surfactant, but also cationic and non-ionic emulsifier are used. In the first two cases, particles are stabilised by electrostatic forces. Anionic and cationic surfactants are amphiphilic molecules that can distribute at the particle-water surface with their hydrophilic head directed towards the aqueous phase and their lipophilic tail dissolved into the particle (organic) phase. Electrically charged polymer particles with

the same polarity are then formed, which repulse each other and limit coagulation. Upon aggregation of particles, particle surface charge density will increase. When they have reached a certain size, these particles will acquire a sufficiently high surface charge density to maintain their colloidal stability, and thus further coagulation ceases. Coagulation is particularly common over a short period of time after nucleation due to the small size and the low surface charge of the first nuclear particles.

Non-ionic surfactants operate instead by steric hindrance and they are usually large polymer molecules that act by building a uniform layer around the particles. This increases the distance of separation between the core particles and decreases their chance to coagulate. Special cases are constituted by reactive surfactant, used in special applications to enhance certain properties of the final latex, such as reduced desorption during film formation and reduced water sensitivity of the latex films, and water-soluble surfactant, used to impart stability for example against added electrolyte and mechanical shear.

Initiation usually involves two stages. In the first stage the initiator molecule generates free radicals. In the second stage this radical reacts with a monomer molecule and produces a primary radical with an active centre where further mononer molecules can add by chain polymerisation reaction. Anionic initiators, such as sodium or potassium persulfate, are the most commonly used. They generate free radicals by homolytic scission of a single bond, which is usually caused by heat (thermal initiation) or γ-radiation. Redox initiators are usually composed of two components, an oxidising and a reducing agent, and radicals are formed by transfer of a single electron to or from an ion or molecule. This second strategy is often used for polymerisation processes carried out at low temperature since it does not need thermal activation. Oil-soluble initiators may also be used, for example when trying to reduce the amount of unreacted monomer or to control the morphology from within the particles.

CTAs are used to decrease the molar mass and molar mass distribution of the polymer latex through chain transfer reactions. Chain transfer reactions terminate the growth of a propagating chain and generate a new radical, which can then react with a monomer molecule to initiate the growth of a new polymer chain. Mercaptans are often used as CTA. Other than

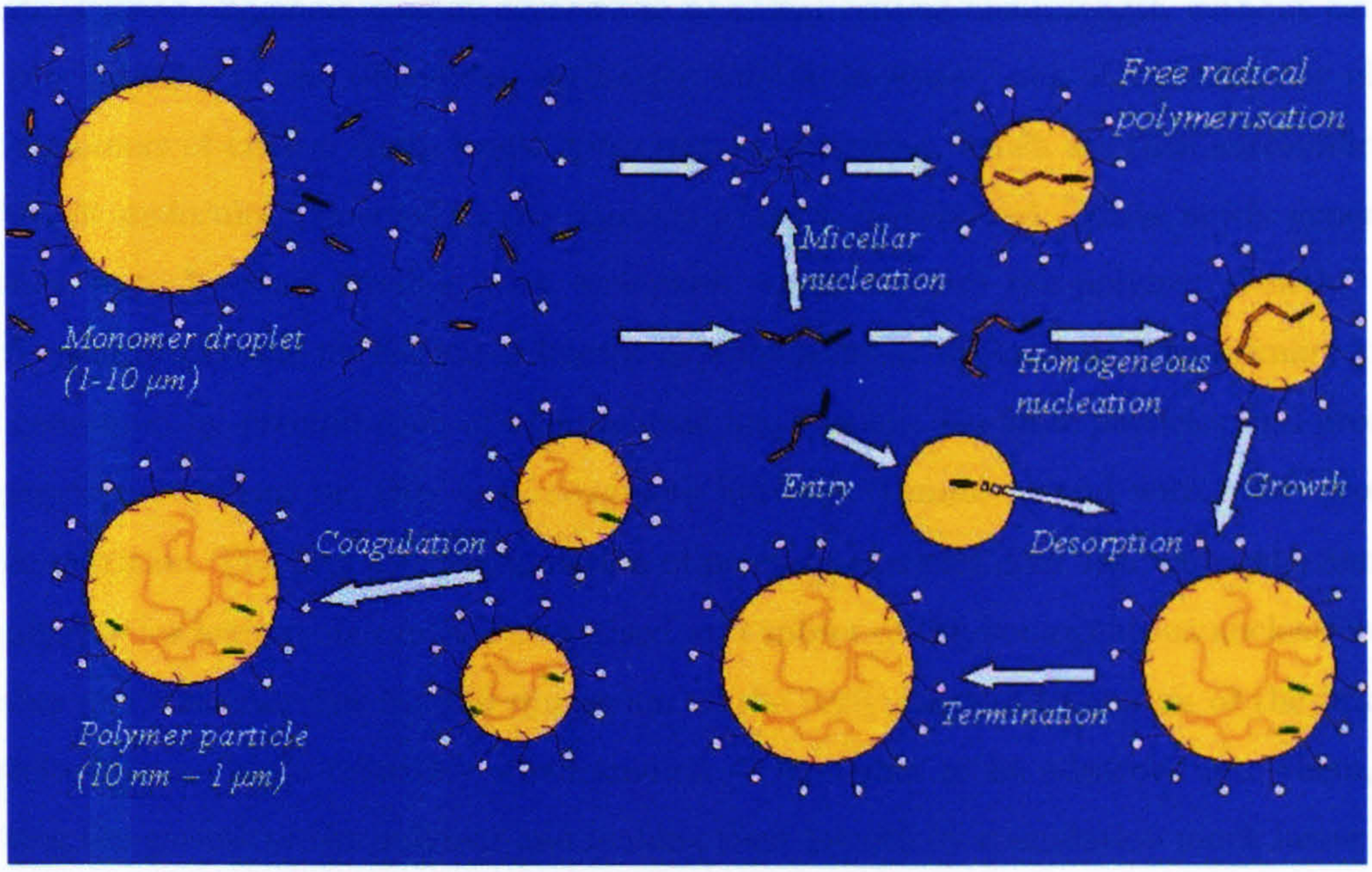


Figure 2.1: Emulsion polymerisation process.

CTAs, also other formulation components, such as monomers and surfactants, can undergo chain transfer reactions (Lovell and El-Aasser, 1997).

2.1.3 Particle nucleation, growth and coagulation

The main phenomena driving the evolution of the particle number, size and distribution in emulsion polymerisation are nucleation, growth and coagulation of the polymer particles. Upon mixing of monomer, surfactant and water, the bulk of the monomer will form droplets, stabilised by surfactant. The rest of the surfactant will tend to aggregate and form micelles, which will swell with monomer by diffusion from the monomer droplets. When the initiator is added to the system, they form free radicals that start the chain polymerisation reaction (Lovell and El-Aasser, 1997). A schematic of the process is shown in figure 2.1.

Free radicals generated in the aqueous phase from initiators may propagate through ad-

dition of monomer molecules dissolved in the aqueous phase to give oligomers. The chain length of these oligomers cannot exceed the so-called critical chain length without causing the precipitation of the oligomers, no longer soluble in water, out of the aqueous phase. The oligomers of critical chain length form primary particles, which are then surrounded by surfactant molecules dispersed in the aqueous phase and stabilised. These newly generated polymer particles start swelling with monomer, which sustains the polymer growth. This mechanism of particle nucleation is known as homogeneous nucleation. The primary particles generated by precipitation of oligoradicals may remain as stable particles and grow by propagation reactions or, they may coagulate between themselves and with other growing stable particles. The process of coagulation of primary particles goes also under the name of coagulative nucleation. It can be categorised as a subset of the homogeneous nucleation and it takes place because the limited dimension at the early stage of formation of the primary particles allows only a relatively small amount of monomer to be adsorbed into them, this limiting the growth of the polymer and making their growth by coagulation much faster than by propagation reactions.

Another way to nucleate polymer particles is known as micellar nucleation. Micellar nucleation takes place when the growing oligomer before reaching the critical chain length is adsorbed inside a micelle and forms a polymer particle. Generally only one micelle in every 100-1000 captures a primary radical or oligoradical and become a polymer particle. The rest of the micelles disappear, redistributing surfactant and monomer to the existing polymer particles. Micellar nucleation terminates when micelles disappear, after which the number of particles usually remains constant. It may eventually decrease due to instability of some of the polymer particles because of insufficient surfactant, with resulting coagulation of the particles. They may also increase in number after the disappearance of the micelles because of the release of surfactant molecules from disappearing droplets and/or particles, causing further nucleation by micelle formation.

When the surfactant concentration is above the critical micelle concentration (cmc), micellar nucleation is the main source of polymer particles. The cmc is the concentration of surfactant above which micelles are formed. On the other hand, homogeneous nucleation

could occur even when the concentration of the surfactant is below the cmc or in surfactant-free systems. It is more prevalent generally at the very early stages of a batch emulsion polymerisation, usually by the first minute of the process.

Also a third way, droplet nucleation, is possible but its contribution is usually negligible in standard emulsion polymerisations while it is considered predominant in processes like miniemulsion (Tang et al., 1991) and microemulsion (Kuo et al., 1987) polymerisation. For this reason, only micellar and homogeneous nucleation are accounted for in the model implemented in this project. In droplet nucleation the primary radicals and oligoradicals enter the monomer droplets and start a propagation reaction. A large number of small-size droplets, compared to the larger droplets in standard emulsion polymerisation, compete effectively for radicals in miniemulsion and microemulsion polymerisation.

Polymer particles, once formed, swell with monomer diffusing from the monomer droplets. The rate of diffusion of monomers from droplets into particles is larger than the particle phase rate of polymerisation. Hence, in the presence of droplets, particles are saturated with monomers and the maximum polymer growth rate is registered. These monomer-swollen polymer particles are the main sites for polymer growth, which takes place by addition of monomer to the growing polymer chains.

Polymer particles can coagulate by aggregation of smaller polymer particles to form larger particles. Particle breakage is not common in emulsion polymerisation and it is generally neglected. Stable colloidal systems can be defined as those in which the particles remain dispersed as single entities for long periods of time. The addition of surfactants and physical stresses imposed to the colloidal particles, such as the stir or shear of the system, both influence the aggregation phenomena.

In addition to nucleation, growth and coagulation, there are other important events that occur during emulsion polymerisations. These are the entry of aqueous phase oligomers into polymer particles, the desorption of monomeric chains formed by chain transfer within the particles back into the aqueous phase and the termination (by combination and disproportionation) within the particles.

2.2 Emulsion polymerisation modelling

2.2.1 Population balance modelling

As specified in section 1.2.1, different approaches can be followed when modelling emulsion polymerisation. A number of mathematical models have been proposed in the literature for the PSD evolution in emulsion polymerisation (Min and Ray, 1974; Penlidis et al., 1985; Dougherty, 1986b,a; Rawlings and Ray, 1988a,b; Coen et al., 1998; Herrera-Ordóñez and Olayo, 2000a,b; Zeaiter et al., 2002b; Immanuel et al., 2003; Doyle III et al., 2003; Fortuny et al., 2005; Park et al., 2005; Vale and McKenna, 2007; Yano et al., 2007; Sood, 2008).

In the first attempts to model the PSD in emulsion polymerisation processes, the authors made use of well-known distributions (e.g. normal, log-normal, Poisson, binomial) to represent polymer particle size distributions with an analytic form. However, this approach requires many restrictive approximations. Yano et al. (2007) built a pure stochastic model, but the capability of this kind of approach may also be restricted and the resulting mathematical description of the system be accurate only for specific operating conditions. This is the reason why most of the work on the modelling of emulsion polymerisation has been carried out in the last decades employing first principles (pure mechanistic) or hybrid models. Often these models have been based on PBEs. This derives from the need for a more accurate description of the phenomena involved in emulsion polymerisation (i.e. nucleation, growth and coagulation), of the way they are linked and of the effect of the available decision variables on them. Nowadays, population balance modelling is the most common tool used to predict the evolution of polymer particle size distribution (Saldívar et al., 1998; Coen et al., 1998; Melis et al., 2000; Immanuel et al., 2002; Meadows et al., 2003; Vale and McKenna, 2005a; Park et al., 2005; Sood, 2008), as well as to describe the dynamics of several other particulate processes, such as crystallisation, granulation and fermentation. The general structure of a PBE is given below

$$\frac{\partial}{\partial t}F(r,t) + \frac{\partial}{\partial r}\left[F(r,t)\Re_{growth}(r,t)\right] = \delta(r - r_{nuc})\Re_{nuc}(r,t) + \Re_{coag}(r,t) \tag{2.1}$$

with the particle size r considered as the internal coordinate. The terms $\Re_{nuc}(r,t)$, $\Re_{growth}(r,t)$,

$\Re_{coag}(r,t)$ are the rate of nucleation, growth and coagulation, respectively.

Tacking a step back, as already specified in section 1.2.1, it is possible to divide particle distribution models in two categories: level-one or particle number models and level-two or PSD models. The first family of models considers the system as monodisperse, with all the particles having the same average size (Richards et al., 1989; Gao et al., 2002). A review on monodispersed approximation models can be found in Dubé et al. (1997).

Level-two models are instead based on PBEs and consider the system as constituted by a distribution of particles of different sizes. When the PSD modelling approach is followed, mass balances are written over the concentration of particles of a given size at a given time and kinetic terms are included for the nucleation, growth and coagulation of particles. This last approach is nowadays the most commonly used. Vale and McKenna (2005a) clearly stated that advances in the modelling of emulsion stability and the availability of more and more sophisticated numerical solution algorithms will make PBEs an even more widespread tool for the modelling of emulsion polymerisation. More detailed considerations on the difference between particle number and PSD models can be found in Dubé et al. (1997) and Gao et al. (2002).

A detailed overview on population balance modelling and its application to emulsion polymerisation and other particulate processes can be found in the book by Ramkrishna (2000). Kiparissides (2006) highlighted the difficulties arising from the numerical solution of PBEs, while Vale and McKenna (2005a) pointed out as major obstacle to a more widespread use of PBEs for the modelling of PSD the lack of detailed physical models of source terms such as coagulation. They also quoted van Herk and German (1998) and their concerns for the uncertainties arising in emulsion polymerisation modelling.

Fortuny et al. (2005) provided a quantitative description of the nucleation stage in batch processes using an hybrid approach. They showed that during the early stage of the nucleation, a large number of short-lived particles are formed. Before coagulating onto larger particles, they contribute for a short period to an accelerated rate of polymerisation. Nucleation occurs very quickly and takes place usually in the early stage of emulsion polymerisation, generating the need to account simultaneously for different complex mechanisms in a short

period of time (El-Aasser and Sudol, 1997). Experimental and theoretical studies on the underlying mechanisms of nucleation (Harkins, 1945, 1946; Hansen and Ugelstadt, 1978; Lichti et al., 1983; Feeney et al., 1984; Hounslow et al., 1988; Giannetti, 1993; Gilbert, 1997; Coen et al., 2004; Fortuny et al., 2005), growth (Lichti et al., 1977; Hounslow et al., 1988; Giannetti, 1990; Kusters et al., 1992; de Arbina et al., 1996) and coagulation (Lowry et al., 1984, 1986; Hounslow et al., 1988; Litster et al., 1995; Chern and Kuo, 1996; Mayer et al., 1996; Chern et al., 1997; Unzueta and Forcada, 1997; Kemmere et al., 1998; Melis et al., 2000; Lattuada et al., 2004) have been carried out and resulted in various mathematical descriptions of these phenomena.

An extensive review on the modelling of emulsion polymerisation was first presented by Min and Ray (1974). They were among the first to develop a comprehensive model that considered the whole spectrum of mechanisms postulated for emulsion polymerisation to calculate the full PSD in a population balance framework, including also particle coagulation. More recently, Saldívar et al. (1998) have developed a comprehensive and generalised model for PSD and MWD, employing the pseudo-homopolymerisation approximation (Storti et al., 1989). In their model they neglected particle coagulation.

Most of the models mentioned in this section are built over mono-dimensional PBEs. Vale and McKenna (2005a) developed a two-dimensional PBE model to describe simultaneously the evolution of PSD and composition of the polymerising particles. A three-dimensional population balance model was implemented by Poon et al. (2008) to granulation processes. Other examples of multi-dimensional PBEs applied to particulate processes can be found in Ma et al. (2002a); Verkoeijen et al. (2002); Immanuel (2004) and Pinto et al. (2007). A comprehensive review on the challenges arising from the use of multi-dimensional PBEs is given by Ramkrishna and Mahoney (2002).

2.2.2 Zero-one/pseudo-bulk kinetics and pseudo-homopolymerisation approach

The underlying kinetics in emulsion polymerisation can be modelled using two different approaches. These are known as zero-one and pseudo-bulk kinetics. The zero-one approach

is typical of, but not limited to (Ballard et al., 1984), systems characterised by sufficiently small particles, where entry of a radical in a particle that contains a growing radical results in instantaneous termination, so that either zero or one radical is present at a time in the particle. It is usually applicable at low conversion, when the Trommsdorff gel effect is less significant. In a zero-one system, radical termination and desorption rates are high, while the overall entry rate is low, causing the rapid disappearance of a polymer radical as soon as another radical adsorbs into the particle (Lovell and El-Aasser, 1997).

One way of modelling these systems is to consider the existence of only particles carrying zero or one radical (Lichti et al., 1977). Another approach consists in considering the particle population with one radical further divided in two families, the one with monomeric radicals, still able to desorb, and the one with a polymeric radical (Coen et al., 1998; Gilbert, 1997; Coen et al., 2004). Gilbert and co-workers have developed a series of tests to verify whether the zero-one kinetics applies to a given system (Casey et al., 1994; Maeder and Gilbert, 1998; Prescott, 2003). For example, a necessary, but not sufficient condition, is that the average number of radicals per particle $\bar{n} \leq 0.5$ (Vale and McKenna, 2005a).

According to Giannetti (1993), when implementing the zero-one kinetic to describe the PSD dynamic we neglect the contribution of latex particles with more than one growing radical and this causes the model to produce physically unreliable results. So, while we can neglect the contribution to the system kinetics from particles with more than one radical (when $\bar{n} \leq 0.5$), we need to account for their contribution to the PSD evolution, with their presence resulting in a broader PSD compared to the one predicted by the zero-one approach.

Even if characterised by some limitations, the zero-one modelling approach has proven to be of great value in mechanistic studies of emulsion polymerisation (Vale and McKenna, 2005a). Gilbert's group have extensively applied this approach to the emulsion polymerisation of styrene to investigate the mechanism of particle formation (Coen et al., 1998; Gilbert, 1997). Doyle's group implemented modified versions of Coen et al. (1998) model to control the PSD in styrene semi-batch emulsion polymerisation (Crowley et al., 2000; Meadows et al., 2003). Zeaiter et al. (2002b) exploited Coen et al. zero-one kinetics and implemented the resulting model to predict the evolution of PSD and MWD in a semi-batch process. Their

model predictions were confirmed experimentally on an automated reactor facility described in Zeaiter et al. (2002a). A distributed parameter model that implements the zero-one kinetics is also that of Saldívar et al. (1998), who developed an extensive model for PSD and MWD.

Also Chen and Wu (1988) implemented a zero-one model, in this case applied to a copolymerisation process. Based on previous work on emulsion homopolymerisation systems by Lichti et al. (1977), they developed a mathematical model to describe the PSD evolution. They implemented the same equations created by Lichti et al. (1977) for homopolymerisation systems to copolymerisation systems using appropriate combinations of kinetic parameters of the co-monomers.

A similar approach for the modelling of copolymer systems was proposed by Storti et al. (1989) and named pseudo-homopolymerisation approach. As in Chen and Wu (1988), they created an approximation procedure to reduce the kinetics of an emulsion polymerisation involving any number of monomer species to that typical of homopolymerisation processes. When in a system we have several monomeric species reacting simultaneously, we need to consider the evolution of several particle populations, each characterised by number and type (i.e. free-radical end group) of radicals contained in each particle. To do so, a set of population balances needs to be derived. Storti et al. (1989) reduced this set to a smaller one, for which any particle population is characterised by an overall number of radicals of any type. The model assigns the polymer chains to one type or to the others based on a pseudo-homopolymerisation probability.

Asua and co-workers applied this concept to a continuous loop reactor (Abad et al., 1994; Araújo et al., 2001). Various binary systems and polymerisation strategies were simulated by Saldivar et al. (Saldívar and Ray, 1997b; Saldívar et al., 1998), who validated their model against experimental data on the copolymerisation of styrene and methyl methacrylate. Immanuel et al. (Immanuel et al., 2002, 2003) developed coagulation-free and coagulation-inclusive models for the copolymerisation of vinyl acetate and butyl acrylate in semi-batch reactors. Kammona et al. (2003) also implemented the pseudo-homopolymerisation kinetics to model a copolymerisation reactor and showed good agreement between the PSDs produced by their model and those obtained experimentally.

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As specified before, the emulsion polymerisation kinetics can be simulated, other than through the zero-one approach, also using the pseudo-bulk approximation. Pseudo-bulk kinetics consider the possibility of more than one free radical to co-exist for a significant period of time in the polymer particle. This approach is commonly applied to systems with large particles or that use monomers which propagate very rapidly, such as acrylates. When applying the pseudo-bulk kinetics to the population balance model, we define an average number of radicals over all particles of a certain size. In the population balance formulation, the particle density distribution $F(r,t)$ and the average number of radicals per particle distribution $\bar{n}(r,t)$ are decoupled. The population balance equation in this case will require an expression for the average number of radicals per particle of size (volume) r, $\bar{n}(r,t)$. Different strategies for the computation of this expression were reviewed by Vale and McKenna (2005a).

Immanuel et al. (2002) derived the average number of radicals/particle $\bar{n}(r,t)$ for particles of a given size r from first principle equations. A global average number of radicals per particle can also be calculated for the whole particle population. Based on this work, an extensive model for PSD and MWD was recently developed by Sweetman and co-workers (Sweetman et al., 2006; Sweetman, 2008) implementing a pseudo-bulk approach.

The number of polymer radicals within the particles depends upon the rate of entry of oligomers from the aqueous phase, the rate of desorption of radicals formed by chain transfer within the particles back into the aqueous phase and the rate of mutual termination of the growing chains within the particles. Smith and Ewart (Smith, 1948; Smith and Ewart, 1949; Smith, 1949) identified three different regimes based on the relative importance of these rates in each one of them. For each regime they defined an expression for the average number of radicals per particle $\bar{n}$. These formulations or the Stockmayer and O'Toole modification (O'Toole, 1965) have been used to formulate a number of lumped parameter models (DeGraff and Poehlein, 1971; Kiparissides et al., 1979; Nomura et al., 1982; Mead and Poehlein, 1988; Dimitratos et al., 1989; Richards et al., 1989; Forcada and Asua, 1990; Dimitratos et al., 1991; Urretabizkaia et al., 1992), in which distributions such as PSD and MWD were approximated by moments. A review on lumped parameters modelling can be found in Penlidis et al. (1985).

When moving to distributed parameter systems, Min and Ray (1974) were among the

first to model the entire PSD. In this case, the population density $F_n(r,t)$ was expressed as a function of time and particle size r. $F_n(r,t)$ was used as a measure of the concentration of particles with n growing radicals, of size r, at time t. A generalisation of this model was developed by Rawlings and Ray (1988a,b) and a distributed parameter model was also used by Storti et al. (1989) in their model implementation of the pseudo-homopolymerisation approach. Coen et al. (2004) explicitly took into account both pseudo-bulk and zero-one approach during the period of particle formation in their particle number model of butyl acrylate emulsion polymerisation. They defined a cross-over radius r_{co} as the radius above which termination of radicals within the particles cannot be considered anymore instantaneous and the pseudo-bulk approximation needs to be implemented.

2.2.3 The process model

The irreversible traits that characterise emulsion polymerisation together with the difficulties in controlling the competitive growth of polymer particles of different sizes (Immanuel and Doyle III, 2004) and the complex interaction between the major phenomena driving the evolution of the PSD, can make corrective control actions not straightforward and, in many cases, also not possible. Furthermore, if control actions are inappropriate and lead to errors, these will carry through the entire batch. For these reasons the development of a model with good predictive ability is essential for application in model-based optimisation and control of emulsion polymerisation processes.

The model used in this project is a pure mechanistic, nonlinear, distributed model developed by Immanuel et al. (2002, 2003). It is a comprehensive population balance model for the evolution of particle size distribution in the emulsion copolymerisation of vinyl acetate (VAc) and butyl acrylate (BuA). The model is designed for a semi-batch reactor. This PSD model applies the pseudo-homopolymerisation approximation (Storti et al., 1989) to the copolymerisation system and implements pseudo-bulk kinetics in modelling the average number of radicals per particle. It is based on the general model structure by Saldívar et al. (1998), with influences from other works (Coen et al., 1998; Crowley et al., 2000). Significant changes were implemented in this model (Immanuel et al., 2002, 2003) compared to those

mentioned above. The formulation of an equation for the average number of radicals per particle based on first principles and the introduction of partitioning equations when using non-ionic surfactants, to account for the absorption of the surfactant into the organic phase, are two of these modifications. As demonstrated by Özdeğer et al. (1997), the partition of surfactant between aqueous phase, organic phase and particle/droplet surface can alter the evolution of the PSD. In Immanuel et al. (2003) the importance of a coagulation inclusive model was pointed out and a kinetic model for the coagulation kernel was developed and included in the original model formulation (Immanuel et al., 2002), showing a qualitative improvement in the match with the experimental data and confirming the importance of particle coagulation even under low solids conditions.

Process (vessel) dynamics were related to the particle-level phenomena in a multi-scale framework, with the process-level particle population driven by nucleation, growth and coagulation. The models for these particle-level phenomena, inferred from kinetic and colloids theory, were expressed in a form that allowed them to be embedded into the process-level model and gives the overall model a multi-scale character. The framework used to embed these models is a population balance equation, which is used to describe the evolution of the PSD. This approach is only one of the possible ways of integrating models at different scales as pointed out by Ingram et al. (2004) in their classification of the methodologies for multi-scale process modelling.

In the original model (Immanuel et al., 2002, 2003) redox initiation was considered, with *t*-butyl hydrogen peroxide (*t*-BHP) and sodium formaldehyde sulphoxylate (SFS) used as redox initiator pair. Redox initiation was chosen because it enables low temperature operation and usually offers better control of the initiation process. Studies on the same system when implementing a thermal initiator were also carried out by Sweetman (2008) due to the wide use of this type of initiators in industry. The original model was modified by Sweetman (2008) also to account for the use of ionic surfactant, with new assumptions on the surfactant partitioning.

The PSD is simulated using the particle density function $F(r,t)$, where $F(r,t)dr$ is defined as the moles of particles of size between r and $r+dr$ at time t. The particle density function

is embedded in the framework of a population balance equation

$$\frac{\partial F(r,t)}{\partial t} + \frac{\partial}{\partial r}\Big(F(r,t)\Re_{growth}(r,t)\Big) = \delta(r - r_{nuc})\Re_{nuc}(r,t) + \Re_{coag}(r,t) \tag{2.2}$$

with the particle size (particle radii, r) used as the internal coordinate. The internal coordinate is an independent variable used to describe the particle properties and can be the particle size or age, for example. It is distinguished from the external coordinates, which are used to describe the physical space external to the particle. The evolution of the PSD is obtained solving equation 2.2 in terms of the particle density function $F(r,t)$.

In the polymerisation reactor under study, the copolymerisation of VAc and BuA is carried out. In this two-monomer system it is possible to find growing polymer radicals of two types, those with free-radical end group derived from VAc and those with free-radical end group derived from BuA. The particle density function for such a copolymer system, employing two monomers, can be in general expressed through the notation $F_{n_1,n_2}(r,t)$, which shows how this function depends both on the particle size r (continuous variable) and on the number of active radicals of the two types present in each particle (discrete variables). Since n_1 and n_2 can assume theoretically any integer value, it results in coupled systems of PBEs for the various combinations of n_1 and n_2. To simplify the model, an average number of radicals/particle was considered in the various size ranges

$$\bar{n}(r,t) = \frac{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}(n_1+n_2)F_{n_1,n_2}(r,t)}{\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}F_{n_1,n_2}(r,t)} \tag{2.3}$$

and the pseudo-homopolymerisation approach (Storti et al., 1989) was employed to allow the formulation of the new term $F_{\bar{n}}(r,t)$ starting from the expression $F_{n_1,n_2}(r,t)$. At this stage another simplification is possible and is achieved lumping the distribution along the discrete dimension n. This allows the decomposition of the two-dimensional distribution into two one-dimensional distributions: $F(r,t)$ and $\bar{n}(r,t)$. The evolution of the first of these two distributions results from the solution of equation 2.2, while the second is calculated from the following new PBE for the average number of radicals/particle $n(r,t)$

$$\frac{\partial}{\partial t}(\bar{n}(r,t)) = \Re'_{entry}(r,t) - \Re'_{desorption}(r,t) - 2\Re'_{termination}(r,t) \tag{2.4}$$

In the model of Immanuel et al. (2002) a population balance framework is used to embed and calculate the number of radicals/particle, avoiding the simplifications introduced by earlier models and incorporating the size-dependence of $\bar{n}$.

$\Re'_{entry}(r,t)$, $\Re'_{desorption}(r,t)$, $\Re'_{termination}(r,t)$ are the entry rate of aqueous phase oligomers into a single particle of size between r and $r+dr$, the rate of desorption of monomeric radicals (radicals of chain length 1) from a single particle of size between r and $r+dr$, and the rate of termination inside a single particle of size between r and $r+dr$, respectively

$$\Re'_{entry}(r,t) = \sum_{l=0}^{j_{cr}-1} \sum_{i=1}^{2} e_i^l(r) p_{wi} \left[P_w^l\right] \tag{2.5}$$

$$\Re'_{desorption}(r,t) = \sum_{j=1}^{2} k_{dM_j}(r) \frac{\sum_{i=1}^{2} k_{trij} p_i n(r,t) \left[M_j\right]_p}{k_{dM_j}(r) + \sum_{i=1}^{2} k_{pji} \left[M_i\right]_p} \tag{2.6}$$

$$\Re'_{termination}(r,t) = \frac{k_{tav} n(r,t)^2}{V_p(r) N_A} \tag{2.7}$$

$e_i^l(r)$ is the entry rate constant of oligomers of type i (*i.e.* free-radical end group derived from a monomer of type i (VAc or BuA in the current system)) and length l into a particle of radius r. p_{wi} is the probability of a radical being of type i in the aqueous phase and $\left[P_w^l\right]$ is the molar concentration of oligomers of length l in the aqueous phase. k_{dMj} is the rate of desorption of monomeric radicals of type j, k_{trij} is the chain transfer rate of a polymer radical of type i with a monomer of type j, where p_i is the probability of the polymer radicals to be of type i in the particle phase, n is the number of polymer radicals in the particle and $\left[M_j\right]_p$ is the molar concentration of monomers of type j in the particle phase. k_{pji} is the rate of propagation of polymer radicals of type j with monomer of type i. k_{tav} is the pseudo-homopolymer rate constant for termination and $V_p(r)$ is the volume of unswollen particles of radius r.

The three key determining phenomena that define the PSD are nucleation, growth and coagulation and these three events are accounted for in equation 2.2 through the terms

$\Re_{nuc}(r,t)$, $\Re_{growth}(r,t)$, $\Re_{coag}(r,t)$, which are the rates of nucleation, growth and coagulation, respectively.

The rate of nucleation is given by

$$\Re_{nuc} = \Re_{homogeneous} + \Re_{micellar} \tag{2.8}$$

where $\Re_{homogeneous}$ and $\Re_{micellar}$ are the rate of homogeneous and micellar nucleation. The rate of homogeneous nucleation is expressed as follows

$$\Re_{homogeneous} = k_{pav}^{w}\left[P_{w}^{j_{cr}-1}\right]V_{aq} \tag{2.9}$$

with

$$k_{pav}^{w} = \sum_{i=1}^{2}\sum_{j=1}^{2} k_{pij}^{w} p_{wi}\left[M_j\right]_w \tag{2.10}$$

which is the pseudo-homopolymerisation rate constant for propagation in the aqueous phase. $\left[P_{w}^{j_{cr}-1}\right]$ is the molar concentration of oligomers of length $j_{cr}-1$ in the aqueous phase and V_{aq} is the volume of the aqueous phase. k_{pij}^{w} is the rate of propagation of polymer radicals of type i with monomer of type j in the aqueous phase and $\left[M_j\right]_w$ is the molar concentration of monomers of type j in the aqueous phase.

The rate of micellar nucleation is given by

$$\Re_{micellar} = \sum_{l=0}^{j_{cr}-1}\sum_{i=1}^{2} e_{i,micelle}^{l} p_{wi}\left[P_{w}^{l}\right]C_{micelle}V_{aq} \tag{2.11}$$

where

$$e_{i,micelle}^{l} = 4\pi r_{micelle}^{n} N_A D_{wi}\ , \qquad l = 0,1 \tag{2.12}$$

$$e_{i,micelle}^{l} = \frac{4\pi r_{micelle}^{n} N_A D_{wi}}{\sqrt{l-1}}\ , \qquad l = 2,...,j_{cr}-1 \tag{2.13}$$

are the entry rate constants in micelles for an oligomer chain of length 0 or 1 (2.12) and between 2 and $j_{cr}-1$ (2.13), respectively. $r_{micelle}$ is the micelle radius and D_{wi} is a model

parameter. In equations 2.9 and 2.11 the concentration, in the aqueous phase, of oligomers of chain length up to $j_{cr} - 1$ needs to be supplied. Material balances are used to calculate these concentrations. In equation 2.11 is also necessary to define the following terms

$$p_{w1} = \frac{\left(k^w_{p21} + k^w_{tr21}\right)\left[M_1\right]_w}{\left(k^w_{p21} + k^w_{tr21}\right)\left[M_1\right]_w + \left(k^w_{p12} + k^w_{tr12}\right)\left[M_2\right]_w} \tag{2.14}$$

$$C_{micelle} = max\left(0, \frac{(S_w - cmc)\alpha_{m,s}}{4\pi r^2_{micelle}}\right) \tag{2.15}$$

which represents the probability factor for the aqueous phase (2.14) (probability that a radical is of type 1 in the aqueous phase) and the micelle concentration (2.15). k^w_{pij} and k^w_{trij} are the rate constants for propagation and chain transfer to monomer in the aqueous phase, respectively. The probability factor comes from the application of the pseudo-homopolymerisation approach to the model formulation. This factor also appears in other expressions such as the pseudo-homopolymerisation rate constant for propagation. S_w is the free-surfactant concentration and $\alpha_{m,s}$ is the area occupied by a surfactant molecule.

The rate of growth is given by

$$\Re_{growth}(r,t) = \frac{dr}{dt} = \frac{1}{4\pi r^2 \rho_p} \sum_{i=1}^{2}\sum_{j=1}^{2} k_{pij} p_i \frac{n(r,t)}{N_A}\left[M_j\right]_p MW_j \tag{2.16}$$

where

$$p_1 = \frac{(k_{p21} + k_{tr21})\left[M_1\right]_p}{(k_{p21} + k_{tr21})\left[M_1\right]_p + (k_{p12} + k_{tr12})\left[M_2\right]_p} \tag{2.17}$$

is the probability factor for the particle phase (probability that a radical is of type 1 in the particle), and k_{pij} and k_{trij} are the rate constants for propagation and chain transfer to monomer in the particle phase. ρ_p is the density of the polymer and MW_j is the molecular weight of monomer j. $\Re_{growth}(r,t)$ is the growth rate of polymer chains inside the particles,

which is different from the growth rate in the aqueous phase. Inside the particles polymers propagate at much higher rates compared to those in the aqueous phase, due to the higher concentration of monomer inside the particles. Only this growth rate is considered since most of the monomer molecules are consumed within the particle phase.

The last term to define in equation 2.2 is the coagulation rate

$$\Re_{coag}(r,t) = H(r_{upper} - r)\Re_{formation}(r,t) - H(r_{cut-off} - r)\Re_{depletion}(r,t) \tag{2.18}$$

which is calculated as difference between the rate of formation and the rate of depletion of polymer particles into and from, respectively, a bin of size between r and $r + dr$. Each term is multiplied by the Heaviside function (which is unity when the argument is non-negative and zero otherwise), with r_{upper} and $r_{cut-off}$ that are, respectively, the maximum size of particles that could result from the coagulation of smaller particles and the size below which the particles tend to coagulate. The modelling of the coagulation event involves integral terms. The rate of formation is given by

$$\Re_{formation}(r,t) = \frac{1}{V_{aq}} \int_{r'=r_{nuc}}^{\frac{r}{2^{(1/3)}}} \beta(r^{'},r^{''})F(r^{'},t)F(r^{''},t)\frac{r^2}{\left(r^3 - (r')^3\right)^{2/3}}dr^{'} \tag{2.19}$$

while the rate of depletion is expressed through the equation

$$\Re_{depletion}(r,t) = \frac{1}{V_{aq}} \int_{r_{nuc}}^{r_{max}} \beta(r,r^{'})F(r,t)F(r^{'},t)dr' \tag{2.20}$$

where r, $r^{'}$ and $r^{''}$ are the radii of the two coagulating particles, and r_{nuc} and r_{max} are the radius of the particle nuclei and the maximum radius for coagulation, respectively.

In both these equations the coagulation kernel $\beta(r,r^{'})$ is given by

$$\beta(r,r^{'}) = c_3\frac{4\pi D_0(r+r^{'})}{W} \tag{2.21}$$

with W that is the Fuch's stability ratio

$$W(r,r^{'}) = (r+r^{'})\int_{D=(r+r')}^{\infty} \frac{e^{\frac{\Psi(D)}{kT}}}{D^2}d(D) \tag{2.22}$$

D_0 the diffusion coefficient and D the distance between the particle centres. The term $\Psi(D)$ represents the net interaction potential

$$\Psi(D) = \Psi_R(D) - \Psi_A(D) \tag{2.23}$$

and k and T are the Boltzmann constant and the temperature.

The net interaction potential is expressed as the difference between the van der Waals attractive potential (A is the Hamaker constant)

$$\Psi_A(D) = \frac{A}{6}\left(\frac{2rr'}{D^2-(r+r')^2} + \frac{2rr'}{D^2-(r-r')^2} + ln\left(\frac{D^2-(r+r')^2}{D^2-(r-r')^2}\right)\right) \tag{2.24}$$

and the repulsive potential, which for a system using non-ionic surfactant is the consequence of steric interaction and can be defined, based on the steric repulsion potential formulation by Israelachvili (1992), as follows (Immanuel et al., 2003)

$$\Psi_R(D) = c_2\frac{2rr'}{r+r'}\frac{100L^2}{\pi}\Gamma^{\frac{3}{2}}kTe^{-\frac{\pi D}{L}} + c_1 \tag{2.25}$$

L is the extensional length of surfactant chain into the aqueous phase and Γ is the surface coverage of the particles with surfactants. c_1 and c_2 in equation 2.25, and c_3 in equation 2.21 are multiplicative and additive correction factors.

All the equations listed above constitute the mathematical model of the emulsion polymerisation reactor, together with material balances for initiator, monomers and aqueous phase oligomers (ODEs), and partitioning equations for monomers and surfactant (algebraic equations). Fortran language was used to code the model. The complete model and more detailed explanations of its assumptions can be found in Immanuel et al. (2002, 2003). Various recipes have been tested employing the above model. There are slight discrepancies between the simulation results obtained using the model stated above and the experimental results, but these can be attributed to parametric uncertainties and possible process disturbances. To account simultaneously for both these parametric and experimental uncertainties, Immanuel and Doyle III (2003c) used a combined parameter/state estimation technique.

As already mentioned, the original model described above was modified by Sweetman

(2008) to account for the use of ionic surfactant and thermal initiation. Sodium Dodecyl Sulfate (SDS) and sodium persulfate were considered as emulsifier and initiator, respectively. This case and the one considered in the original model are only two of the various scenarios that can be simulated with the implemented model through modulation and reformulation of the rate equations and partitioning equations. Homopolymerisations as well as copolymerisations, and the use of different sets of monomers can also be accounted for.

When using an ionic surfactant such as SDS, its partitioning is limited to the particle/droplet surface and the aqueous phase. Also, surfactant influence all the three major phenomena driving the evolution of the PSD, *i.e.* nucleation, growth and coagulation. Of these three, the most sensitive to the nature of the surfactant employed is the coagulation. When moving from a non-ionic to an ionic surfactant, the forces of interaction between the particles change and go from steric interaction to electrostatic interaction. The coagulation rate expression used in Sweetman (2008) was derived from Coen et al. (1998) and is based on the Healy-Hogg extension of the DLVO theory (Hogg et al., 1966; Wiese and Healy, 1970). The attractive force between particles is given by the van der Walls interaction and expressed, as in Immanuel et al. (2002), through the Hamaker attractive potential. The repulsion potential between two curved surfaces electrically charged is used to define the repulsion potential between the particles and is expressed through the Healy-Hogg-Fursteneu equation (Hogg et al., 1966)

$$\Psi_R = \frac{\epsilon r_{si} r_{sj}(\zeta_i^2 + \zeta_j^2)}{4(r_{si} + r_{sj})} \left[\frac{2\zeta_i \zeta_i}{\zeta_i^2 + \zeta_j^2} \ln\left(\frac{1 + e^{-kL}}{1 - e^{-kL}}\right) + \ln(1 - e^{-2kL}) \right] \tag{2.26}$$

In this equation ϵ is the permittivity of the water, and r_s and ζ are the swollen radius and the zeta potential of the particles.

2.3 Solution algorithm

2.3.1 PBE numerical solution methods

Population balance equations may be seen as hyperbolic balance laws with special source terms (Ramkrishna, 2000). The application of population balance modelling to a system re-

sults in a mathematical description based on partial differential equations or integro-partial differential equations (the integral arising from the coagulation rate term in emulsion polymerisation) (Immanuel and Doyle III, 2003a). The solution of the dynamic PBE is a notably difficult problem. Difficulties arise from numerical complexities and model uncertainties in the source terms embedded in the PBE (Alexopoulos et al., 2004). The high computational load associated with these equations derives both from the terms that appear in the PBE (complex integrals) and from the calculations involved in the phenomenological laws (*e.g.* the coagulation term has to be computed for each combination of the particle pairs). The solution of population balance equations usually involves the discretisation of the internal coordinate domain into a number of discrete elements, which results in a system of stiff, nonlinear differential or algebraic/differential equations solved numerically (Kiparissides, 2006). Solving these equations numerically presents two major challenges (Vale and McKenna, 2005a):

- the hyperbolic nature of the PDE leads to numerical dispersion and/or numerical diffusion (propagation of the errors through the approximating mesh when a continuous differential equation is discretised, which results from the inaccuracy of the interpolation in space and time)
- any error in the computation of the rate functions affect the final solution

The difficulties faced when solving PBEs limited their application in the past, but advances in computation techniques have made these equations applicable nowadays to more and more complex systems. The use of PBEs may constitute a great contribution to the design and control of these processes. Reviews on the available numerical methods for the solution of population balance equations can be found in different papers (Rawlings et al., 1993; Immanuel and Doyle III, 2003a; Attarakih et al., 2004). Validation against analytical solution of simpler cases has to be performed whenever a new solution technique is presented. Several numerical methods have been developed to solve steady-state and dynamic PBE. They include, based on the classification of Alexopoulos et al. (2004), the full discrete method (Hidy, 1965), the method of classes (Marchal et al., 1988; Chatzi and Kiparissides, 1992), the discretised PBE method (Hounslow et al., 1988; Litster et al., 1995; Kumar and

Ramkrishna, 1997), the fixed and moving pivot discretised PBE methods (Kumar and Ramkrishna, 1996a,b), the sectional method (Gelbard et al., 1980), the high order discretised PBE methods (Bleck, 1970; Gelbard and Seinfeld, 1980; Sastry and Gaschignard, 1981; Landgrebe and Pratsinis, 1990), the orthogonal collocation on finite elements (Gelbard and Seinfeld, 1979; Rigopoulos and Jones, 2003), the Galerkin method (Nicmanis and Hounslow, 1998), the wavelet-Galerkin method (Chen et al., 1996), the hierarchical two-tier algorithm (Immanuel and Doyle III, 2003a), and the spline collocation method (Eyre et al., 1988; Steemson and White, 1988). Comparative studies of the different numerical methods (Kostoglou and Karabelas, 1994; Nicmanis and Hounslow, 1996; Zhang et al., 1999) and more detailed description of these solution techniques (Rawlings et al., 1993; Kumar and Ramkrishna, 1996a; Ramkrishna, 2000; Vanni, 2000; Ramkrishna and Mahoney, 2002) can be found in the open literature.

Attarakih et al. (2004) grouped the numerical methods for the solution of PBEs into four categories: method of moments, stochastic methods, higher order methods and zero-order methods. From a computational point of view the method of moments (Mitra et al., 1998; Diemer and Olson, 2002a,b,c) is the most attractive. One ordinary differential equation is used to represent each moment of the distribution (Hulburt and Katz, 1964). It is a perfect method when only the average properties of the population need to be computed. Even if the solution of the resulting system of ODEs is simple, this technique presents some drawbacks starting from the numerical instability arising from the reconstruction of the distribution from its moments (Randolph, 1971) and the intrinsic distribution reconstruction intricacies (Diemer and Olson, 2002a,b). Also, the application of this technique requires the number of moments to be limited. Thus, the definition of a proper closure condition is important. The definition of a cut-off moment limits the number of moments in those cases where certain moments of the distribution depend on higher terms. All these issues often limit this method to smooth and ideally monomodal distributions. Immanuel and Doyle III (2003a) pointed out that there are anyway few exceptions, where the method of moments was used to solve complex models and was able to simulate multi-modal distributions (see, for example Marchisio et al. (2002, 2003) and their quadrature method of moments).

In stochastic methods random values are generated for the identification of the probability functions governing the system behaviour (Ramkrishna, 2000). Stochastic (or probabilistic) methods include the Monte Carlo method (*e.g.* Hollander et al. (2001)), which employs a probability function known as Markov conditional probability. Ramkrishna (2000) pointed out the ability of the Monte Carlo method to predict both average properties and fluctuations of a distribution. Goodson and Kraft (2004) compared the performances of two algorithms for the stochastic simulation of PBEs, namely the direct simulation algorithm (Eibeck and Wagner, 2000) and the mass flow algorithm (Eibeck and Wagner, 2001), when applied to a liquid-liquid extraction process. The great advantage of all stochastic methods is their ability to simulate multivariate PBE with respect to the internal coordinates whenever the application of the other methods would become computationally too expensive.

Immanuel and Doyle III (2003a) distinguished the stochastic methods and the method of moments from a third family of solution techniques, the discretisation methods. Discretisation methods are the most popular techniques for the solution of PDEs, in which category the PBEs fall. Given the full domain of the internal coordinate, these techniques seek to satisfy the PBE only for certain values in this domain. The larger the number of points chosen to reconstruct the PBE, the higher the computational load. This broad group of PBE solution methods also include what were defined as zero and higher-order methods by Attarakih et al. (2004). In fact, discretisation methods can be divided in two categories, the finite difference (FD) method and the method of weighted residuals (MWR), with zero and higher order methods that refer to the different approaches used when implementing the MWR.

The FD method can be used to solve more complex and multi-modal distribution compared to the method of moments. This method is based on the approximation by finite differences of the derivatives with respect to the internal coordinate, usually, or both time and internal coordinate. Based on the order of the finite differences (*i.e.* 1, when using Taylor's expansion, or 2), the PDE can be reduced either to a set of ODEs or of algebraic equations. Drawbacks of this method are that it cannot avoid problems such as spurious oscillations and numerical dispersion in the distributions, which derive from the truncation error introduced in approximating the derivatives. A solution to limit these numerical insta-

bilities was proposed by Ma et al. (Ma et al., 2002a,b). Other than spurious oscillations and numerical dispersion, also closure problems from backtracking may arise when using the FD method (Crowley et al., 1999; Melis et al., 2000). Patankar (1980) also pointed out how number and mass conservation is guaranteed in this method only in the limit of infinite resolution. A comparison of different FD approaches can be found in Wójcik and Jones (1998).

The second type of discretisation methods is the MWR. In this method functions are used to approximate the PBE. As in the finite difference method, the MWR tries to simulate the PBE exactly only in certain points of the independent variable domain. The domain of interest can be considered as a whole or divided in sub-domains and the approximating functions defined in each one of these sub-intervals. The functions used in the MWR are always a combination of basis functions and weighting functions. To avoid using an high degree polynomial, which would arise from the use of a single basis function to cover the whole domain, usually the domain of interest is discretised into sub-intervals (or finite elements (FEs)) and a local basis function is used to simulate the PBE within each FE. Those known in the literature as finite element (FE) methods can then be considered as a subset of the MWR. An example of MWR in which the domain is not discretised into finite elements and a single function is used to simulate the whole PBE can be found in Bhatia and Chakraborty (1992). Usually FE methods allow for more general solutions.

The distinction between zero and higher-order methods by Attarakih et al. (2004) refers to the type of basis function implemented to approximate the PBE in the different FEs, *i.e.* a constant function (zero-order function) or a higher-order function. The aim of the MWR is to drive to zero (minimise) the weighted sum of the residuals between the PBE and its approximation at certain chosen points within each FE. While in the finite difference method only one or both neighboring points of the one we compute the derivative at are utilised, in the MWR all the points in which a single finite element is discretised in are used in the simulation of the PBE. This reduces numerical dispersion and spurious oscillations typical of FD methods.

The MWR is further divided by Immanuel and Doyle III (2003a) into two categories, the collocation techniques and the Galerkin's method. In the collocation methods orthog-

onal polynomials are used as basis functions and the Dirac delta function as the weighting function. When the basis functions are orthogonal polynomials this method takes the name of orthogonal collocation on finite elements (OCFE) (see, for example Gelbard and Seinfeld (1978); Crowley et al. (2000) and Immanuel et al. (2002)). Also other basis functions can be employed in the collocation techniques. An example can be found in Liu and Cameron (2001), who used orthonormal wavelets to approximate the PBE in each FE. Also, moving finite elements techniques have been proposed (Rawlings and Ray, 1988a) to reduce the number of FEs and limit the risk of incurring in closure problems. The Galerkin's method differs from the collocation techniques because it implements the same function as basis and weighting functions (Nicmanis and Hounslow, 1996, 1998; Godin et al., 1999; Chiu and Christofides, 1999; Mahoney and Ramkrishna, 2002). Mahoney and Ramkrishna (2002) pointed out some of the advantages of the MWR:

- convergence on the entire distribution
- availability of adaptive mesh techniques

and its disadvantages:

- inability to capture discontinuities
- computational overhead arising from double integral evaluations in Galerkin's formulations

The independent variable lumped is usually the internal coordinate and after its lumping the PDE is reduced to a set of ODEs in time. Sometimes the time is discretised and the discretisation of the PBE in time results in a set of ODEs in the internal coordinate. When this approach is followed, the discretisation method takes the name of Rothe's method. This method has been successfully applied by Wulkow et al. (2001) to simulate a PSD model for crystallisation processes. Also, the width of the finite elements in discretisation methods is usually fixed *a priori* and kept constant throughout the simulation. But, in the attempt to reduce the computation time, different researchers recognised the need for adaptive mesh sizes (Rawlings and Ray, 1988a; Rawlings et al., 1993; Wulkow et al., 2001).

A special sub-class of discretisation techniques are those used to solve the aggregation/breakage problem. The terms accounting for these phenomena are integral expressions, so the PBE becomes an integro-partial-differential equation (Hounslow et al., 1988; Kumar and Ramkrishna, 1996a; Lee, 2001) when aggregation/breakage phenomena are included. Kumar and Ramkrishna (1996a) presented a detailed review on this class of problem. In this and in the sequel publication (Kumar and Ramkrishna, 1996b), they implemented a fixed and moving pivot technique. The pivotal point was defined as the point in each finite element where the newly formed coagulating or breaking particles are assigned after one of these size changing event takes place. The appropriate redistribution of the newly formed particles allows to preserve the properties of two moments of interest (*e.g.* number and mass of particles). Kumar and Ramkrishna (1997) were also able to handle sharp discontinuities by allowing the discretisation to move or deform with particle growth. Discontinuities may be present due to the hyperbolic nature of the system and arise from the initial distribution or nucleation (Mahoney and Ramkrishna, 2002).

Other papers have dealt with the solution of different special cases of PBE arising from the modelling of various processes (Rubisov and Papangelakis, 1997; Bennett and Rohani, 2001; Hamilton et al., 2003; Kiparissides et al., 2004; Vale and McKenna, 2005b; Hu et al., 2005b,a; Dorao and Jakobsen, 2008). Most of the papers mentioned so far try to solve mono-variate PBEs. In many cases certain characteristics of the system under study are largely influenced by more than a single internal variable. This generates the need for multi-variate PBEs. Different solution techniques for multi-dimensional PBEs have been proposed and can be found in the literature, of which the method of classes (Puel et al., 2003a,b; Gerstlauer et al., 2001), the finite differences, finite elements and spectral method (Mantzaris et al., 2001a,b,c, 2002), the finite volumes method (Ma et al., 2002a; Gunawan et al., 2004), the Galerkin's method (Gelbard and Seinfeld, 1978) and the hierarchical two-tier algorithm (Immanuel, 2004; Immanuel and Doyle III, 2005; Pinto et al., 2007) are examples. Challenges and requirements in the solution of multi-dimensional PBEs are reviewed by Ramkrishna and Mahoney (2002). As already said, when solving higher-dimensional PBEs stochastic methods also constitute a valid alternative to more complex and computational demanding numerical

techniques (Henson et al., 2002). Applications of Monte Carlo simulations to the solution of multivariate PBE systems can be found in Kostoglou and Konstandopoulos (2001); Lin et al. (2002); Adityawarman et al. (2005) and Voigt et al. (2005).

There is always a fine balance between the need for accuracy of the solution and the speed in the computation, with the latter that becomes crucial, for example, in model-based online control strategies. The fact that such a large number of numerical techniques has been used to solve the PBE highlight the inherent difficulties in obtaining accurate and stable numerical solutions for this equation (Alexopoulos et al., 2004). An extensive review on PBE solution techniques applied to emulsion polymerisation can be found in Vale and McKenna (2005a).

2.3.2 Hierarchical two-tier algorithm and multi-level discretisation

The solution technique used to simulate the model implemented in the project (Immanuel et al., 2002, 2003) is the hierarchical two-tier algorithm (Immanuel and Doyle III, 2003a). It is a finite volume (FV) method and presents features compared to previous techniques that make it a valid and efficient alternative to other proposed methods. The sixth order implicit Simpson method is employed to integrate the PBE in each FV. To capture with greater fidelity the PSD the FE width chosen is considerably lower than normal (Crowley et al., 1999).

Advantages of the FV technique compared to other solution methods are summarised by Vale and McKenna (2005a)

- the difficulties related to the hyperbolic nature of the PBE (dispersion and dissipation) are subdued by the use of high resolution scheme
- the FV method ensures that the number of particles is conserved
- point sources, such as particle nucleation, can be easily treated
- the FV is fully compatible with the simple yet efficient discretisation methods developed for particle aggregation (*e.g.* Kumar and Ramkrishna (1996a))

A major drawback when solving PBEs is the difficulty of decoupling the time-dependent rates from the time-dependent variables (Attarakih et al., 2004). This problem is solved by

Immanuel and Doyle III (2003a) through the implementation of a two-tier strategy. In this two-tier integration framework, the computation of the rates and the update of the PSD are performed in two subsequent steps (two-tier). The time-dependent variable particle density $F(r,t)$ is computed solving a system of ODEs and algebraic equations based on the values of the source terms computed off-line. A complete scheme of the hierarchical two-tier algorithm is provided in figure 2.2.

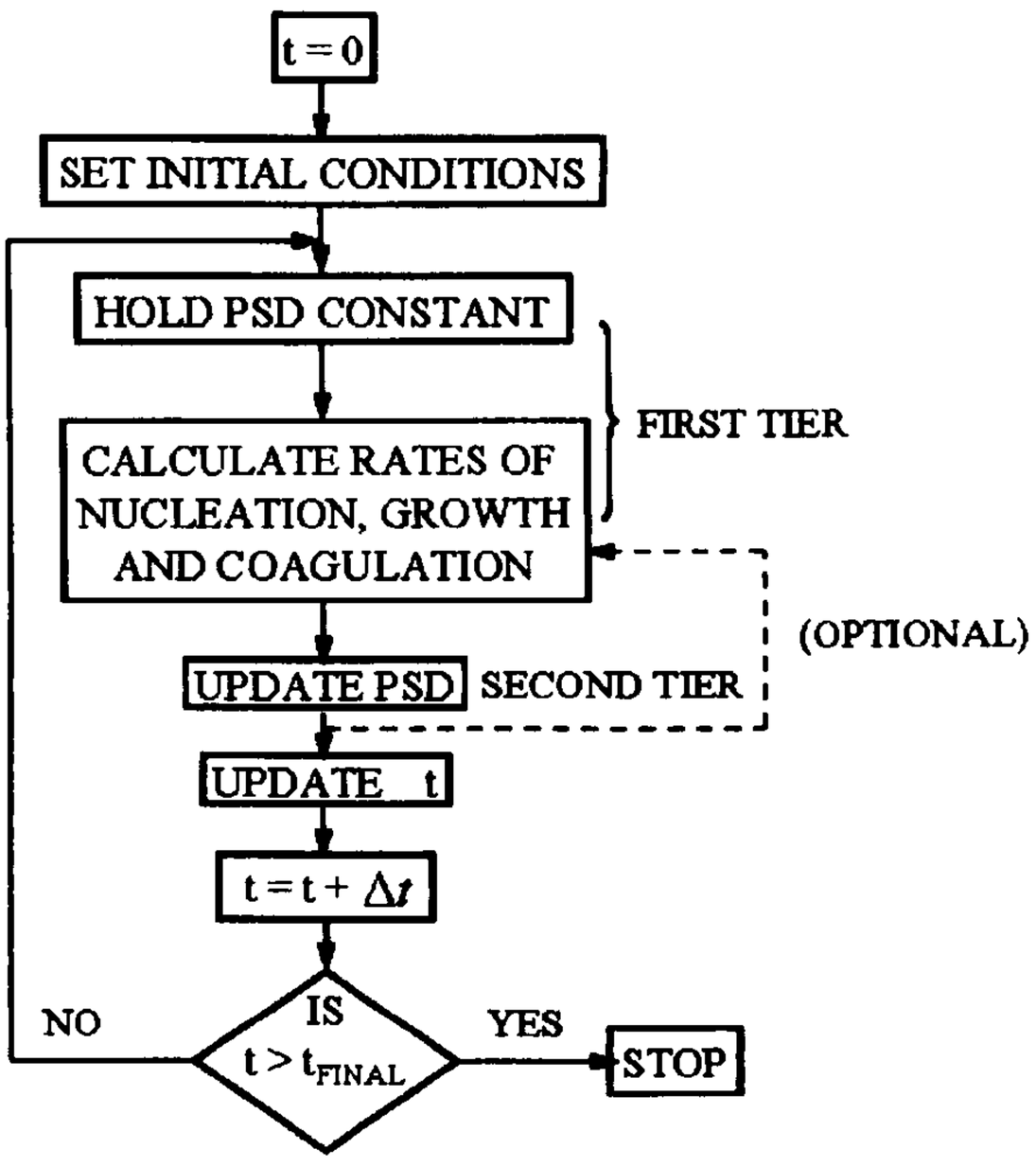


Figure 2.2: Schematic of the hierarchical two-tier algorithm.

The hierarchical two-tier algorithm has the same two-tier structure as some model reduction strategies (*e.g.* Pope (1997)). The two-tier model reduction is achieved through the understanding of the interplay between nucleation, growth and coagulation. The method is based on a hierarchical strategy that employs the individual rates of nucleation, growth and coagulation to update the PSD. Hence, in solving the PBE this algorithm can effectively decompose fast and slow kinetics and this reduces the stiffness in the solution of the equation.

This method is not based on the discretisation of the PBE, but on the re-formulation of population balances in each FE (or bin) after the discretisation of the population along the

particle size domain. The entire set of ODEs and algebraic equations is effectively divided in two sub-sets, those used for the computation of the source terms and those deriving from the re-formulation of the PBE. This reduces the associated stiffness in the solution, which derives from the huge disparity in the time constants of the nucleation, growth and coagulation events. Also, no approximation is necessary for the derivatives, resulting in a reduction of the truncation-related instabilities.

The ability to pre-process the computationally intensive coagulation term also partly contribute to the efficiency of the technique. The coagulation kernel is computed employing a semi-analytical solution method that reduces the computational load and, at the same time, ensures preservation of the particles mass and the consistency of the number of particles as in Hounslow et al. (1988) and Kumar and Ramkrishna (1996a,b), subject to the assumption of a uniform particle density within each bin. In this case the particles are not considered as concentrated all in one point of the FE (pivot point), but as uniformly distributed within each FE (*i.e.* constant particle density in each FE), making this approach more similar to a second strategy also presented in Kumar and Ramkrishna (1996a).

Time domain and particle size domain are both discretised. The algorithm is structured in two tiers, solved at each time step. In the first, the rates of nucleation, growth and coagulation are calculated individually for each FE, while holding the PSD constant. During the second, these rates are used to update the PSD. Each time step $\triangle t$ is divided in four sub-intervals. While the rates are computed at each sub-interval, the PSD is updated only at the end of each main time interval. This is re-iterated at each time step $\triangle t$. An optional loop in which the updated PSD is used to recalculate the rates of nucleation, growth and coagulation can also be implemented.

$\Re_{nuc}(r,t)$, $\Re_{growth}(r,t)$ and $\Re_{coag}(r,t)$ are modelled through appropriate material balances and partitioning equations. Some of these expressions are ODEs, some are algebraic equations, resulting in a system of DAEs. Different methods can be used to solve each one of these two categories of equations. Immanuel and Doyle III (2003a) apply a fourth order predictor-corrector technique to compute the ODEs and an iterative solution strategy coupled with Newton-Raphson methods to solve the algebraic equations.

Once calculated the rate of nucleation, growth and coagulation, the PSD is updated in the second tier using the following expression

$$\begin{aligned} F_{new,1} &= F_1 - F_1\frac{rb_1 - ri_1}{\Delta R_1} + (\Delta t/4)(14\Re_{nuc,1} + 64\Re_{nuc,2} + 24\Re_{nuc,3} + 64\Re_{nuc,4} \\ &+14\Re_{nuc,5})\left(\frac{1}{45}\right) + (\Delta t/4)(14\Re_{formation_{1,1}} + 64\Re_{formation_{1,2}} \\ &+24\Re_{formation_{1,3}} + 64\Re_{formation_{1,4}} + 14\Re_{formation_{1,5}})\left(\frac{1}{45}\right) \\ &-(\Delta t/4)(14\Re_{depletion_{j,1}} + 64\Re_{depletion_{j,2}} + 24\Re_{depletion_{j,3}} + 64\Re_{depletion_{j,4}} \\ &+14\Re_{depletion_{j,5}})\left(\frac{1}{45}\right) \end{aligned} \tag{2.27}$$

for $j = 1$ and

$$\begin{aligned} F_{new,j} &= F_j - F_j\frac{rb_j - ri_j}{\Delta R_j} + F_{j-1}\frac{rb_{j-1} - ri_{j-1}}{\Delta R_{j-1}} \\ &+H(j_{upper} - j)(\Delta t/4)(14\Re_{formation_{j,1}} + 64\Re_{formation_{j,2}} + 24\Re_{formation_{j,3}} \\ &+64\Re_{formation_{j,4}} + 14\Re_{formation_{j,5}})\left(\frac{1}{45}\right) \\ &-H(j_{cut-off} - j)(\Delta t/4)(14\Re_{depletion_{j,1}} + 64\Re_{depletion_{j,2}} + 24\Re_{depletion_{j,3}} \\ &+64\Re_{depletion_{j,4}} + 14\Re_{depletion_{j,5}})\left(\frac{1}{45}\right) \end{aligned} \tag{2.28}$$

for $j = 2, ..., N$, with j representing the bins of the size domain. F_j is the particle density function and ΔR_j the width of the finite element (bin) j. $\Re_{nuc,j}$ is the nucleation rate at the jth time sub-step, and $\Re_{formation_{i,j}}$ and $\Re_{depletion_{i,j}}$ are the rate of formation and depletion of the particles in and from the finite element i, at the time sub-step j. The two radii rb_j and ri_j are the upper boundary of FE j and the representative size for FE j, respectively. The representative radius ri_j is the cut-off particle size in FE j defined such that all particles above that size in this FE will move onto the next FE at the next time step. This cut-off size is calculated using the expression

$$\begin{aligned} ri_j^3 &= rb_j^3 + (\Delta t/4)(14\Re_{growth_{j,1}} + 64\Re_{growth_{j,2}} + 24\Re_{growth_{j,3}} + 64\Re_{growth_{j,4}} \end{aligned}$$

$$+14\Re_{growth_{j,5}})\left(\frac{1}{45}\right) \tag{2.29}$$

and is used to compute the terms in equations 2.27 and 2.28 that accounts for the polymer particles growth. The expressions 2.27 and 2.28 are obtained through the integration of the PBE (2.2) using, as integration strategy, the implicit sixth order Simpson method. This integration strategy is also used to derive equation 2.29.

The hierarchical two-tier algorithm was used to solve the PSD model in section 2.2.3 and the results found by Immanuel and Doyle were encouraging. In Immanuel and Doyle III (2003a) a comparison with the orthogonal collocation on finite elements (OCFE) is presented showing the drastic reduction in computation time that derives from the implementation of this technique. They solved the same model in orders of magnitude shorter time than using the OCFE, without any considerable loss in accuracy of the solution. The discretisation of the model results in approximately 510 ordinary differential equations and 30 algebraic equations, which were solved in 37 s on a SunBlade 1000 processor (800 MHz processor with 1GB memory) for a batch spanning 150 min, when implementing an adaptive step size strategy.

An analysis of the sensitivity of the different sub-processes of nucleation, growth and coagulation to the discretisation of the particle size domain was carried out by Sun and Immanuel (Sun, 2004; Sun and Immanuel, 2005). It showed that the coagulation sub-model, while being the most computational intensive, is also the least sensitive to the discretisation of the internal coordinate. On the other hand, the growth sub-model seemed to be quite sensitive to the level of discretisation, with numerical diffusion errors that increase sensibly with the increase of the finite element widths. The nucleation sub-model, being restricted to the smallest bin, does not give any considerable contribution to the numerical error.

Starting from these considerations a multi-level discretisation approach was developed (Sun, 2004; Sun and Immanuel, 2005), where different widths of the FEs were used to discretise the particle size domain. This discretisation technique was implemented within the hierarchical two-tier algorithm to solve the population balance model (Immanuel et al., 2002, 2003). A finer grid was used to compute growth rate, material balances and partitioning

equations, to ensure the accuracy of the computation, while a coarser grid was chosen to calculate the coagulation rate as a way to reduce the computational load while retaining the accuracy limits obtained based on a finer discretisation.

Each one of the FEs at the finer level can be seen as a sub-division of the element at the coarser level. The PSD (probability density function) is updated at the coarser level only for the coagulation event

$$\begin{aligned} F^c_{new,i} &= F^c_i + H(i_{upper} - i)(\Delta t/4)(14\Re_{formation_{i,1}} + 64\Re_{formation_{i,2}} \\ &\quad +24\Re_{formation_{i,3}} + 64\Re_{formation_{i,4}} + 14\Re_{formation_{i,5}})\left(\frac{1}{45}\right) \\ &\quad -H(i_{cut-off} - i)(\Delta t/4)(14\Re_{depletion_{i,1}} + 64\Re_{depletion_{i,2}} + 24\Re_{depletion_{i,3}} \\ &\quad +64\Re_{depletion_{i,4}} + 14\Re_{depletion_{i,5}})\left(\frac{1}{45}\right) \end{aligned} \tag{2.30}$$

while is updated at the finer level for the nucleation and the growth events

$$\begin{aligned} F^f_{new,1} &= F^f_1 - F^f_1\frac{(rb_1 - ri_1)}{\Delta R_1} + (\Delta t/4)(14\Re_{nuc,1} + 64\Re_{nuc,2} + 24\Re_{nuc,3} + 64\Re_{nuc,4} \\ &\quad +14\Re_{nuc,5})\left(\frac{1}{45}\right) \end{aligned} \tag{2.31}$$

$$F^f_{new,i} = F^f_i - F^f_i\frac{(rb_i - ri_i)}{\Delta R_i} + F^f_{i-1}\frac{(rb_{i-1} - ri_{i-1})}{\Delta R_{i-1}} \tag{2.32}$$

The superscripts c and f in the above equations refer to the coarser and finer level of the size domain discretisation. It is important to transfer information between these two levels. This is obtained implementing the following equations

$$\begin{aligned} F^c_{new,1} &= F^c_1 - F^f_{N_{FE}}\frac{Growth_{N_{FE}}}{\Delta V_{N_{FE}}} + (\Delta t/4)(14\Re_{nuc,1} + 64\Re_{nuc,2} + 24\Re_{nuc,3} \\ &\quad +64\Re_{nuc,4} + 14\Re_{nuc,5})\left(\frac{1}{45}\right) - H(1_{cut-off} - 1)(\Delta t/4)(14\Re_{depletion_{1,1}} \\ &\quad +64\Re_{depletion_{1,2}} + 24\Re_{depletion_{1,3}} + 64\Re_{depletion_{1,4}} \\ &\quad +14\Re_{depletion_{1,5}})\left(\frac{1}{45}\right) \end{aligned} \tag{2.33}$$

$$
\begin{aligned}
F^{c}_{new,j} \;=\; & F^{c}_{j} - F^{f}_{(j-1)N_{FE}} \frac{Growth_{(j-1)N_{FE}}}{\Delta V_{(j-1)N_{FE}}} + F^{f}_{jN_{FE}} \frac{Growth_{jN_{FE}}}{\Delta V_{jN_{FE}}} \\
& + H(j_{upper} - j)(\Delta t/4)(14\Re_{formation_{j,1}} + 64\Re_{formation_{j,2}} + 24\Re_{formation_{j,3}} \\
& + 64\Re_{formation_{j,4}} + 14\Re_{formation_{j,5}}) \left(\frac{1}{45}\right) \\
& - H(j_{cut-off} - j)(\Delta t/4)(14\Re_{depletion_{j,1}} + 64\Re_{depletion_{j,2}} + 24\Re_{depletion_{j,3}} \\
& + 64\Re_{depletion_{j,4}} + 14\Re_{depletion_{j,5}}) \left(\frac{1}{45}\right)
\end{aligned} \tag{2.34}
$$

for the first and subsequent FEs, respectively, to transfer information from the finer to the coarser level and update the PSD on the coarser level. Following the same strategy the equation

$$
F^{f}_{corrected,i} \;=\; F^{f}_{new,i} \frac{F^{c}_{new,j}}{\sum_{k=1}^{N_{FE}} F^{f}_{new,k}} \tag{2.35}
$$

is used to recalculate the particle density, at each finer grid of the coarser bin, once it has been updated at the coarser level, generating a two-way interaction between discretisation levels. $Growth_{jN_{FE}}$ and $\Delta V_{jN_{FE}}$ are the integrated growth rate and volume for the coarser bin j, which are computed from the growth rates and volumes at the finer level.

The computation time required to implement the hierarchical two-tier algorithm using the two-level/two-way discretisation is considerably reduced compared to the original algorithm, while retaining the accuracy of the solution. This strategy was implemented using two grids fixed *a priori*, a finer one with a constant FE width of $\triangle R = 2$ nm and a coarser one with FEs width of $\triangle R = 10$ nm, the last used to compute the coagulation rate. The overall computation time of a typical batch spanning 150 min is 8 s on a Pentium IV, 1.8 GHz processor with 2 GB memory.

2.4 Process Control and Optimisation

2.4.1 PSD control in particulate processes

Particulate processes are widely used and applied in industry for the manufacturing of a large variety of products. Typical applications include crystallisation of proteins, production

of latexes by emulsion polymerisation and aerosol synthesis of titania powders, just to mention some. Particulate processes are characterised by the co-presence of a continuous phase and a dispersed phase strongly interacting with each other and leading to phenomena such as particle nucleation, growth, coagulation, breakage, melting and solidification. The PSD of the particulate (dispersed) phase heavily influences both mechanical and physicochemical properties of the particulate materials. This motivated a growing attention on the control of particulate processes and often resulted in model-based control approaches due to the underlying complexities of the phenomena involved.

A natural framework for the mathematical modelling of PSD in particulate processes is provided by papulation balances (*e.g.* Doyle III et al. (2002); Rawlings et al. (1993); Dimitratos et al. (1994) and Kalani and Christofides (2000)). It usually results in systems of nonlinear partial integro-differential equations describing the rate of change of the PSD. The major drawback in the synthesis of model-based controllers for the nonlinear feedback control of particulate processes is the distributed nature of the PBE. The different solution techniques implemented to derive finite dimensional approximations of these models also typically lead to systems of ODEs of very high order. In the past, these factors made the synthesis of low-order controllers for real-time implementation of feedback controllers not practical (Christofides et al., 2007). It limited researchers to the application of conventional control schemes such as proportional-integral (PI), proportional-integral-derivative (PID) and self-tuning control (Rohani and Bourne, 1989; Dimitratos et al., 1994; Semino and Ray, 1995b), and to controllability and observability theoretical studies on systems described by population balance models (Semino and Ray, 1995a).

In the last decade much effort has been devoted to the development of model-based control strategies for PSD (cell mass distribution in biological systems, crystal size distribution in crystallisation processes, etc.) of crystallisation (Rawlings et al., 1993; Chiu and Christofides, 1999; Ma et al., 1999; Braatz, 2002; Braatz and Hasebe, 2002; Ma et al., 2002b; Shi et al., 2005, 2006; Christofides et al., 2008), emulsion polymerisation (Dimitratos et al., 1994; Crowley et al., 2000; Doyle III et al., 2002; Immanuel and Doyle III, 2003c; Dokucu et al., 2008a), granulation (Gantt and Gatzke, 2004; Wang et al., 2006), fermentation (Zhu

et al., 2000; Schügerl, 2001; Daoutidis and Henson, 2002; Henson, 2003), cellular biological (Stelling et al., 2004), aerosol (Kalani and Christofides, 2000, 2002), thermal spray coating (Li and Christofides, 2004; Li et al., 2004a) processes, due to the enhancements in computational capacities of modern computers and the implementation of solution techniques able to reduce complex population balance models into low-order DAE systems. An overview of recently developed methods for model-based control of particulate processes are presented by Christofides et al. (2008) and Henson (2003). A general approach to the control of systems described by dissipative and hyperbolic PDE arising from the description of spatially distributed processes was developed by Christofides and co-workers (Christofides and Daoutidis, 1998; Armaou and Christofides, 2002).

Some of the major challenges in the development of distribution control methodologies for a particulate process are

- limited degrees of freedom, thereby necessitating optimal strategies
- complexity of the underlying optimisation problem deriving from non-convexity and possible discontinuities in employing a multi-scale process model for control
- sparsity of measurements
- complexity in the underlying processes arising from integrated and interacting nature of the particle-level processes and irreversibility traits

When building optimisation/control systems for particulate polymerisation processes, such as emulsion polymerisation, the major problems to address are (Kiparissides, 2006)

- better understanding of process dynamics (through experimentation and mechanistic/stochastic modelling)
- ability to measure and characterise polymer quality variables (via on-line sensors and estimators/observers)
- development of nonlinear model-based predictive controllers with superior performances and constraint handling capabilities

Kiparissides (2006) pointed out that there is still a lack of closed-loop property control in industry for particulate polymerisation processes and underlined the following as the causes

- these processes are highly nonlinear and contain a large number of time-varying kinetic and transport parameters
- modelling of particulate polymerisation systems usually results in nonlinear integro-differential equations of infinite-dimensional nature, which makes their direct implementation in real-time controllers not easy
- on-line measurement of PSD and other important properties such as MWD and copolymer composition distribution (CCD) are difficult to obtain and the available secondary measurements are often not adequate for the accurate inference of these properties
- changes in the manipulated variables can cause opposite reactions on the controlled variables due to the complexity of the process and makes the formulation of a proper objective function challenging, especially when trying to build inferential controls of end-use properties through control of molecular and morphological properties, *e.g.* an attempt to match the desired PSD may result in mismatches with other desired targets, such as solids content or CCD

The model parameter identification is a challenging task. Most of the strategies used rely on lumped parameters, selected using sub-optimal methods. The discrepancies with the experimental data are usually reduced through the adjustment of only few sensitive parameters. This makes the updated model/parameters valid only in the vicinity of the current operating conditions. In light of this, a knowledge-based approach to the problem, based on the actual understanding of the process, the implementation of a detailed mechanistic model and a robust run-to-run model update are crucial aids to the parameter identification. Different strategies have also been proposed to identify the parameters to be updated based on estimability considerations (Asprey and Macchietto, 2000; Li et al., 2004b,c; Gadkar et al., 2005; Kou et al., 2005).

In recent years, the availability of always more accurate mathematical models, solution techniques for complex mathematical systems, advances in on-line measurements (Kammona

et al., 1999) and control theory (Doyle III, 1998; Chiu and Christofides, 1999; Crowley et al., 2000; Christofides, 2001; Valappil and Georgakis, 2002, 2003), created the ground for advancements in the field of nonlinear optimisation and control of PSD in particulate polymerisation processes. Examples of different strategies applied to semi-batch emulsion polymerisation processes for the control of PSD can be found in the literature. They include feed-forward control (Crowley et al., 2000; Immanuel and Doyle III, 2002, 2003c; Meadows et al., 2003; Rajabi-Hamane and Engell, 2007) batch-to-batch strategies (Crowley et al., 2001; Doyle III et al., 2003), on-line model-based control (Liotta et al., 1997a; Park et al., 2004; Zeaiter et al., 2006; Dokucu et al., 2008a,b) and mid-course corrections (Flores-Cerrillo and MacGregor, 2002; Wang and Doyle III, 2004).

2.4.2 Observers and estimators in control applications

The mathematical description of a system is usually not able to reproduce its real evolution due to model-plant mismatches, the presence of time-varying model parameters and of unknown process disturbances. This is where the importance of a state estimator arises when building a real-time optimisation/control application. Observers and estimators supply the fundamental feedback from the process needed to correct modelling errors. Also, they may be used for early detection of undesired reactor conditions that may lead to violation of operating constraints and product quality specifications (Kiparissides, 2006).

In the implementation of feedback control schemes generally only some of the variables of interest in the process (states) are measured online. In an emulsion polymerisation process these generally are basic quantities such as temperatures, pressure and flow rates. The PSD can be measured using techniques such as, for example, turbidity spectra, size exclusion chromatography and dynamic light scattering. Usually PSD measurements are available at a frequency not sufficient for the needs of an accurate online control scheme. Furthermore, important process variables that require more sophisticated analysis such as composition of the bulk and molar mass, molar mass distribution, copolymer composition of the products, and, in general, most of the product quality variables, are often unavailable. If a reasonably accurate mathematical model of the polymerisation process is available it may be possible to

estimate those states that are not available (not measurable or measurable only at certain time) based on the values of those states that are. Some events in emulsion polymerisations are rapid and irreversible and because the measurements are often sparse and delayed, these can be of reduced utility in a feedback control strategy, which then needs efficient state estimation techniques to be implemented.

The state variables can be calculated using a variety of estimation strategies. Among these the Kalman filter (Kalman, 1960; Kalman and Bucy, 1961) has shown to be one of the most popular and powerful techniques. The Kalman filter can be used for noise filtering, estimation of unmeasured states and prediction of future values of states in cases where modelling inaccuracies, process disturbances and limited measurements are present. Dimitratos et al. (Dimitratos et al., 1989, 1991) used an adaptive design of the Kalman filter (hybrid extended Kalman filter) to obtain optimal estimates of the process states in a VAc/BuA emulsion copolymerisation. A reiterative extended Kalman filter (EKF) was also used by Kozub and MacGregor (1992b), who applied it to the online control of a semi-batch emulsion copolymerisation process (Kozub and MacGregor, 1992a). State estimation using extended Kalman filter applied to emulsion polymerisation has also been addressed by several other authors (see, for example Dimitratos et al. (1991); Liotta et al. (1997a) and Astorga et al. (2002)). Applications of Kalman filtering to other polymerisation processes can be found in Ellis et al. (1988) and Adebekun and Schork (1989).

Another state estimation technique extensively applied to optimisation and control problems is based on Luenberger observers (Luenberger, 1966, 1971). The Luenberger observers enable reconstruction of the entire state vector of a system when no measurements or a limited number of them are available. The observer characteristics can be properly selected by the designer to ensure stability and a faster dynamics of the system when applied to a feedback control. A study on Luenberger observers applied to emulsion polymerisation can be found in Fevotte et al. (1998), where considerably accurate estimation of the reaction evolution was achieved using an only approximate physical model of the process. In this study they also underlined many of the issues related to the model-based control of emulsion polymerisation. Kalani and Christofides (1999) applied a nonlinear output feed-back control strategy in com-

bination with a Luenberger-type observer to an aerosol process with simultaneous chemical reaction, nucleation, condensation and coagulation. Immanuel and Doyle III (2003c) applied Luenberger observers to follow the evolution of the full PSD for a VAc/BuA emulsion copolymerisation. The online measurements available to monitor the process were the relative PSD, latex density and feed rates. They underlined the importance of an optimisation-based robust state estimation method and the need for a combined state/parameter estimation strategy.

Another possible approach to state estimation is the moving (or receding) horizon estimation (MHE) (Allgöwer et al., 1999; Russo and Young, 1999; Rao et al., 2003; Wang et al., 2003c,b). The MHE is used to determine the current states and unmodelled disturbances from inputs and observed measurements using a moving estimation window of fixed size. The stability that characterises estimation techniques such as Kalman filter and observers has been demonstrated feasible also for the MHE methods, through proper formulation of the problem. Rao et al. (Rao et al., 2001, 2003) investigated MHE strategies for constrained linear state estimation, while Allgöwer et al. (1999) developed optimization strategies to estimate the states of nonlinear systems.

A critical evaluation of EKF and MHE is presented by Haseltine and Rawlings (2005). The MHE allows for incorporation of constraints into the optimisation strategy and uses trajectories of states and measurements rather than values at a single time, as in the EKF. Haseltine and Rawlings pointed out that this leads to an improved state estimation and a greater robustness to both poor guesses of the initial states and tuning parameters compared to the EKF, with the only drawback of a greater computational expense required to solve the MHE optimisation. Another drawback arises from the use of a local optimisation strategy in the MHE framework. To track multiple optima in the estimator, they proposed the use of Monte Carlo particle filters (Chen et al., 2004). Another case in which the EKF was shown to be outperformed by an optimisation-based estimator is presented by Jang et al. (1987).

The EKF is still a valuable and efficient estimation strategy, as demonstrated by Dimitratos et al. (1989, 1991); Ellis et al. (1994); Mutha et al. (1997); Crowley and Choi (1998) and Ahn et al. (1999). Various authors (de Vallière and Bonvin, 1989; Kozub and MacGregor, 1992b) showed that to eliminate the bias from the state estimates in nonlinear Kalman

filtering and make it a more robust strategy, the state vector needs to be augmented with additional stochastic states accounting for the non-stationary disturbances and model mismatches.

Detailed information on the general application of Kalman filter, Luenberger observers, MHE and other state estimation techniques for nonlinear systems can be found in the book on nonlinear process control by Henson and Seborg (1997). A different categorisation of the design methods for nonlinear state estimators can also be found in Soroush (1998). More recent surveys on Kalman filtering, MHE and the simulation-based particle filtering (PF) are those of Haseltine and Rawlings (2005) and Rawlings and Bakshi (2006).

2.4.3 From open-loop to in-batch feedback control in semi-batch emulsion polymerisation

Control of batch/semi-batch emulsion polymerisation reactors can be achieved using two different approaches, namely feed-forward (Crowley et al., 2000; Vicente et al., 2002; Immanuel and Doyle III, 2002, 2003c; Meadows et al., 2003; Rajabi-Hamane and Engell, 2007) and feed-back control (Kozub and MacGregor, 1992a; Saldívar and Ray, 1997a; Liotta et al., 1997a; Echevarría et al., 1998; Crowley et al., 2001; Vicente et al., 2001; Flores-Cerrillo and MacGregor, 2002; Lee et al., 2002; Doyle III et al., 2003; Wang and Doyle III, 2004; Park et al., 2004; François et al., 2005; Zeaiter et al., 2006; Immanuel et al., 2008; Dokucu et al., 2008a,b). Feed-forward are open-loop control systems where the process outputs have no effect on the inputs, while feed-back control systems are implemented in a closed-loop setting with the outputs that affect the inputs in such a way to keep the outputs at the desired value. Control loops react to changes in the controlled system environment, usually to maintain some of its desired states. Feed-forward control systems respond to a measured disturbance in a pre-defined way. The disturbance is measured and fed forward to an earlier part of the control loop so that the corrective action can be initiated in advance of the disturbance having an adverse effect on the system response. Many prerequisites are required to implement a feed-forward control scheme: the disturbance must be measurable, the effect of the disturbance on the output of the system must be known and the time it takes for the disturbance

to affect the output must be longer than the time it takes to the feed-forward controller to affect it. If these conditions are met, feed-forward controllers can be tuned to be extremely effective. Feed-forward control can respond more quickly to known and measurable kinds of disturbances, but cannot do much with novel disturbances. Still, a robust formulation of the open-loop control strategy might be employed to account for possible model errors and potential disturbances (Nagy and Braatz, 2004) and eventually render the feedback control only a means to reduce the conservatism in operation.

Feed-back control deals with any deviation from desired system behaviour, but requires the system's measured variable (output) to react to the disturbance in order to notice the deviation. In feed-back control strategies some proportion of the output signal of the system is fed back to the input. The controller needs some way to measure the process output and requires corrective actions (feed-back actions) to exist (Kailath, 1980) in order to counter the errors introduced in the process and achieve the target output. Feed-back control is often used to control the dynamic behaviour of the system. In process control, the most common general-purpose controller using a feed-back mechanism is the proportional-integral-derivative (PID) controller (Ogunnaike and Ray, 1994).

When initialisation errors, disturbances and model uncertainties (non-ideal operating conditions) are present, open-loop control policies can lead to poor control of the product properties. Corrective feed-back control actions are then necessary to correct optimal open-loop input trajectories in the presence of these non-ideal operating conditions. On the other hand, open-loop control studies are very important because they constitute the base cases to build a closed-loop control system. Optimal open-loop control policies to be implemented in online feed-back control schemes were studied by Saldívar and Ray (1997a) and Kozub and MacGregor (1992a). Immanuel and Doyle III (2003c) highlighted the importance of feed-back corrective actions to account for non-ideal operating conditions, such as model uncertainties and disturbances, in a semi-batch emulsion co-polymerisation process. In their paper, they also analysed the potential for an on-line feed-back control strategy.

Immanuel and Doyle III (2003c) used a multi-objective formulation of the optimisation problem to deal with the conflicting nature of the sub-processes in emulsion polymerisation.

The multi-objective strategy was implemented in open and closed batch-to-batch control loops for the control of the individual processes of nucleation, growth and coagulation following a hierarchical strategy. As an optimisation technique they used the nondominated sorting genetic algorithm (NSGA), a global optimisation technique whose strategy is based on the evolutionary mechanism of biological species.

Another particular optimisation approach was used by Flores-Cerrillo and MacGregor (2002, 2003). They computed control actions through an optimisation algorithm that minimises the 2-norm of the difference, at discrete points, between the target PSD and the profile calculated with a PLS (partial least square) regression model.

Off-line optimisation criteria to derive set of process variable trajectories that are to be applied to the batch in open-loop control scheme were used by Crowley et al. (2000) and Immanuel and Doyle III (2002). Due to the direct implementation of the optimal trajectories calculated off-line these methods need very good process models. Batch-to-batch optimisation methods (Clarke-Pringle and MacGregor, 1998; Crowley et al., 2001; Doyle III et al., 2003) instead overcome this problem by combining reasonably accurate models and the results from previous batches to define the optimal set of operating conditions for the subsequent batches, in a feedback sense. The batch-to-batch control methodology has been used for distribution control of various particulate processes, including emulsion polymerisation (Srinivasan et al., 2001; Doyle III et al., 2003; Lee and Lee, 2003; François et al., 2004; Flores-Cerrillo and MacGregor, 2005; Xiong and Zhang, 2005; Owens et al., 2006).

Model-based batch-to-batch optimisation of PSD in a semi-batch emulsion reactor is realised through a hybrid modelling approach by Crowley et al. (2001), who augmented the fundamental model with a partial least square (PLS) model to account for the coagulation events and, in general, for the model mismatches. They showed that a moving batch data history is more effective in matching the target than an expanding batch data set. An hybrid model can be obtained augmenting a mechanistic model with a statistical model. Batch-to-batch control in emulsion polymerisation has been achieved using this type of hybrid model (Crowley et al., 2001) as well as pure statistical (Clarke-Pringle and MacGregor, 1998; Jaeckle and MacGregor, 1998) or pure mechanistic models (Sayer et al., 2001; Doyle III et al., 2003).

As mentioned before, open-loop control studies are very important because they constitute the base cases when building a closed-loop control system. Saldívar and Ray (1997a) produced optimal open-loop control policies and applied them to an on-line feedback control scheme accounting for disturbances. Positive tests on this scheme underlined the importance of open-loop control studies and the advantages in re-computing them on-line in a feedback control configurations.

There are two distinct strategies for the implementation of feed-back control: within-batch and batch-to-batch control. Within-batch (or in-batch) control is achieved via actions performed during the batch and needs online optimisation to yield the required products at the end of the batch. It may involve either online continuous control (Kozub and MacGregor, 1992a; Saldívar and Ray, 1997a; Liotta et al., 1997a) or mid-course corrections (Flores-Cerrillo and MacGregor, 2002; Wang et al., 2003a; Wang and Doyle III, 2004). On the contrary, the aim of batch-to-batch control is not to perform corrective actions during the batch, but use information derived from previous batches to elaborate the control actions needed for the subsequent batches (Crowley et al., 2001; Doyle III et al., 2003).

A detailed controllability study on the semi-batch emulsion copolymerisation of VAc and BuA was carried out by Immanuel and Doyle III (2004) and revealed

- restrictions in the use of in-batch feed-back for the control of PSD and the need for a batch-to-batch strategy in those cases where in-batch feed-back is not effective, which suggested the possibility of combining the two strategies for the control of PSD in emulsion polymerisation

- the effectiveness of open-loop control if associated with robust optimisation formulations accounting for potential uncertainties and disturbances

2.4.4 Control of PSD and other latex properties in emulsion polymerisation reactors

Measurement limitations Studies on the control of the entire PSD have been addressed only in recent times and coincide with advances in computational techniques and the use of novel on-line instrumentation that allows sufficiently rapid measurements of PSD and other

important properties. Problems in on-line monitoring of polymerisation reactions are, for example, long measurement delay and poor reliability, at which it is necessary to add practical difficulties in tracking the evolution of polymerisation systems due to their complex and viscous nature. The same off-line measurement can be a difficult task, as it requires sometimes sophisticated and time-consuming analytical techniques. Kammona et al. (1999) presented a literature survey on online hardware sensors for monitoring polymerisation reactions and investigated the more recent developments in this field as well as the accuracy and robustness of on-line techniques employed to measure important properties such as molecular weight distribution (MWD), copolymer composition and PSD. Comparative studies on different methods for the measurement of the PSD can also be found in Elizalde et al. (2000) and Schneider and McKenna (2002), where the difficulties of measuring very small particles produced in the early stages of the reaction was pointed out. Acoustic attenuation measurements were used by Hipp et al. (2002a,b) to measure the PSD of colloidal dispersions.

Sensitivity studies and controllability analysis Before attempting any kind of control on a system, sensitivity studies and a controllability analysis highlighting the best set of manipulated variables to use for driving the process to the desired output is often crucial. This is especially true if the process involves complex interaction between the different phenomena involved and the control problem is defined by highly nonlinear objective functions, as in emulsion polymerisation. To demarcate the controllable regime, a mathematical analysis using the population balance model can be performed as shown in El-Farra et al. (2001); Russell and Braatz (2002); Wang and Doyle III (2004) and Immanuel and Doyle III (2004).

Model-based sensitivity studies for the control of the full PSD in emulsion polymerisation were performed by Sood (2004). These studies showed that the initial initiator and the emulsifier amount can be used to control the broadness of both initial and final PSDs. Sensitivity studies on the semi-batch VAc/BuA copolymerisation process were carried out by Immanuel and co-workers (Immanuel et al., 2002; Immanuel and Doyle III, 2003b). The same research group (Doyle III et al., 2003; Immanuel and Doyle III, 2004) also carried out detailed reachability analysis of potential PSDs on the same system and evaluated different control strategies, demonstrating the ability to employ on-line feed-back control of the process. Ex-

perimental studies on the same system were also carried out to study the sensitivity of the process to the properties of the reagents and to the initial conditions and operational uncertainties (Immanuel and Doyle III, 2003b, 2004). Experiments carried out using non-ionic surfactant indicated the following

- the need of multiple process inputs for the control of PSD
- the importance of VAc and surfactant feed rates as manipulated variables
- the ability to produce a desired PSD through the direct control of the particle level phenomena in a hierarchical framework
- the negative effect of the irreversibility of phenomena such as growth rate and coagulation rate in the control of the PSD
- the limitation in the possible distributions attainable
- the negative effect of control actions to tailor the distribution on the final solids content
- the need for a detailed first principles model for the control of the PSD

Controllability studies highlighted the importance of competitive growth on the relative breadth of a bi-disperse emulsion polymerisation system (Liotta et al., 1997b). The influence of the weight fraction of polymer (W_P) inside the particle on the relative narrowing of the bi-modal PSD indicated W_P as an attractive manipulated variable for PSD control. Liotta et al. (1997b,a) were also the first to attempt the control of the PSD (the ratio of mean particle diameters in a seeded bi-disperse population) in emulsion polymerisation. They pointed out that one key determinant factor in determining the particle size distribution is the average number of radicles/particle in each population of growing particles inside the emulsion polymerisation system due to its influence on the particle growth and, consequently, on the competitive growth of the different populations. The control of the lumped parameter, the ratio of mean particle diameters of the peaks of a bimodal PSD, was achieved through the modulation of the relative particle growth using as main tools an adaptive Kalman filter, to estimate the average number of radicals/particle, and a nonlinear model predictive control (NMPC) (Liotta et al., 1997a).

Crowley et al. (2000) were the first to employ a detailed population balance model for the computation of optimal recipes in a semi-batch emulsion polymerisation. They used both surfactant feed and surfactant concentration in the aqueous phase as manipulated variables. Due to the low solids content and high surfactant concentration registered in the early stages considered by Crowley et al., they neglected the particle coalescence. Successive studies from the same research group (Immanuel et al., 2003) showed that a more accurate description of the phenomena should include also the coagulation process in the early stages.

Integrated control of multiple outputs and inferential control of latex properties

The first successful attempt to match a target full particle size distribution, limited to short reaction times (interval I of the Smith-Ewart theory for emulsion polymerisation), was made by Crowley et al. (2000), while the first success in controlling more than a single average property of the emulsion polymer products was achieved by Saldívar and Ray (1997a). They addressed the control of copolymer composition and average molecular weight in a semi-batch copolymerisation through an online generation of monomer and chain transfer agent feed trajectories using a nonlinear multiple input and multiple output (MIMO) controller.

Other strategies for the simultaneous control of MWD and copolymer composition in emulsion polymerisation were also developed by Echevarría et al. (1998); Clarke-Pringle and MacGregor (1998); Sayer et al. (2001); Vicente et al. (2001, 2002); Tian et al. (2002) and Elizalde et al. (2004). A combined controllability analysis of PSD and MWD was presented by Sweetman (2008) for a semi-batch process. Perturbations on initiator, surfactant, monomer and chain transfer agent were simulated through a mechanistic model and implemented experimentally. The coupling between PSD and MWD clearly emerges from these studies and the ability to control the MWD with CTA with minimal alteration of the PSD was evinced.

The work towards the inferential control of end-use product properties is what motivated different scientists in their attempt to control simultaneously more than one output. In fact, latex quality properties are usually determined by a combination of different particle-level and molecular-level properties, of which PSD, MWD and copolymer composition are probably the most important. A combined control of reaction time and polymer composition was also presented in several publications (Gentric et al., 1999; Araújo and Giudici, 2003; Lima et al.,

2004; François et al., 2005; Sayer et al., 2006), because of the importance of a cost effective reduction in the processing time.

MWD and copolymer composition were related to the end-properties of the final emulsion latex by Elizalde et al. (2004). On-line inferential control of adhesive properties was performed by manipulating decision variables such as the feed rates of monomers and CTA. This was done as an attempt to control the final properties of the product, rather than their molecular properties (Prasad et al., 2002). Progress has been also made in quantitatively relating the PSD to the rheological properties of the emulsion latex (Sudduth, 1993a,b; Luckham and Ukeje, 1999; Arevalillo et al., 2006).

PSD control strategies Extended theoretical studies on the controllability of PSD are those of Semino and Ray (Semino and Ray, 1995a,b), who studied the PSD controllability in emulsion polymerisation as a particular case of their general study on the controllability of systems described by population balance equations (Semino and Ray, 1995a). They underlined the importance of unconstrained manipulation of the feed concentrations of surfactant, initiator and inhibitor, coupled with the knowledge of the reactor states, in controlling the PSD in presence of sustained oscillations, and also that is possible to expand the controllability region of the PSD in the constrained case by altering two manipulated variables with opposite effects (*i.e.* initiator and inhibitor feed concentrations). A different strategy was used by Meadows et al. (2003), who employed as manipulated input the temperature of the reactor to control the PSD in the emulsion polymerisation of styrene.

Immanuel and Doyle III implemented optimal open-loop recipes to the semi-batch emulsion polymerisation of VAc and BuA, with the purpose to achieve a full target PSD, controlling directly the PSD (Immanuel and Doyle III, 2002) or using a hierarchical approach (Immanuel and Doyle III, 2003c). In their study they identified the feed rates of surfactant and monomers as suitable manipulated variables for the control of the full distribution, stated the irreversibilities in emulsion polymerisations and supported the use of the hierarchical approach to control the full PSD.

While Immanuel and Doyle III (2003c) controlled the PSD in a multi-objective framework in which the tracking of solids content and total number of particles profiles were used as

constraints, Rajabi-Hamane and Engell (2007) used a different approach in which the focus was on the reduction of the batch time, which was minimised, and the difference between the specified and obtained PSD and the heat removal capacity of the reactor jacket were entered as constraints.

Wang and Doyle III (2004) addressed the definition of the reachable regions for the PSD, in the emulsion homopolymerisation of styrene, through the solution of optimisation problems. In their study, the response of the system to mid-course correction highlighted the importance of early PSD measurements. These were replaced by the solids content data available from the more frequent densitometer and load cell (feed rates weight) measurements by Immanuel and Doyle III (2003c) for the early control actions, before PSD measurements were available, with good results. Wang and Doyle III controlled the reaction using the same criterion applied by Flores-Cerrillo and MacGregor (2002), setting a certain tolerance ϵ on the original target. If the error on the intermediate PSD value falls into this acceptable tolerance no mid-course correction is applied; if not, the reachability analysis results are used to see if the target PSD is still achievable and to decide either to record the data from the actual batch for the application in a batch-to-batch strategy, for an improvement in the subsequent batches, or to calculate the optimal recipe to obtain a close match to the target at the end of the current batch. This strategy underlines the limitation in the applicability of in-batch control methods, when the target to be reached through online control actions do not fall in the feasible region. Flores-Cerrillo and MacGregor (2003) implemented directly a combination of within-batch and batch-to-batch control actions to semi-batch reactors using this concept of "no-control region", with control actions taken during the batch only to correct errors deemed to be statistically significant.

Immanuel and Doyle III (2003c) highlighted the necessity to combine batch-to-batch and in-batch control strategy due to the impossibility, in certain cases, to rectify the discrepancy in the distribution with feasible in-batch control actions (target outside the reachable region). These limitations also motivated the study of Crowley et al. (2001) on batch-to-batch optimisation of the PSD.

Model predictive control All these previous studies on the optimal control of the PSD

have been pushing, in the past years, towards the implementation to the process of advanced control strategies such as model predictive control (MPC). In MPC the feedback signal is given by the difference between the predicted and actual output variables. Based on these residuals, the controller performs the calculation of the new set point and of the control actions at each sampling time and for specified time horizons. MPC is posed as an optimisation problem and one of its unique features is that inequality constraints can be incorporated in both future prediction of plant behaviour and calculations of control actions. Methods such as matrix algorithm control (MAC), dynamic matrix control (DMC) (García and Morshedi, 1986; Gattu and Zafiriou, 1992) and other control strategies of similar structure (García and Morari, 1982, 1985a,b; Eaton and Rawlings, 1990; Ricker, 1990; Morari and Ricker, 1994) are classified as MPC (Ogunnaike and Ray, 1994). Detailed reviews on MPC and its industrial applications are provided by Morari and Lee (1999); Mayne et al. (2000) and Qin and Badgwell (2003).

An optimisation-based control strategy like MPC is perfectly suitable when a detailed model of the system is available and a robust estimator can be used to infer all the data needed from available and more frequent measurements. MPC was employed by Dokucu et al. (2008a) to control the full PSD in the emulsion copolymerisation of VAc and BuA. The high dimensionality of the discretised full PSD was reduced through a model order reduction method based on principal component analysis. Dokucu et al. (2008b) also compared different in-batch feed-back control strategies and saw that while a quadratic dynamic matrix controller (QDMC) used to track the nominal trajectories of the moments of the distribution fails in achieving the required solids content target, a nonlinear multi-rate MPC formulation based on a detailed model of the process is able to reject this off-specification, while matching the full PSD. The overall performance of the multi-rate MPC is superior to that of a PID controller used to regulate the nucleation and growth events and of the above mentioned QDMC. But, they also pointed out that the better performance of the MPC has to be ascribed mainly to the coupling of this with a multi-rate estimator. Availability of more PSD measurements would diminish the superiority of MPC compared to the other strategies.

Another application of MPC to a semi-batch emulsion polymerisation for the control of the PSD can be found in Park et al. (2004). They used a statistical model based on

the PLS method as prediction model in the predictive control algorithm. The data set to regress the statistical model was generated from the mechanistic model of Immanuel et al. (2002). The MPC operates over open-loop optimal control trajectories and the database is updated with experimental data in a batch-wise manner. The knowledge of the actual system allows the controller to compensate for model mismatches and improve its performance. Still, low frequency PSD measurements do not allow for early control action and may reduce the ability to correct errors on the primary peak, generated in the early stage of the process by homogeneous nucleation.

Alhamad et al. (2005) were able to produce a real-time multi-variable DMC for the constrained optimal control of particle size polydispersity index, average molecular weight and monomer conversion in the semi-batch emulsion copolymerisation of styrene and methyl methacrylate. The dynamic matrix in a general DMC application is built with the step responses of the system to manipulation of the controlled variables over the control horizon and is used to predict the changes in the process output (Ogunnaike and Ray, 1994).

Control of continuous processes Considerations on the control of continuous emulsion polymerisation reactors can be found in Schork et al. (1993) and Lovell and El-Aasser (1997). In Schork et al. (1993), unwanted dynamics such as the sustained oscillations that characterise, for example, trains of CSTRs, are deemed to be one of the causes responsible for undesired outputs in continuous reactors. These dynamics may be corrected through reactor design to facilitate regulatory control. The main goal of reactor design in continuous processes is the decoupling of the particle level phenomena, so that the control of nucleation, growth and coagulation can be targeted separately. Different control strategies are presented by Richards and Congalidis (2006), with a specific focus on a commercial continuous emulsion polymerisation reactor. As pointed out by Schork (1997), most of what has been done in the area of control of continuous emulsion systems is based on operating experience rather than optimisation approaches.

2.5 Summary

In this chapter a review on emulsion polymerisation, on the modelling strategies used to describe the integrated phenomena involved in this process, and on the solution techniques implemented to solve the resulting models, was presented. A description of optimisation, state estimation and control strategies applied to particulate processes was also provided, with a particular focus on PSD control in semi-batch emulsion polymerisation.

The emulsion polymerisation process Emulsion polymerisation is a free-radical chain polymerisation. It is a non-homogeneous polymerisation technique where an organic phase is dispersed in an aqueous solution to form a colloidal system. The colloidal particles dispersed in the aqueous phase are the main locus for the polymerisation reaction. All the reactions, namely initiation, propagation, termination and chain transfer, that characterise free-radical polymerisations take place in emulsion polymerisation. Fundamental ingredients of an emulsion polymerisation are monomers, water, surfactant, initiators and chain transfer agents (CTA). Chain transfer agents are used primarily to control the molar mass of the polymer.

In emulsion polymerisation processes both the polymerisation rate and molar mass of the polymer can be simultaneously increased. Water acts to maintain a low viscosity of the reaction bulk and has good heat transfer capacity. Emulsion polymerisation produces water-borne latexes, which are an ideal alternative to solvent-borne polymer products, which production has generated growing environmental concerns. The Trommsdorff gel effect is also reduced in emulsion polymerisation compared to other polymerisation processes.

The main phenomena driving the evolution of the particle size distribution in emulsion polymerisation are nucleation, growth and coagulation of the polymer particles. Polymer particles, once formed by homogeneous or micellar nucleation, swell with monomer diffusing from monomer droplets. These monomer-swollen polymer particles are the main sites for polymer growth, which takes place by addition of monomer to the growing polymer chains. Polymer particles can coagulate by aggregation of smaller particles to form larger polymer particles. The addition of surfactants and physical stresses imposed to the colloidal particles, such as stir or shear of the system, both influence the aggregation phenomena.

Emulsion polymerisation modelling Most of the work on the modelling of emulsion poly-

merisation has been carried in the last decades employing first-principles (pure mechanistic) or hybrid models, often based on PBEs. Population balance modelling is one of the most common tool used to predict the evolution of polymer particle size distribution in emulsion polymerisation (Saldívar et al., 1998; Coen et al., 1998; Immanuel et al., 2002; Vale and McKenna, 2005a), as well as to describe the dynamics of several other particulate processes.

It is possible to divide particle distribution models in two categories: level-one or particle number models and level-two or PSD models. The first family of models considers the system as monodisperse, with all the particles having the same average size. Level-two models are instead based on PBEs and consider the system as constituted by a distribution of particles of different sizes. When the PSD modelling approach is followed, mass balances are written over the concentration of particles of a given size at a given time and kinetic terms are included for nucleation, growth and coagulation of particles. This last approach is nowadays the most commonly used.

The underlying kinetics in emulsion polymerisation can be modelled using two different approaches. These are known as zero-one and pseudo-bulk kinetics. The zero-one approach is typical of systems characterised by sufficiently small particles, where entry of a radical in a particle that contains a growing radical results in instantaneous termination, so that either zero or one radical is present at a time in the particle. It is usually applicable at low conversion, when the Trommsdorff gel effect is less significant. In a zero-one system, radical termination and desorption rates are high, while the overall entry rate is low, causing the rapid disappearance of a polymer radical as soon as another radical adsorbs into the particle.

According to Giannetti (1993), when implementing the zero-one kinetic to describe the PSD dynamic we neglect the contribution of latex particles with more than one growing radical and this causes the model to produce physically unreliable results. Even if characterised by some limitations, the zero-one modelling approach has proven to be of great value in mechanistic studies of emulsion polymerisation.

The emulsion polymerisation kinetics can be simulated, other than through the zero-one approach, also using the pseudo-bulk approximation. Pseudo-bulk kinetics consider the possibility of more than one free radical to co-exist for a significant period of time in the

polymer particle. This approach is commonly applied to systems with large particles or that use monomers which propagate very rapidly, such as acrylates. When applying the pseudo-bulk kinetics to the population balance model, we define an average number of radicals over all particles of a certain size. In the population balance formulation, the particle density distribution $F(r,t)$ and the average number of radicals per particle distribution $\bar{n}(r,t)$ are decoupled. The population balance equation in this case will require an expression for the average number of radicals per particle of size r, $\bar{n}(r,t)$.

To model copolymer systems Storti et al. (1989) created an approximation procedure to reduce the kinetics of an emulsion polymerisation involving any number of monomer species to that typical of homopolymerisation processes and named it pseudo-homopolymerisation approach. When in a system we have several monomeric species reacting simultaneously, we need to consider the evolution of several particle populations, each characterised by number and type (i.e. free-radical end group) of radicals contained in each particle. To do so, a set of population balances needs to be derived. Storti et al. (1989) reduced this set to a smaller one, for which any particle population is characterised by an overall number of radicals of any type. The model assigns the polymer chains to one type or to the others based on a pseudo-homopolymerisation probability.

The use of a model with good predictive ability is essential for application in model-based optimisation and control of emulsion polymerisation processes. The model used in this project is a pure mechanistic, nonlinear, distributed model developed by Immanuel et al. (2002, 2003). It is a comprehensive population balance model for the evolution of particle size distribution in the emulsion copolymerisation of vinyl acetate (VAc) and butyl acrylate (BuA). The model is designed for a semi-batch reactor. It is a PSD model that applies the pseudo-homopolymerisation approximation (Storti et al., 1989) to the VAc/BuA copolymerisation system and implements pseudo-bulk kinetics in modelling the average number of radicals per particle. It is based on the general model structure by Saldívar et al. (1998), with influences from other works (Coen et al., 1998; Crowley et al., 2000). In the model of Immanuel et al. (2002) a population balance framework is used to embed and calculate the number of radicals/particle, avoiding the simplifications introduced by earlier models and

incorporating the size-dependence of $\bar{n}$.

In this model Immanuel et al. (2002, 2003) considered redox initiation, with t-butyl hydrogen peroxide (t-BHP) and sodium formaldehyde sulphoxylate (SFS) used as redox initiator pair. Redox initiation was chosen because it enables low temperature operation and usually offers better control of the initiation process. Studies on the same system when implementing a thermal initiator were also carried out by Sweetman (2008) due to the wide use of this type of initiators in industry. The original model was modified by Sweetman (2008) also to account for the use of ionic surfactant, with new assumptions on the surfactant partitioning.

Solution algorithm The application of population balance modelling to a system results in a mathematical description based on partial differential equations or integro-partial differential equations. The solution of the dynamic PBE is a notably difficult problem and is characterised by a high computational load. Difficulties arise from numerical complexities and model uncertainties in the source terms embedded in the PBE. The solution of population balance equations usually involves the discretisation of the internal coordinate domain into a number of discrete element, which results in a system of stiff, nonlinear differential or algebraic/differential equations solved numerically.

The difficulties faced when solving PBEs limited their application in the past, but advances in computation techniques have made these equations applicable nowadays to more and more complex systems. Several numerical methods have been developed to solve steady-state and dynamic PBE. They include the method of classes (Marchal et al., 1988; Chatzi and Kiparissides, 1992), the discretised PBE method (Hounslow et al., 1988; Litster et al., 1995; Kumar and Ramkrishna, 1997), the fixed and moving pivot discretised PBE methods (Kumar and Ramkrishna, 1996a,b), the high order discretised PBE methods (Sastry and Gaschignard, 1981; Landgrebe and Pratsinis, 1990), the orthogonal collocation on finite elements (Gelbard and Seinfeld, 1979; Rigopoulos and Jones, 2003), the Galerkin method (Nicmanis and Hounslow, 1998), the hierarchical two-tier algorithm (Immanuel and Doyle III, 2003a), and the spline collocation method (Eyre et al., 1988; Steemson and White, 1988).

The numerical methods for the solution of the PBEs can be grouped into three major categories: method of moments, stochastic methods and discretisation methods. Discretisation

methods are the most popular techniques for the solution of PDEs, in which category the PBEs fall. Discretisation methods can be divided in two further families, the finite difference (FD) method and the method of weighted residuals (MWR).

The FD method is based on the approximation by finite differences of the derivatives with respect to the internal coordinate, usually, or both time and internal coordinate. Based on the order of the finite differences, the PDE can be reduced either to a set of ODEs or of algebraic equations.

In the MWR functions are used to approximate the PBE. The domain of interest can be considered as a whole or divided in sub-domains and the approximating functions defined in each one of these sub-intervals. The functions used in the MWR are always a combination of basis functions and weighting functions. To avoid using an high degree polynomial, which would arise from the use of a single basis function to cover the whole domain, usually the domain of interest is discretised into sub-intervals (or finite elements (FEs)) and a local basis function is used to simulate the PBE within each FE. Usually these FE methods allow for more general solutions.

The independent variable lumped is usually the internal coordinate and after its lumping the PDE is reduced to a set of ODEs in time. Sometimes the time is discretised and the discretisation of the PBE in time results in a set of ODEs in the internal coordinate. When this approach is followed, the discretisation method takes the name of Rothe's method. Another special sub-class of discretisation techniques are those used to solve the aggregation/breakage problem. The terms accounting for these phenomena are integral expressions, so the PBE becomes an integro-partial-differential equation when aggregation/breakage phenomena are included.

The solution technique used to simulate the model implemented in the current project (Immanuel et al., 2002, 2003) is the hierarchical two-tier algorithm (Immanuel and Doyle III, 2003a). It is a finite volume (FV) method and presents characteristics that make it a valid and efficient alternative to other proposed methods.

A major drawback when solving PBEs is the difficulty of decoupling the time-dependent rates from the time-dependent variables. This problem is solved by Immanuel and Doyle

III (2003a) through the implementation of a two-tier strategy. In this two-tier integration framework, the computation of the rates and the update of the PSD are performed in two subsequent steps (two-tier). The time-dependent variable particle density $F(r,t)$ is computed solving a systems of ODEs and algebraic equations based on the values of the source terms computed off-line.

This method is not based on the discretisation of the PBE, but on the re-formulation of population balances in each FE (or bin) after the discretisation of the population along the particle size domain. The entire set of ODEs and algebraic equations resulting from this procedure is effectively divided in two sub-sets, those used for the computation of the source terms and those deriving from the re-formulation of the PBE. This reduces the associated stiffness in the solution, which derives from the huge disparity in the time constants of the nucleation, growth and coagulation events. Also, no approximation is necessary for the derivatives, resulting in a reduction of the truncation-related instabilities. The coagulation kernel is computed employing a semi-analytical solution method that reduces the computational load and, at the same time, ensures preservation of the particles mass and the consistency of the number of particles, subject to the assumption of a uniform particle density within each bin.

Process control and optimisation Particulate polymerisation processes are highly nonlinear and contain a large number of time-varying kinetic and transport parameters. Modelling of particulate polymerisation systems usually results in nonlinear integro-differential equations of infinite-dimensional nature, which makes their direct implementation in real-time controllers not easy. On-line measurement of PSD and other important properties such as MWD and copolymer composition distribution (CCD) are difficult to obtain and the available secondary measurements are often not adequate for the accurate inference of these properties. Changes in the manipulated variables can cause opposite reactions on the controlled variables due to the complexity of the process and makes the formulation of a proper objective function challenging, especially when trying to build inferential controls of end-use properties through control of molecular and morphological properties. These are some of the reasons why there is still a lack of closed-loop property control in industry for emulsion polymerisation processes.

In recent years, the availability of always more accurate mathematical models, solution

techniques for complex mathematical systems and advances in on-line measurements and control theory, created the ground for advancements in the field of nonlinear optimisation and control of PSD in emulsion polymerisation.

The mathematical description of a system is usually not able to reproduce its real evolution due to model-plant mismatches, the presence of time-varying model parameters and of unknown process disturbances. Observers and estimators supply the fundamental feedback from the process needed to correct modelling errors. Also, they can be used for early detection of undesired reactor conditions that may lead to violation of operating constraints and product quality specifications. Among the estimation strategies, the Kalman filter has shown to be one of the most popular and powerful techniques. Another state estimation technique extensively applied to optimisation and control problems is based on Luenberger observers. Between the other possible approaches to state estimation there is the moving (or receding) horizon estimation (MHE), which allows for incorporation of constraints into an optimisation strategy and uses trajectories of states and measurements rather than values at a single time.

Control of batch/semi-batch emulsion polymerisation reactors can be achieved using two different approaches, namely feed-forward (Vicente et al., 2002; Immanuel and Doyle III, 2002, 2003c; Meadows et al., 2003) and feed-back control (Kozub and MacGregor, 1992a; Liotta et al., 1997a; Flores-Cerrillo and MacGregor, 2002; Lee et al., 2002; Zeaiter et al., 2006; Immanuel et al., 2008; Dokucu et al., 2008a,b). Feed-forward are open-loop control systems where the process outputs have no effect on the inputs, while feed-back control systems are implemented in a closed-loop setting with the outputs that affect the inputs in such a way to keep the outputs at the desired value.

Feed-forward control systems respond to a measured disturbance in a pre-defined way. Feed-forward control can respond more quickly to known and measurable kinds of disturbances, but cannot do much with novel disturbances. Feed-back control deals with any deviation from desired system behaviour, but needs some way to measure the process output and requires corrective actions (feed-back actions) to exist in order to counter the errors introduced in the process through the correction of the input values and achieve the target output. Corrective feed-back control actions are necessary to correct optimal open-loop

input trajectories in the presence of non-ideal operating conditions. On the other hand, open-loop control studies are very important because they constitute the base cases to build a closed-loop control system. Positive tests on the open-loop control scheme underlined the importance of open-loop control studies and the advantages in re-computing them on-line in feedback control configurations. Due to the direct implementation of the optimal trajectories calculated off-line, open-loop schemes need very good process models.

Before attempting any kind of control on a system, sensitivity studies and a controllability analysis highlighting the best set of manipulated variables to use for driving the process to the desired output is often crucial. This is especially true if the process involves complex interaction between the different phenomena involved and the control problem is defined by highly nonlinear objective functions, as in emulsion polymerisation.

There are two distinct strategies for the implementation of feed-back control: within-batch and batch-to-batch control. Within-batch (or in-batch) control is achieved via actions performed during the batch and requires online optimisation to yield the required products at the end of the batch. It may involve either online continuous control or mid-course corrections. On the contrary, the aim of batch-to-batch control is not to perform corrective actions during the batch, but use information derived from previous batches to elaborate the control actions needed for the subsequent batches.

There are limitations in the applicability of in-batch control methods when the target to be reached through online control actions do not fall in the feasible region. Flores-Cerrillo and MacGregor (2003) implemented directly a combination of within-batch and batch-to-batch control actions to semi-batch reactors. Immanuel and Doyle III (2003c) highlighted the necessity to combine batch-to-batch and in-batch control strategy due to the impossibility, in certain cases, to rectify the discrepancy in the distribution with feasible in-batch control actions (target outside the reachable region).

Previous studies on the optimal control of the PSD have been pushing, in the past years, towards the implementation to the process of advanced control strategies such as model predictive control (MPC). In MPC the feedback signal is given by the difference between the predicted and actual output variables. Based on these residuals, the controller performs the

calculation of the new set point and of the control actions at each sampling time and for specified time horizons. MPC is posed as an optimisation problem and one of its unique features is that inequality constraints can be incorporated in both future prediction of plant behaviour and calculations of control actions. An optimisation-based control strategy like MPC is perfectly suitable when a detailed model of the system is available and a robust estimator can be used to infer all the data needed from available and more frequent measurements.

Chapter 3

Optimal Recipes towards Target PSDs: an Open-Loop Control Approach

Results are presented in this chapter that show the inherent difficulties and the strategies employed in tuning optimisation routines towards the match of defined PSDs. Single-objective and multi-objective formulations of the optimisation problem were tested and an analysis of the different possible manipulated variables was performed and resulted in the definition of an ideal set of decision variables for implementation in the PSD control of emulsion polymerisation processes (Bianco and Immanuel, 2006a,b).

3.1 Background information and control strategy

3.1.1 Introduction

While a considerable amount of work has been done on the modelling of emulsion polymerisation processes and the numerical solution of the models, there are relatively few control studies. Control of properties such as PSD (Doyle III et al., 2003; Flores-Cerrillo and MacGregor, 2003; Immanuel and Doyle III, 2003c; Dokucu et al., 2008a) and MWD (Sayer et al., 2001; Vicente et al., 2002; Elizalde et al., 2004) have been addressed only in recent years as

a direct consequence of advances in computational techniques and on-line measurement instrumentation (Kammona et al., 1999). To account for all the issues arising from the control of emulsion polymerisation and, simultaneously, to have a whole picture of the process, the implementation of a model-based control strategy seems to be the most suitable approach to meet the complex and multi-modal PSD objectives required by industrial practice.

The studies presented in this chapter follow the work by Immanuel and Doyle III (Immanuel and Doyle III, 2002, 2003c) on the semi-batch emulsion copolymerisation of VAc and BuA. They implemented open-loop control strategies with the aim of controlling the full profile of the PSD. The optimal recipes were produced following two different strategies. In the first, the PSD was controlled directly using single-objective cost functions (Immanuel and Doyle III, 2002). Experimental validations of the optimal recipes were performed on a semi-batch reactor.

In the second, a hierarchical approach was used accounting, in this case, for the contribution of the different particle-level phenomena to the evolution of the PSD (Immanuel and Doyle III, 2003c). With this strategy the control at the macroscopic level of the PSD is realised through the modification of the underlying particle-level rate processes. The manipulations at the macroscopic (vessel) level are used to tailor particle-level behaviour to obtain the desired population distribution. To cope with the integrated and interacting nature of the particle-level phenomena and their irreversibility traits, a multi-objective strategy lends itself naturally.

The optimal recipes were calculated through a multi-objective optimisation strategy based on the above mentioned hierarchical considerations, aiming at minimising deviations from the target PSD, as well as the target profiles of the number of particles and solids content. The rationale behind this multi-objective approach is the decoupling of the particle rate processes of nucleation and growth. The design nucleation and growth rates are presented as profiles of the total particles and solids content over the course of the batch, because these two distributions are easier to estimate than the rates of nucleation and growth. The decoupling of these particle-level processes and the resulting inferential control approach facilitates the control of the process and may be used in the implementation of feedback control strategies

(*e.g.* in a nonlinear MPC). The optimisations were carried out employing a genetic algorithm (GA), a global optimisation technique (Immanuel and Doyle III, 2002, 2003c).

Computational complexities associated with the solution of the highly nonlinear PSD model and discontinuities in the process with regard to the nucleation and growth phenomena (saturation effects), and the coagulation phenomena, would enforce the use of a global technique to solve the associated model-based optimisation problem. Direct global optimisation techniques such as GA and iterative programming techniques (see, for example Adjiman et al. (1997)) have been demonstrated to be more suitable than gradient-based methods in solving the sort of highly non-convex problems characterised by discontinuities (Crowley et al., 1999) arising from processes such as emulsion polymerisation.

Nevertheless, the results presented here demonstrate that the implementation of gradient-based techniques to the optimal control problem under study gives excellent results in terms of the match between targets and simulated distributions. Different gradient-based methods have been applied to the current optimisation problem and have been able to identify local solutions that reproduce accurately the desired distributions. Process understanding and the implementation of an accurate mathematical description of the process makes the selection of the most suitable decision variables possible. An accurate formulation of the optimisation problem greatly contributes to the efficacy of the optimisation strategy. The efficient computation technique developed by Sun and Immanuel (2005) was implemented to speed up the computation in view of the online implementation of the open-loop results.

3.1.2 Hierarchical strategy

A control system can be used to drive a property towards a specific target through inferential control of other related outputs. This concept is at the base of the hierarchical control strategy. Certain decision variables can be used to control different product properties. These properties may include the output that needs to be regulated and other related properties. In the case under study, the PSD of the emulsion latex is the output that has to be controlled to a specified target.

As can be seen in figure 3.1, initiator, monomers and surfactant concentration/feed rates

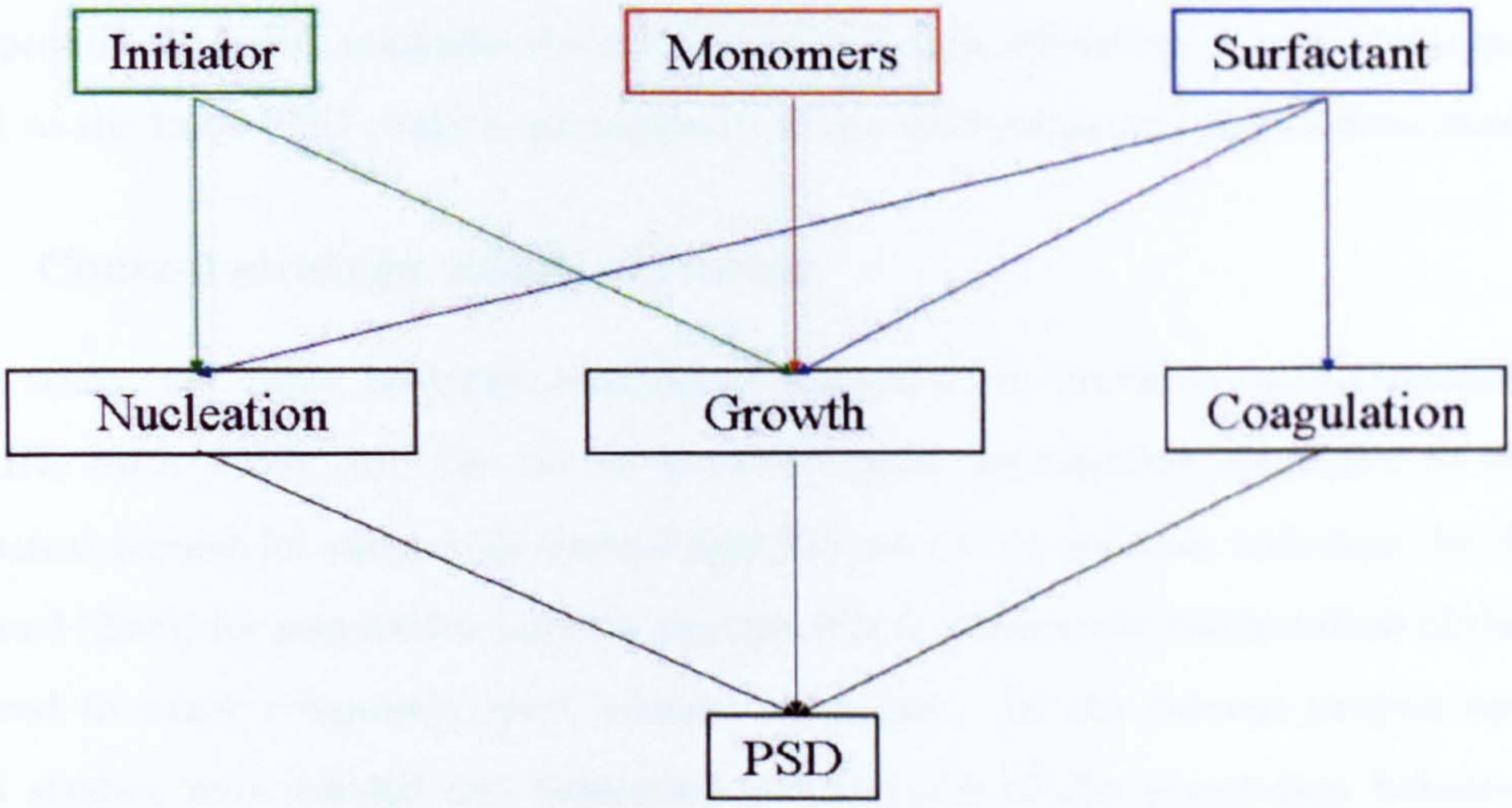


Figure 3.1: Integrated process hierarchy in PSD control.

can be used to control the PSD. They also directly regulate the individual rates of nucleation, growth and coagulation, with the nucleation and growth rates directly linked to the total number of particles and solids content of the latex.

Thus, the PSD dynamic can be indirectly controlled regulating the evolution of these process variables through the manipulation of initiator, monomers and surfactant feed rates. The control of the particle-level phenomena may provide a facilitated and more accurate strategy for the control of the PSD. The development of an effective hierarchical control strategy requires the understanding of how the different phenomena interact and of the integrated effect that the different inputs have on them. This strategy is an alternative to the direct control of the PSD.

Which one of these control strategies, direct or hierarchical, gives better performances may change from process to process and also depends on the choice of the properties to control

and decision variables to use within a certain process. The variability from case to case of the performance of the two strategies is confirmed by the results presented in this chapter. At the same time, the good results obtained for the different systems, operating conditions and target profiles analysed, confirms the robustness and high reliability of both strategies when applied to the latex PSD control, particularly of the multi-objective hierarchical approach.

3.1.3 Control strategy implementation

In this study, the main novelties introduced compared to previous work (Immanuel and Doyle III, 2002, 2003c) are the use of gradient-based optimisation strategies to calculate the optimal recipes for open-loop control and the use of the solution technique by Sun and Immanuel (2005) for population balance models, which quicken the computation of the model compared to other commonly used solution strategies. In the current project open-loop control studies were carried out exploiting the features of the population balance model developed by Immanuel and co-workers (Immanuel et al., 2002, 2003) to produce optimal recipes towards target PSDs.

The effectiveness of different optimisation strategies in finding the optimal feed trajectories towards multi-modal and complex target PSDs was tested. The copolymerisation of Vinyl Acetate (VAc) and Butyl Acrylate (BuA) under non-ionic surfactant and redox initiator in a semi-batch reactor was first considered. A modified model (Sweetman, 2008) accounting for the use of ionic surfactant and thermal initiator was also employed.

Three objective functions were considered in the present study:

$$\theta_1 = \int_{r_{nuc}}^{r_{max}} \Big(W(r,t_f) - W_{ref}(r)\Big)^2 dr \tag{3.1}$$

$$\theta_2 = \int_{t=0}^{t_f} \Big(sc(t) - sc_{ref}(t)\Big)^2 dt \tag{3.2}$$

$$\theta_3 = \int_{t=0}^{t_i} w_i \Big(Np(t) - Np_{ref}(t)\Big)^2 dt + \int_{t_i}^{t_f} \Big(Np(t) - Np_{ref}(t)\Big)^2 dt \tag{3.3}$$

θ_1 was built as the 2-norm of the error between the end-point ($W(r,t_f)$) and the target

($W_{ref}(r)$) weight-averaged PSD. θ_2 accounts for the error on the solids content (sc) and θ_3 for the error on the total number of particles (Np). sc_{ref} and Np_{ref} are the target profiles for solids content and number of particles, respectively. θ_3 was written as the sum of two contributions, with the weight w_i used on the first term accounting for the sudden increase of number of particles after the secondary nucleation in a bi-modal distribution. It is used to reduce the difference in the order of magnitude between the total number of particles after the first nucleation and the final total number of particles after the second nucleation, to make these two values comparable. The same strategy can be used also for a three- or, in general, multi-modal target distribution, with the weights chosen based on the relative magnitude of the different peaks.

These three objective functions were used in different formulations of the optimisation problem

1. *Single objective* $\quad Minimise\ \theta_1$

2. *Weighted sum* $\quad Minimise\ \theta = \theta_1 + w_2\theta_2 + w_3\theta_3$

3. *Weighted min − max* $\quad Minimise\ \theta = max(\theta_1, w_2\theta_2, w_3\theta_3)$

4. *Pareto optimisation* $\quad Minimise\ \theta_1$ under the conditions:

   (a) $w_2\theta_2 \leq \epsilon_2$

   (b) $w_3\theta_3 \leq \epsilon_3$

   (c) $w_2\theta_2 \leq \epsilon_2 \ \ and \ \ w_3\theta_3 \leq \epsilon_3$

The first of these is a single objective formulation for the minimisation of the error between the simulated end-point and the target weight-averaged PSDs (θ_1). The next two are also single-objective strategies, but built to minimise a combination of more than one objective function. In these formulations, other than the error between target and simulated end-point PSD profile, also the error on the solids content (θ_2) and number of particles (θ_3) profiles are accounted for. A weighted sum of θ_1, θ_2 and θ_3 and a weighted maximum among θ_1, θ_2 and θ_3 are the objective functions for these two cases. In the fourth case a multi-objective

problem is solved. A complete set of pareto solutions is obtained minimising the error on the PSD profile while imposing ϵ-constraints on one or two of the other objective functions, when implementing the two and three-objective formulation, respectively.

Weights (w_2 and w_3) for the objective functions θ_2 and θ_3 were used in all the above formulations. This was done to make the error on the different targets comparable. The choice of these weights was made based on process understanding and on the study of the different profiles evolution. Based on these information the weights were tuned. Different sets of values were identified, of which

$$w_2 = 0.2 \qquad\qquad w_3 = 10^{-17}$$

are the weights used for all the bi-modal distributions analysed in the current project. The validity of these weights for a wide range of different bi-modal distributions and the reduced sensitivity of the routines to their values constitute an advantage when implementing this control scheme, since these weights will only need an initial tuning before implementation by an operator. A trial and error strategy was used for the computation of these weights.

The ϵ-constraints used for the pareto optimisation were selected based on the magnitude of the objective functions. These penalties were imposed as upper and lower bounds on the weighted objective functions θ_2 and θ_3. The value 0 (*i.e.* exact match with the target profiles) was used as lower bound, while as upper bounds different sets of values, ranging from 10^{-6} to 10^{-2}, were chosen. The pareto solutions were selected from the different sets of objective functions obtained imposing different upper bounds to the same optimisation problem.

The optimisation problems were solved subject to the following constraints

$$l \leq \begin{pmatrix} x \\ A_L x \\ c(x) \end{pmatrix} \leq u$$

These are the simple bound penalties applied to each decision variable, the linear constraints relating the time intervals and the nonlinear inequality constraints imposed on θ_2 and θ_3 in the pareto optimisation.

The control of the end-point PSD can be realised by controlling the three sub-processes of nucleation, growth and coagulation. The direct influence of the feed rates of surfactants,

monomers and initiators on these three events suggests their use in the control of the PSD. The copolymer system VAc-BuA was considered and monomers, surfactant and initiator feed rates, together with the duration of the time interval for the injection of these reactants, were used as manipulated variables. The batch was divided in time intervals, and the feed rates were defined as piece-wise constants within each time interval. The decision variables for optimisation are the duration of the time intervals and the piece-wise constant values of the flow rate of reactants. Different combinations of these decision variables were tested.

3.1.4 Gradient-based optimisation strategies

The need to reduce the computation time in view of a possible implementation of the open-loop results in an online feedback framework and greater accuracy of gradient-based optimisation strategies in identifying local minima when proper boundaries are used, are the main reasons that put forward the idea of using these strategies as an alternative to global optimisation techniques. Two different gradient-based optimisation strategies were implemented using routines from NAG in FORTRAN (NAG, 2005). The first routine (E04JYF) implements a quasi-Newton algorithm for finding a minimum of a function $f(x_1, x_2, ..., x_n)$, subject to fixed upper and lower bounds of the independent variables $x_1, x_2, ..., x_n$, using function values only

$$\text{Minimise } f(x_1, x_2, ..., x_n) \quad \text{subject to} \quad l_j \leq x_j \leq u_j,\ j = 1, 2, ..., n$$

The NAG routine E04JYF was used in its standard setting. Objective functions, targets, decision variables and an initial guess were supplied to the routine. This routine is employed when derivatives of $f(x)$ are not available. Finite-difference approximations to the derivatives of $f(x)$ with respect to the decision variables are computed by the routine using forward differences, but also central differences when required. If one of the decision variables reaches its boundary, it is fixed and the iterative search continues with a reduced number of variables. The fixed variables are eventually released and made active again in case only a weaker convergence criteria pre-defined by the routine is satisfied.

Newton's method uses first and second derivatives (gradient and Hessian) of the function to find a local stationary point, where the gradient is 0, *i.e.* it employs second-order

(quadratic) approximations of the function and calculates the minimum equating to 0 the expression resulting from the differentiation of the quadratic approximation. In quasi-Newton methods a positive-definite approximation of the Hessian is used and the search direction is computed using only first derivatives. The Hessian matrix is initialised as any positive-definite symmetric matrix and is updated using the gradient vector, which makes the second derivatives not required (Edgar et al., 2001).

The second gradient-based optimisation strategy (E04UCF) implemented is designed to minimise an arbitrary smooth function subject to constraints using a sequential quadratic programming (SQP) method. Constraints may include simple bounds on the variables, linear constraints (matrix of linear constraint functions A_L) and smooth nonlinear (vector of nonlinear constraint functions c) constraints

$$\text{Minimise} \quad f(x) \qquad \text{subject to} \qquad l \leq \begin{pmatrix} x \\ A_L x \\ c(x) \end{pmatrix} \leq u$$

Smooth functions are those with derivatives of all orders, but the NAG routine E04UCF requires for them only to be at least twice continuously differentiable. Moreover, the routine is able to solve the problem even if isolated discontinuities are present, but away from the solution. The unspecified derivatives are approximated by finite differences. Due to the complexity of the model used in these studies, none of the derivatives were specified explicitly and all of them were approximated with finite differences by the optimiser. The standard setting of this routine was also modified including a finite difference check on the gradient elements computed by the user-supplied programs (containing targets and objective function formulations), lowering the initial step for the line search to 10^{-4}, using a finite difference interval equal to 10^{-5}, increasing the upper limit for the number of iteration due to the complexity of the problem, and using tolerances for the error on objective functions and constraints up to 10^{-6}.

The SQP can be seen as a generalisation of Newton's method in that it minimises a quadratic model of the problem. It replaces the objective function with the quadratic ap-

proximation and the constraints with linear models. A nonlinear program (NLP) in which the objective function is quadratic and the constraints are linear is called quadratic program (QP). An SQP solves a QP approximation to a NLP problem at each iteration (Edgar et al., 2001).

3.2 Results and discussion

3.2.1 Batch time discretisation

The ability of single-objective and multi-objective optimisation strategies to produce optimal recipes that generate target PSDs was tested. Feasible targets were used to study the optimisation routines. More attention was given to bi-modal distributions, as a consequence of the large request in industry for this type of PSDs. Different combinations of manipulated variables were used. These included feed rates of surfactant, monomers and initiator. In some of the simulations the redox couple *t*-BHP/SFS and a non-ionic surfactant were used, while in others sodium persulfate, as thermal initiator, and SDS, as ionic emulsifier, were considered. The feasible target PSDs were computed simulating the model for given recipes.

The first simulations were carried out discretising the entire batch time (150 minutes) in a number of time intervals, often 11, and using as decision variables the feed rate in each one of these intervals. Subsequent considerations resulted in the reduction of the time frame in which the feed rates were manipulated, with the reactant feed rates that were set equal to 0 towards the end of the batch to prevent the distribution to evolve behind the end-batch point. In a number of cases, of the original 11 feed rates spanning the 150 minutes of the batch, 5 feed rates of surfactant in the first 71 minutes and 6 feed rates of VAc in the first 80 minutes of the batch were considered as decision variables. In other cases 5 feed rates of initiator and 5 feed rates of surfactant in the first 60 minutes of the batch were used. Many other cases may and have been taken into consideration. The number of time intervals was defined by the selected maximum batch time for feed rate manipulation (between 60 and 80 minutes) and by the criteria of selection of the interval widths. In each time interval the feed rates were formulated as zero-order hold. Both gradient-based optimisation routines were

implemented.

The widths of the time intervals were chosen based on the expected timings of the particle-level events and/or the frequency of the PSD measurements, for a reaction spanning 150 minutes. PSD measurements from the capillary hydrodynamic fractionator (CHDF) used in the experiments are available approximately every 11 min. Thus, the width of the intervals can be chosen to be equal to 11 min each so that a PSD measurement from the CHDF is available every time a new recipe computation needs to be performed, in view of an online implementation of the control strategy.

Alternatively, the intervals can be chosen based on the PSD dynamics. For example, shorter and more frequent intervals can be used at the beginning of the batch to tailor more accurately the nucleation and short term coagulation events and larger time intervals can be chosen at later times into the batch, so that shape and size of second and further modes of the distribution can also be controlled. From the implementation of the different possible cases, it emerged that once the batch discretisation is tailored on the system, the same discretisation can be used for a large range of different targets and operating conditions (*e.g.* different initial composition, stirring rate, concentration of the reactants, etc.). This is a consequence of the observed reduced sensitivity of the system to the batch discretisation. This is a positive finding, since after an initial tuning the optimisation routines may not need further adjustments, making the implementation of these routines more straightforward. This easy-to-implement characteristic was also observed, as seen in section 3.1.3, when tuning the routines with respect to the objective function weights. An operator would eventually be able to use this open-loop control algorithm without further tuning of the routines for a wide range of targets and operating conditions. A common batch time discretisation implemented in most of the cases analysed is presented in table 3.1.

A further alternative is to use the duration of the time intervals as manipulated variables. These can be used in combination with the piece-wise constant values defined for each feed rate in these intervals. This case has been studied and some results are presented in section 3.2.2.

batch time (sec)	batch time (min)	$\triangle t$ (min)
150	2.5	2.5
600	10	7.5
1000	16.7	6.7
2250	37.5	20.8
4260	71	33.5
4800	80	9
5540	92.3	12.3
6300	105	12.7
7380	123	18
7800	130	7
9000	150	20

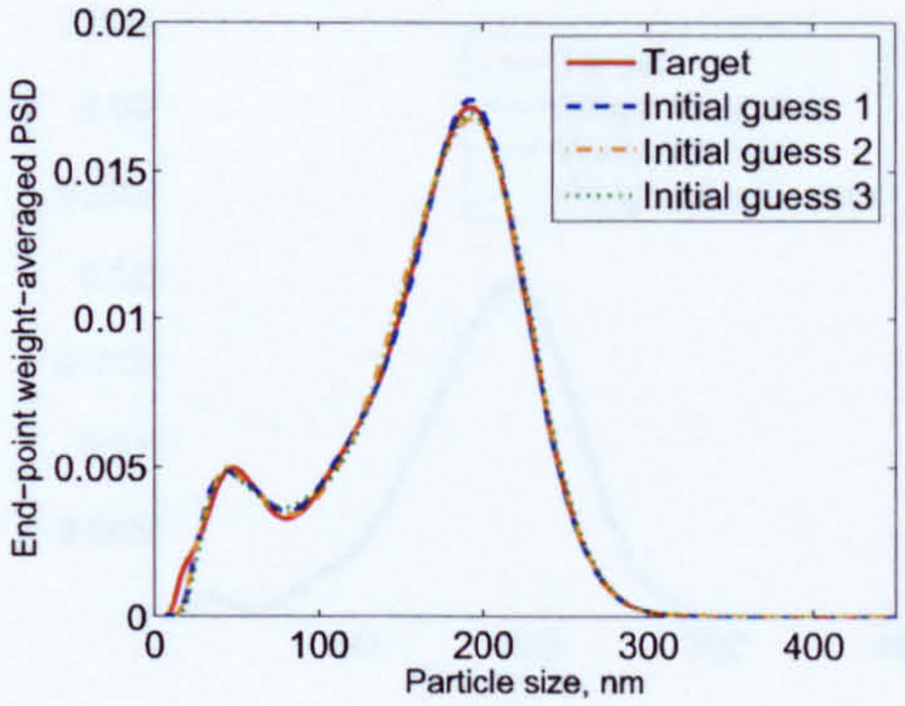
Table 3.1: Batch time discretisation of a semi-batch process for feed supply.

3.2.2 Off-line computation of optimal recipes using a single-objective approach

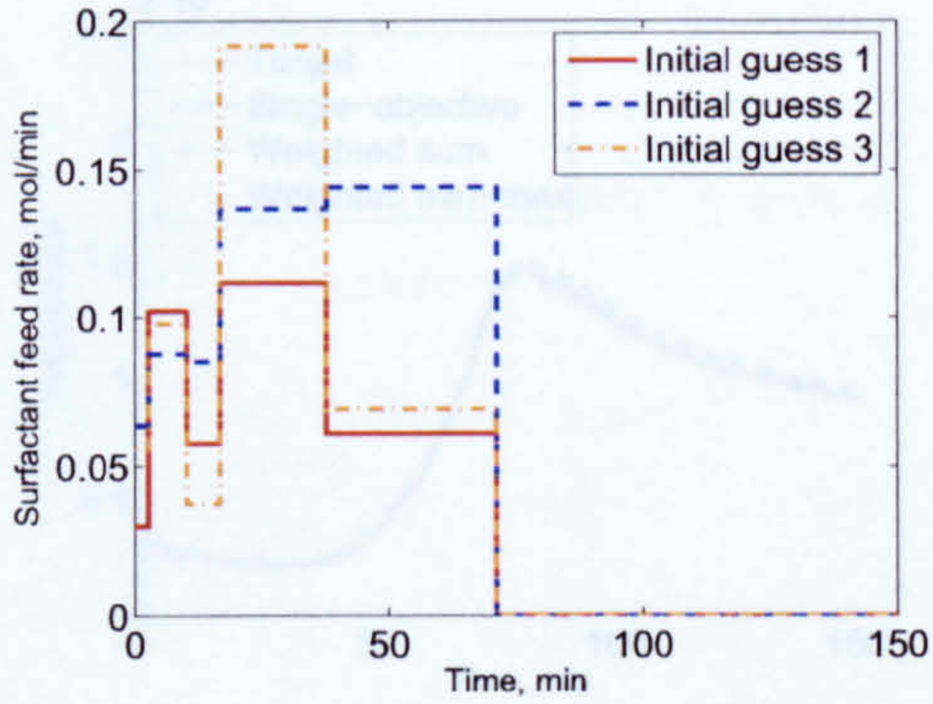
To confirm the non-convexity of the problem, for each target different initial trajectories were tested. In figure 3.2 a series of results for different initial input trajectories applied to a single-objective problem are shown. The batch time was discretised and a non-uniform width of the intervals was used. Eleven piece-wise constant values for the VAc and surfactant feed rates were implemented as decision variables.

Different local minima are found by the optimiser for different initial guesses, this confirming the multiplicity of the solution for this optimisation problem. At the same time, it shows that working with a sufficiently large number of carefully selected manipulated variables the optimality criteria set by the routines are satisfied by a number of local minima. Sensitivity of the system to the chosen decision variables and an adequate range of search directions both contribute to the excellent performance of the optimiser. They seem to reduce the chance the optimiser has to come upon discontinuities and to find local minima that do not satisfy the required tolerance. The optimiser is able to spot more than a single local minima that satisfy the optimal criteria imposed by the routines. For each optimal solution the match with the target is almost perfect.

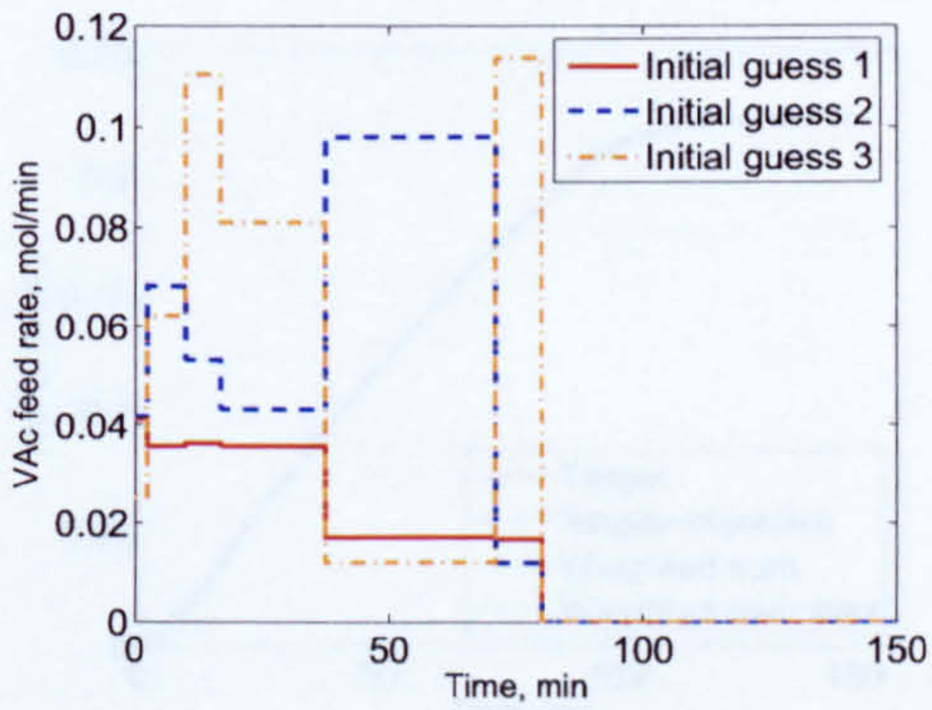
Single-objective, weighted min-max and weighted sum formulation of the objective func-



(a) End-point weight-averaged PSDs.



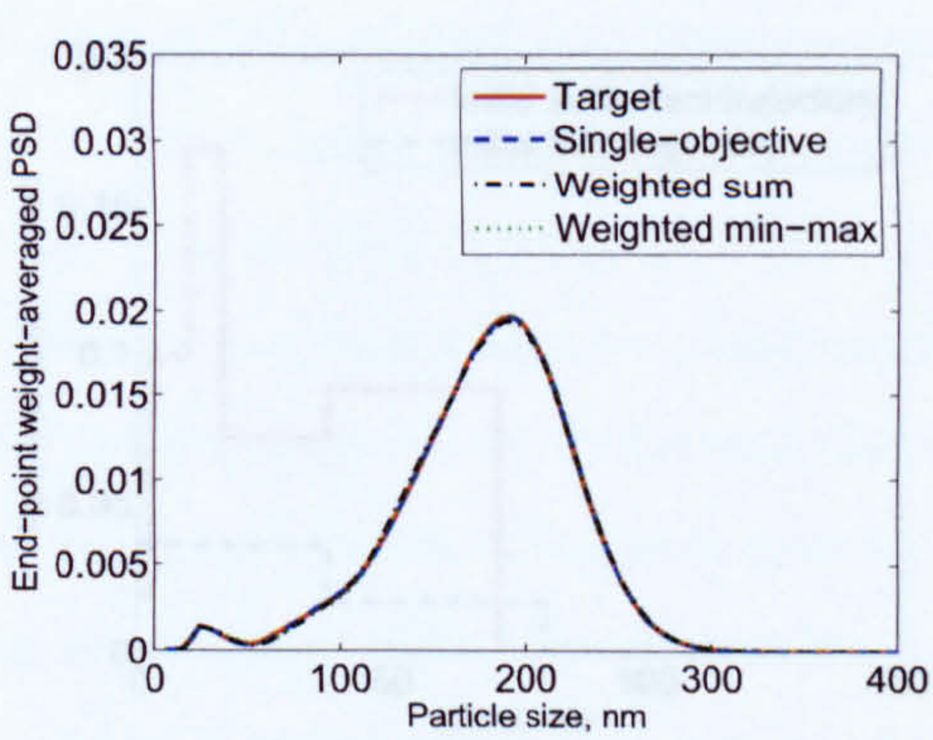
(b) Optimal feed rates of surfactant.



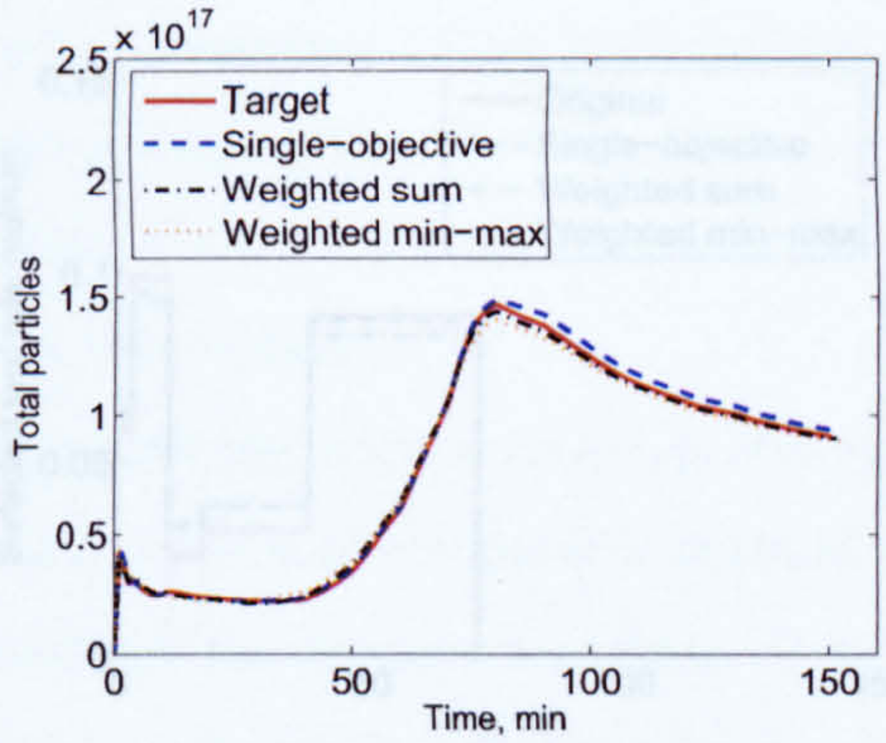
(c) Optimal feed rates of VAc.

Figure 3.2: End-point PSDs and optimal input trajectories for different initial guesses.

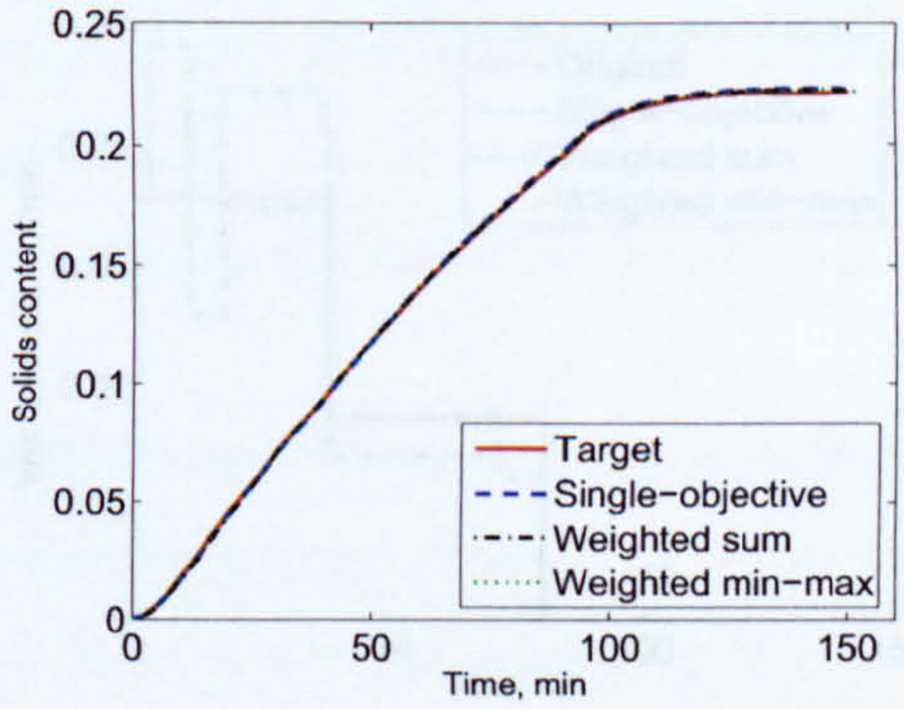
tion were all considered and a comparison between them is presented in figure 3.3. An almost perfect match between target and simulated PSD, solids content and number of particles profiles was observed. Good results were also obtained for all the targets when implementing the single-objective formulation tailored on the PSD (case 1). Slightly better matches with the solids content and number of particles targets were produced using the other two formulations. While case 1 in section 3.1.3 is a pure single-objective optimisation problem, case 2 and 3 can be seen as pseudo multi-objective formulations, involving the optimisation of three objective functions. This contributes to the enhanced performance of the weighted sum and weighted min-max formulations relatively to the solids content and number of particles profiles. Still, they are single-objective strategies, optimising a single objective function at



(a) End-point weight-averaged PSDs.



(b) Total number of particles.

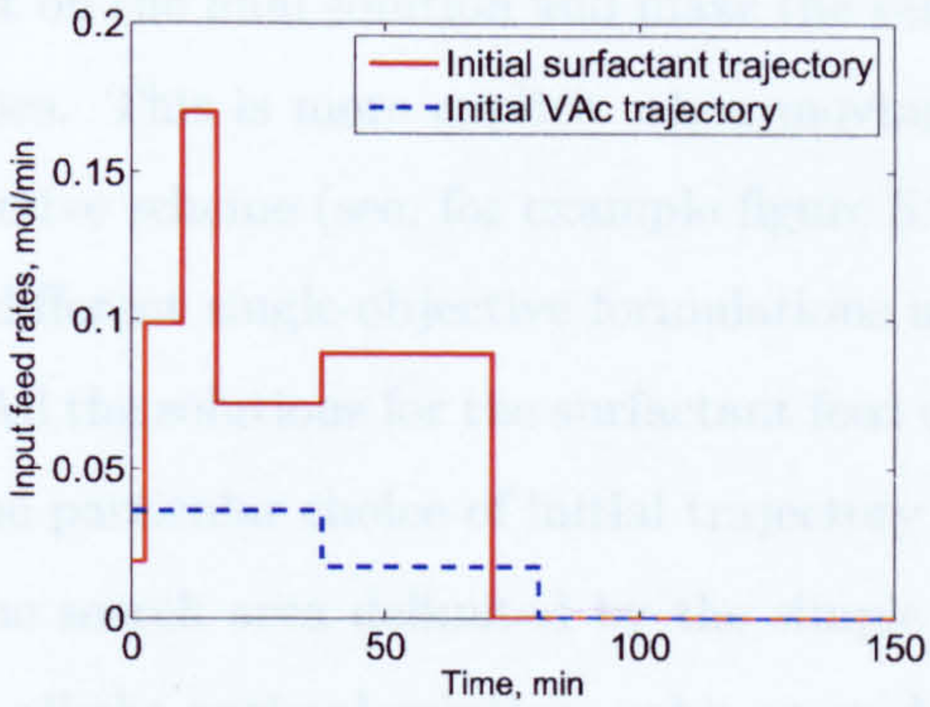


(c) Solids content.

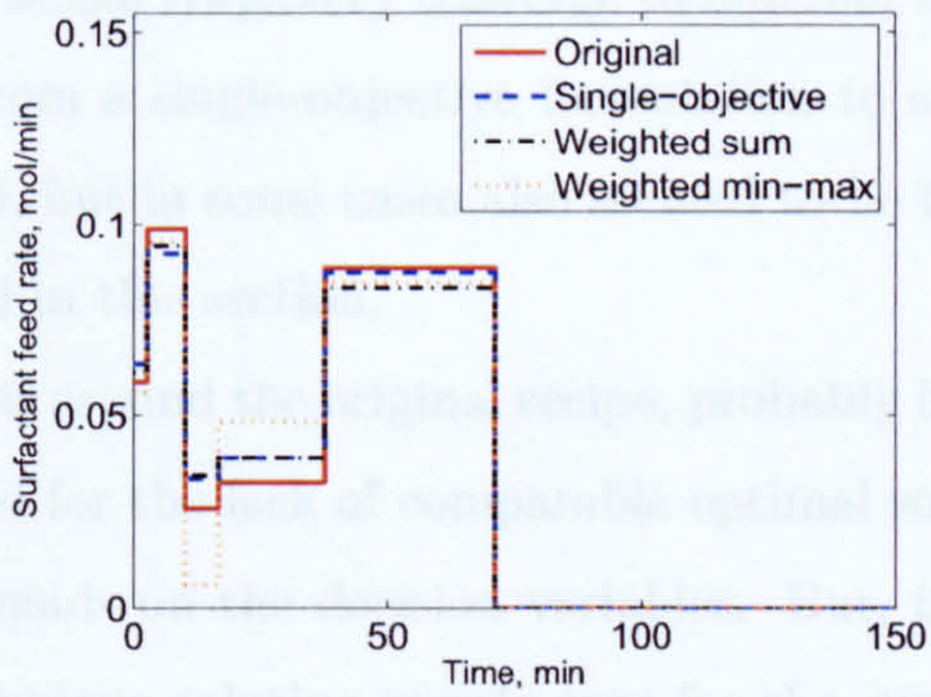
Figure 3.3: Comparison of weight-averaged PSD, total number of particles and solids content obtained from the three different formulations of the optimisation problem: single-objective, weighted sum and weighted min-max.

each iteration.

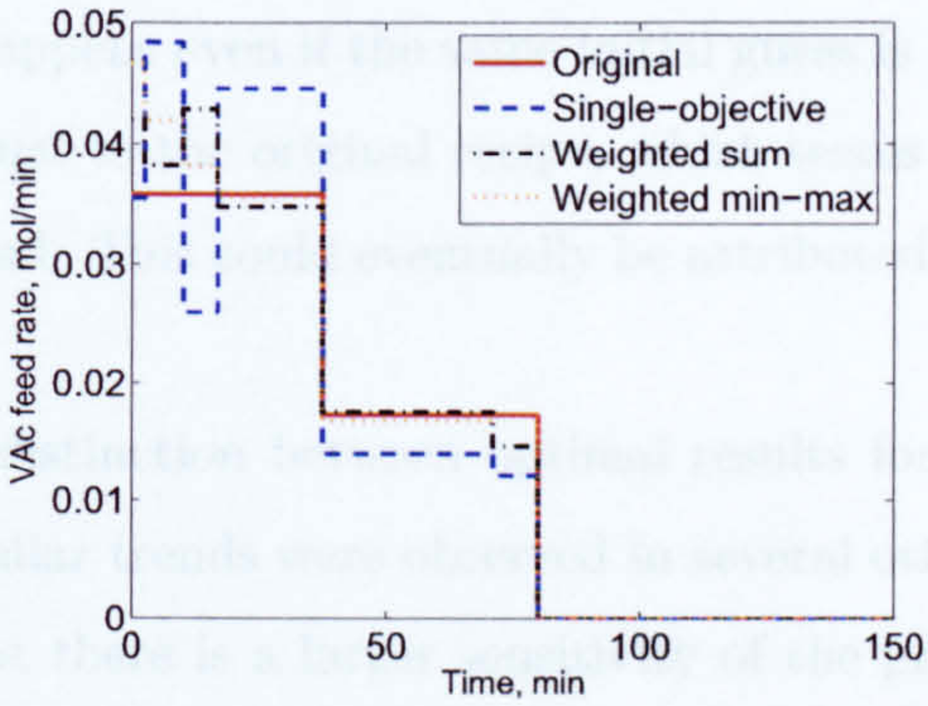
In figure 3.4 the optimal input trajectories for the three cases analysed in figure 3.3 are compared together with the original trajectory, *i.e.* the set of input variables used to produce the targets. The initial input trajectories are also reported to show how the optimiser works its way to the specified targets. Both gradient-based optimisation routines were used and a comparable match with the targets was obtained. The computation time when using the SQP algorithm resulted to be in general a bit larger (10-20 % more) than the one required by the routine implementing the quasi-Newton method. A typical computation time for the optimal recipe when implementing the SQP routine was 30 minutes.



(a) Initial surfactant and VAc feed rates.



(b) Optimal surfactant feed rates.



(c) Optimal VAc feed rates.

Figure 3.4: Initial guess for surfactant and VAc feed rates and comparison between original and optimal decision variables trajectories for the three different formulations of the optimisation problem: single-objective, weighted sum and weighted min-max.

Different information can be deduced from the results in figure 3.4. In the particular case reported in this figure, the initial guess (3.4(a)) for the VAc feed rate was set equal to the original recipe used to produce the target. For the surfactant an initial guess completely different from the original recipe was used. To compare the performance of the three problem formulations, the same set of feed rates was used as the initial trajectory for the three cases. This explains why the optimal recipes for the surfactant all tend to converge to a unique similar solution, with the slight difference in the feed rates that can be attributed, for example, to noise in the optimiser calculations.

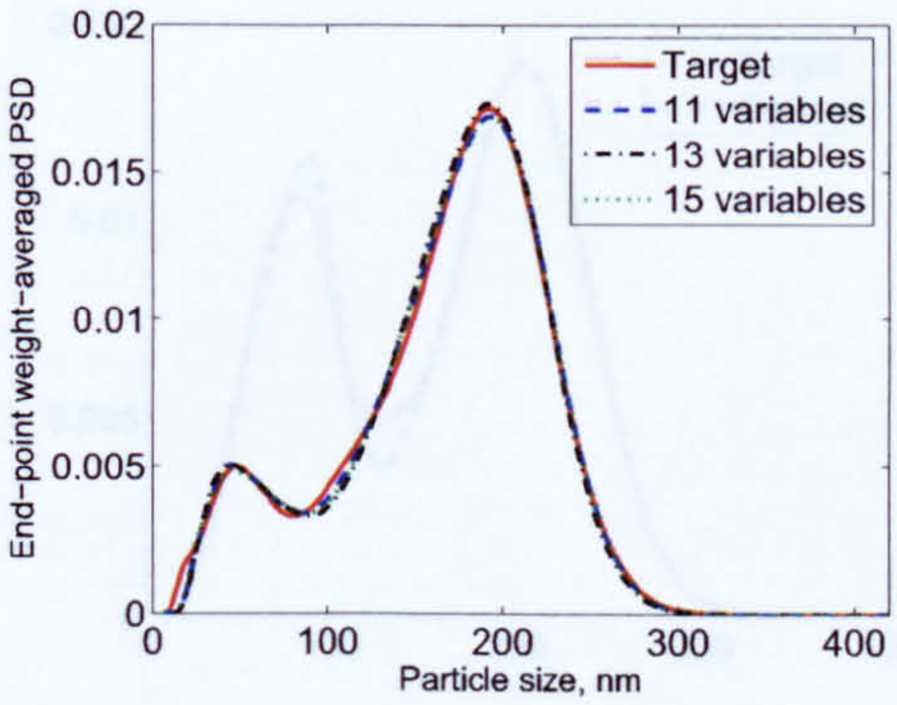
Of course, even the use of different formulations of the objective functions can have an

effect on the final solution and make the same initial trajectory converge to different optimal recipes. This is more explicit when moving from a single-objective formulation to a multi-objective scheme (see, for example figure 3.16), but in some cases also seemed to be true for the different single-objective formulations used in this section.

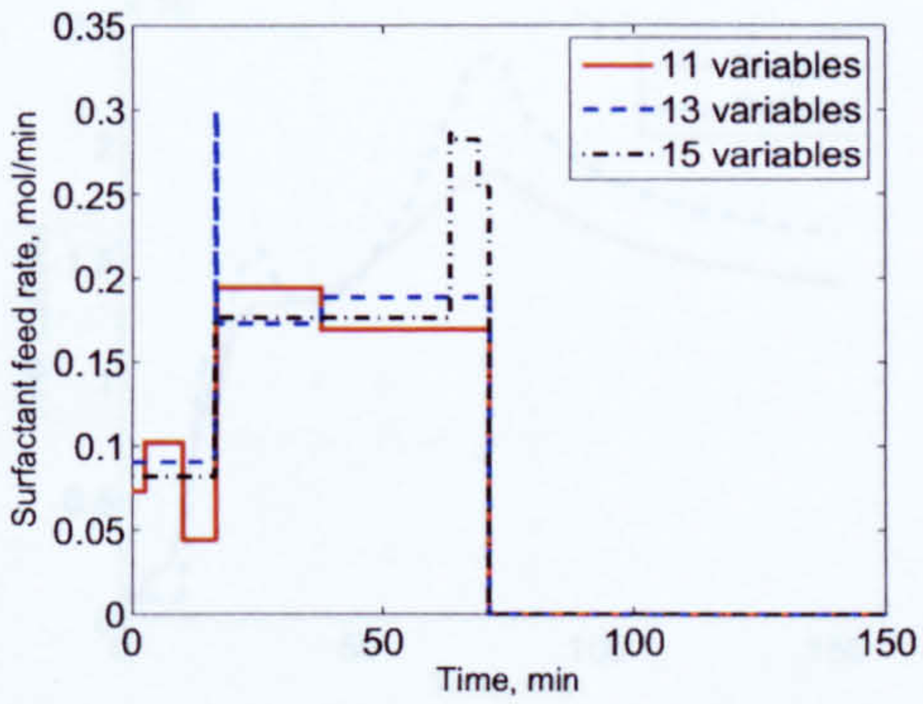
All the solutions for the surfactant feed orbit around the original recipe, probably because of the particular choice of initial trajectory and for the lack of comparable optimal solutions in the search area delimited by the simple bounds on the decision variables. But, the fact that all the optimal solutions orbit around a unique solution is only true for the surfactant feed rates. The VAc optimal feeds show a much larger variation and are basically different from case to case. This happens even if the same initial guess is used in all the cases and the VAc feed profile is set equal to the original recipe, which seems to be the best local optima the routines are able to find. This could eventually be attributed to the observed multiplicity of the solution.

Because of the clear distinction between optimal results for the surfactant and for the VAc and also because similar trends were observed in several other cases, a more reasonable explanation would be that there is a larger sensitivity of the process to the surfactant feed rates compared to the VAc feed rates. In most of the cases studied, when starting from a certain initial trajectory, the surfactant feed rates converged to a unique profile, the original or a different recipe, as expected. On the contrary, the VAc trajectory often presented wide differences. An hypothesis that would explain it is that the larger sensitivity of the system to the surfactant feed rates makes the routines use this sub-set of the decision variables, which are then driven towards the optimal solution, neglecting the contribution of the VAc feed rates. These are left behind by the optimiser during the search for the local optima at random values resulting from the search criteria used by the routines.

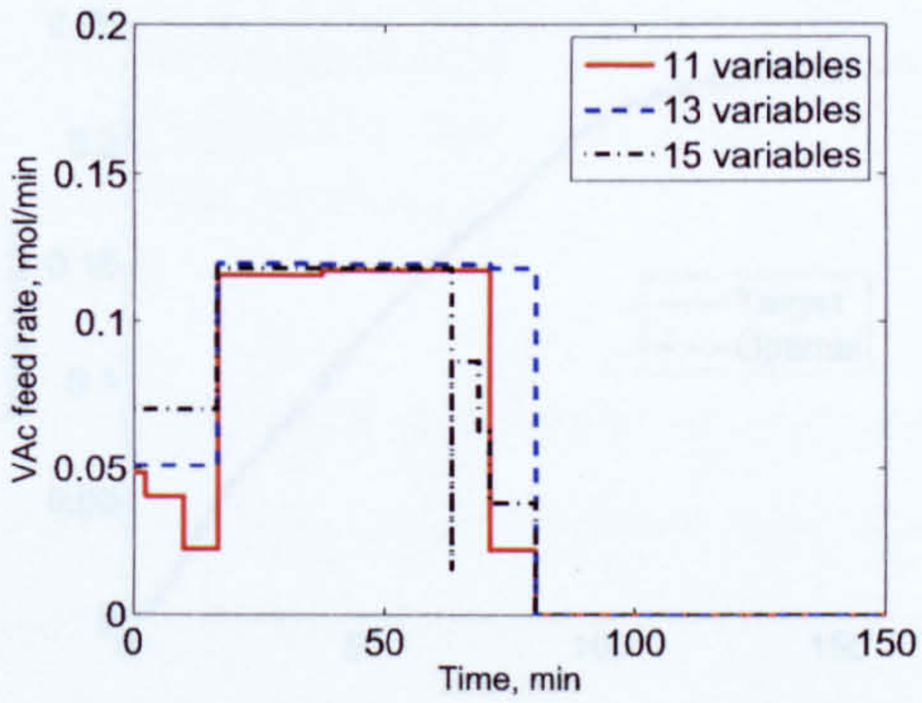
From the various cases analysed, it was observed that a combination of two different feed rates, *e.g.* VAc and surfactant, BuA and surfactant, initiator and surfactant and so on, limited to the first time intervals, is sufficient to drive the optimiser towards the desired target with a satisfactory accuracy. The use of feed rates of more than two reactants did not result in considerable improvement. At the same time, to limit the search vector to the feed



(a) End-point weight-averaged PSDs.



(b) Optimal surfactant feed rates.

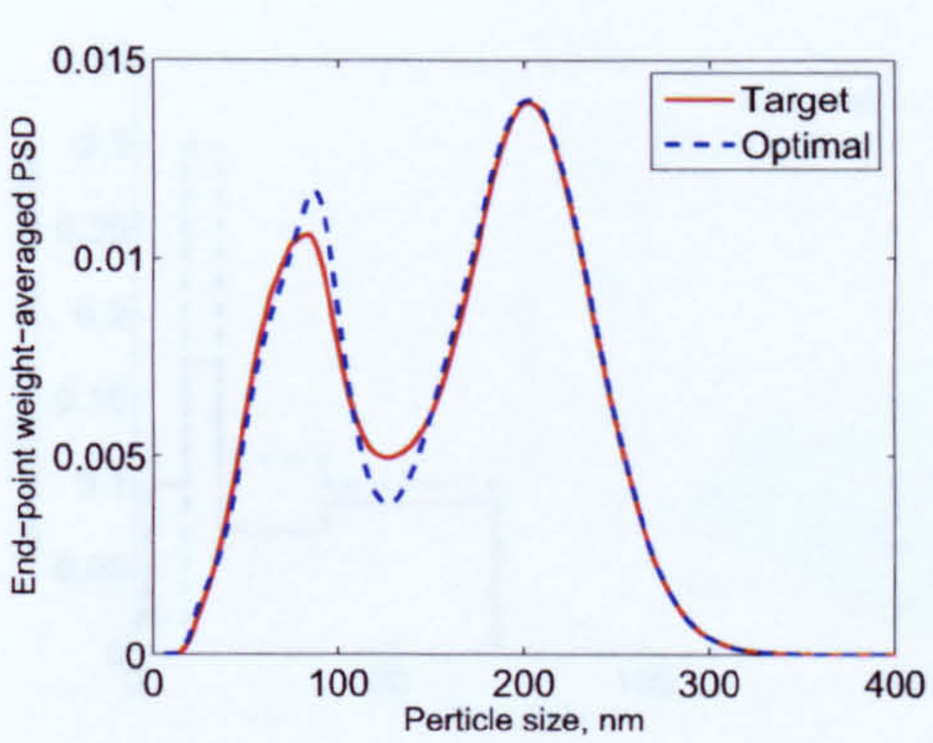


(c) Optimal VAc feed rates.

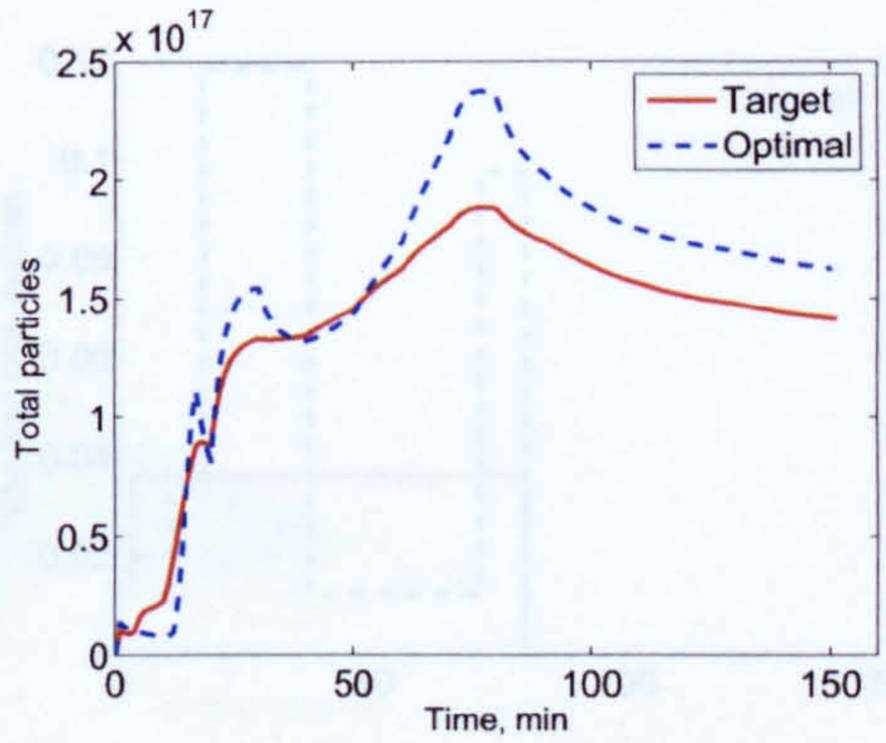
Figure 3.5: Comparison between end-point weight-averaged PSDs and optimal input trajectories when applying the direct single objective PSD optimisation for different number of decision variables.

rates of only one reactant does not always give an acceptable match with the desired target. From the different studies, it emerged that surfactant feed rates need always to be included in the control vector for the open-loop scheme to be effective. In a number of cases also the use of surfactant feed rates alone was satisfactory. This is understandable when realising that, as shown in section 3.1.2, all three the major phenomena that drive the evolution of the PSD depends on the surfactant concentration. The importance of this control variable has to be taken into account when building a control scheme for the PSD in emulsion polymerisation.

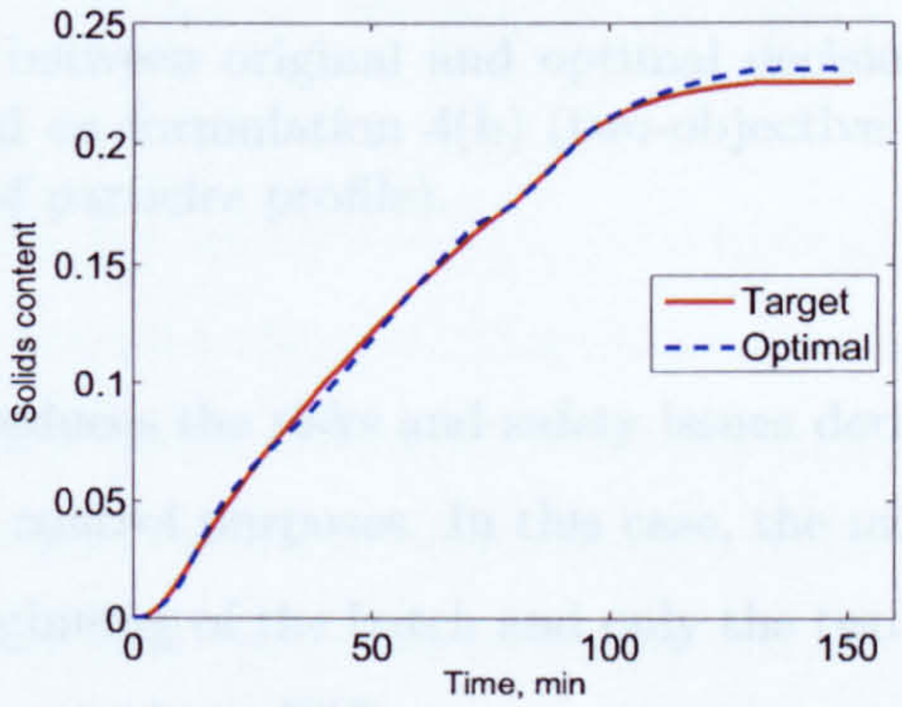
A major number of tests were done using surfactant combined with VAc and initiator feed rates. When combined with VAc feed rates, the resulting open-loop control scheme seemed to



(a) End-point weight-averaged PSDs.



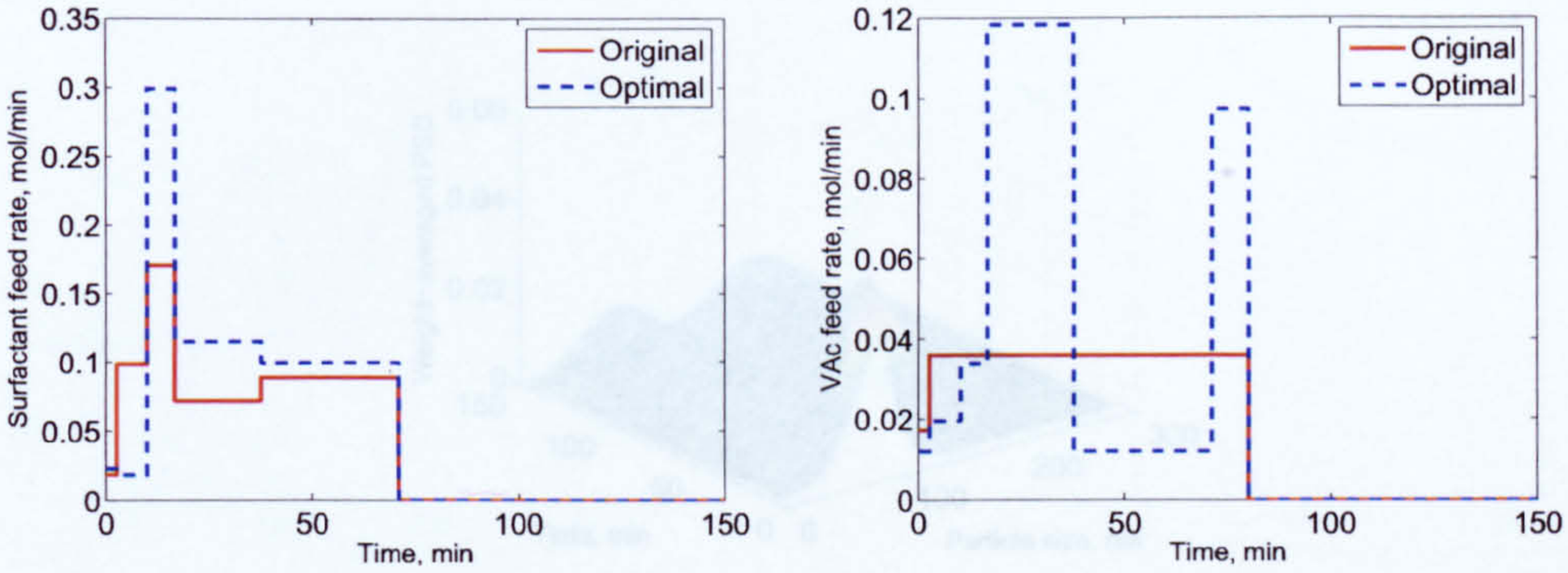
(b) Total number of particles.



(c) Solids content.

Figure 3.6: Comparison between the weight-averaged PSD, total number of particles and solids content for a pareto optimisation based on formulation 4(b) (two-objective optimisation, ϵ-constraint on the error of the number of particles profile, see section 3.1.3).

be applicable to most of the cases analysed. Comparable results where obtained when the BuA feed rates were used instead of VAc feed rates as control variables. Because of the increased difficulties in handling liquid BuA compared to the VAc, it was decided to concentrate on this second monomer. When the initiator feed rates were used in combination with surfactant feed rates, the match with the targets was still good and only less accurate in some cases when compared to the results obtained for the same systems with the surfactant/VAc feed rates. When using initiator feed rates as decision variables, the optimiser produces recipes that are easy to implement experimentally. In fact, liquid VAc and BuA are quite difficult to handle, while both surfactant and initiator can usually be dissolved in water and used as



(a) Original and optimal feed rates of surfactant. (b) Original and optimal feed rates of VAc.

Figure 3.7: Comparison between original and optimal decision variables trajectories for a pareto optimisation based on formulation 4(b) (two-objective optimisation, ϵ-constraint on the error of the number of particles profile).

aqueous solutions. This reduces the risks and safety issues deriving from the need to handle (feed) these reactants for control purposes. In this case, the monomers can both be inserted into the reactor at the beginning of the batch and only the two solutions fed into the reactor in a semi-batch mode to control the PSD.

The duration of the time intervals can also be used as decision variable. The 11 manipulated variables from the VAc/surfactant feed rates case analysed previously were augmented in two further cases with the first two and four injection time intervals used as decision variables. The choice of the first time intervals was suggested by the underlying difficulties associated with the initial stage of the process. The time interval was limited to a certain minimum width through boundaries on the time intervals and linear constraints were applied to have a progressive batch time. Different targets and optimisation problem formulations were implemented. In figure 3.5 are shown the final PSD and the optimal feed rate profiles for a single-objective case.

A very good match was observed between simulated and target PSD when using only the flow rates as decision variables. Thus, the further addition of injection time intervals as manipulated variables does not produce tangible improvements. At the same time, the capacity of the optimiser to match desired target PSDs is confirmed.

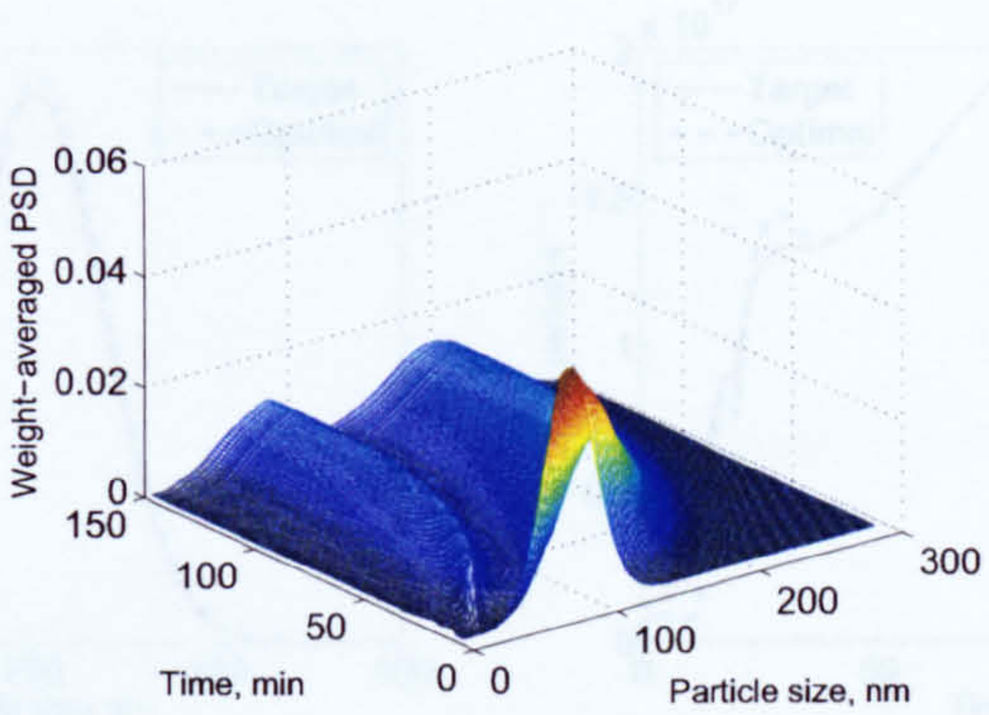
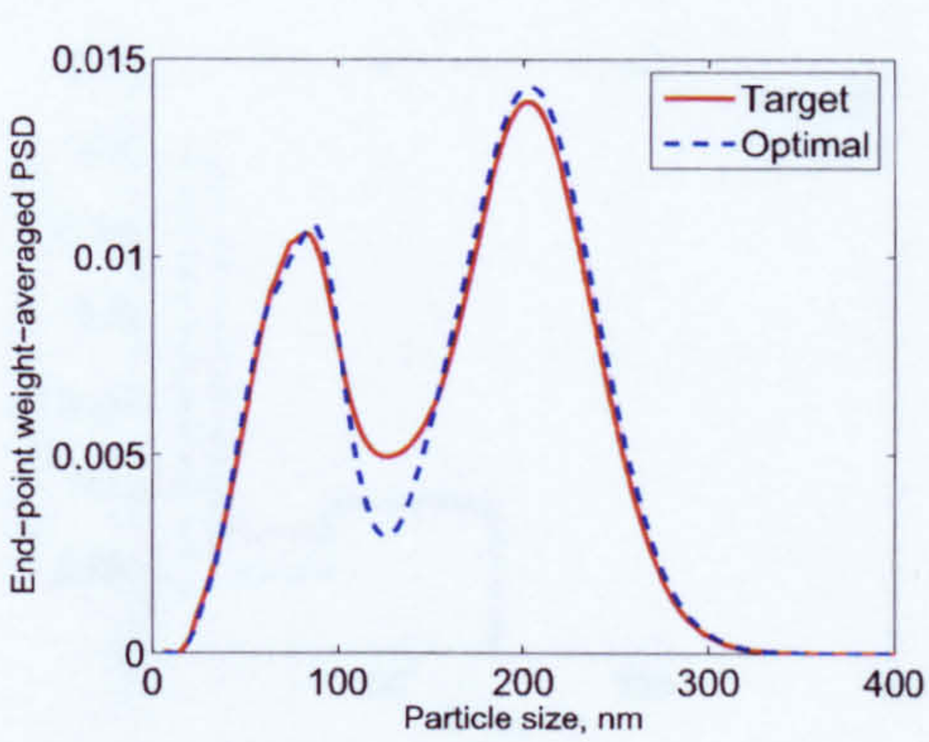


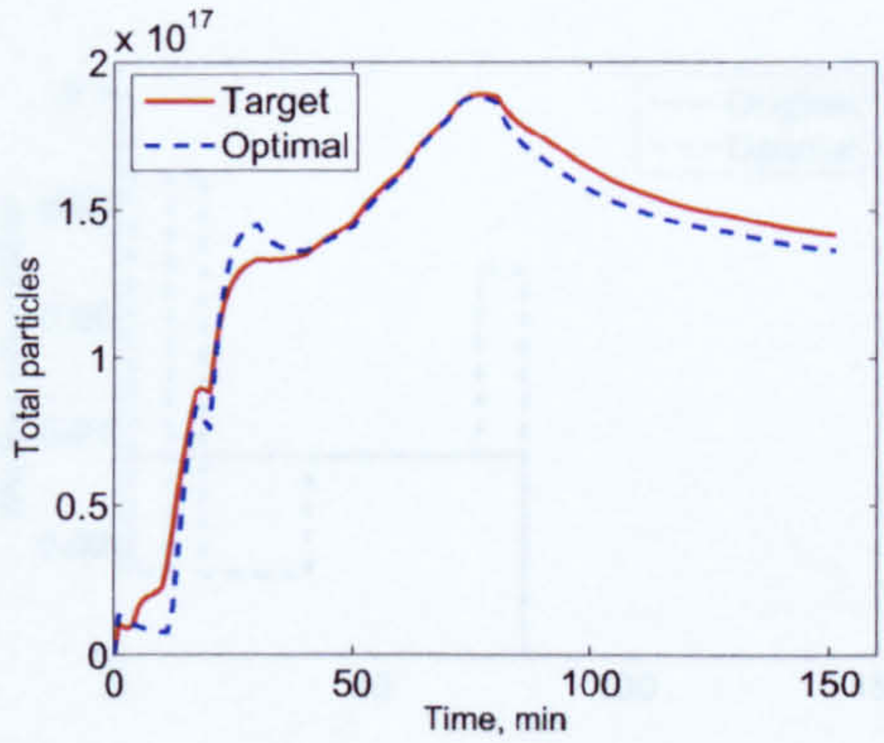
Figure 3.8: Weight-averaged PSD for a pareto optimisation based on formulation 4(b) (two-objective optimisation, ϵ-constraint on the error of the number of particles profile).

As can be observed from figures 3.5(b) and 3.5(c) the resulting optimal input trajectories may present transient and sudden changes. This shows the ability of the optimiser to track the desired target even when drastic modifications of the manipulated variables are required, but at the same time, it raises a practical issue regarding the implementation of the computed optimal recipe, in the sense that the pump used may not be able to produce quick enough response to such sudden and brief changes of flow rate. Anyway, boundaries my be adjusted to limit the extent of these variations and to impose larger minimum width for the time intervals. The presence of feed peaks with short durations in figures 3.5(b) and 3.5(c) gives us also a further information, which is the need of a fine tailoring of the process in the early stages of the batch.

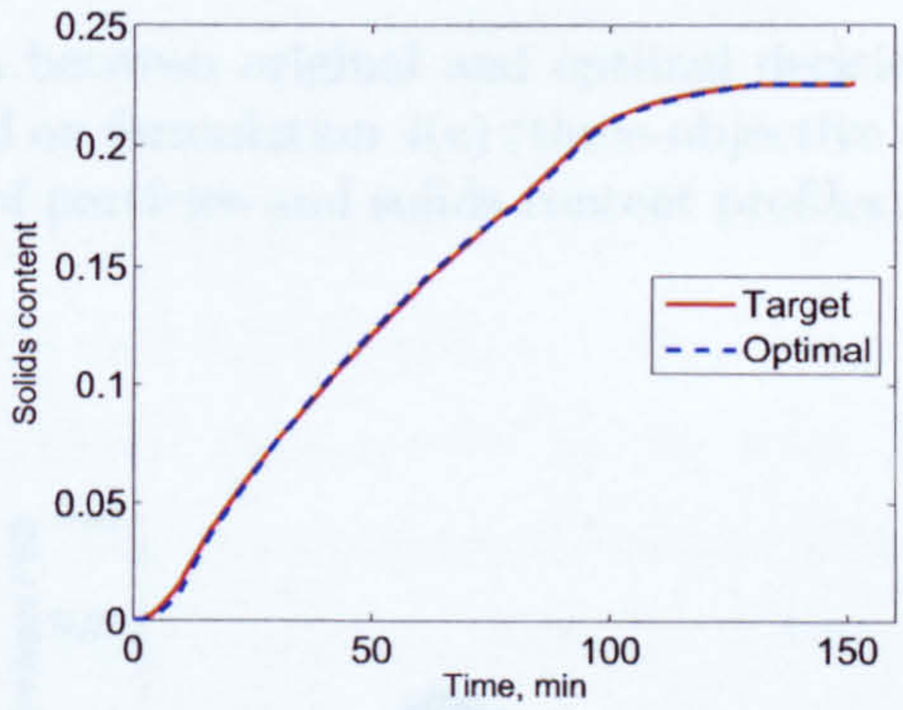
When using the duration of the time interval as decision variables a slightly worse match with the targets was observed in a number of cases. This is probably a consequence of the increase in the number of constraints imposed to the optimisation routine. This limits the search area and adds complexities to the optimisation process. For this reason, and because of the accurate discretisation already performed on the batch time, most of the open-loop control studies were performed using feed rates only as decision variables. Still the larger flexibility offered by this formulation has the potential to produce more accurate and robust optimisation routines, as observed for the multi-objective framework in section 3.2.3. The need for a limited number of variables for a considerable number of problems is a positive



(a) End-point weight-averaged PSDs.



(b) Total number of particles.



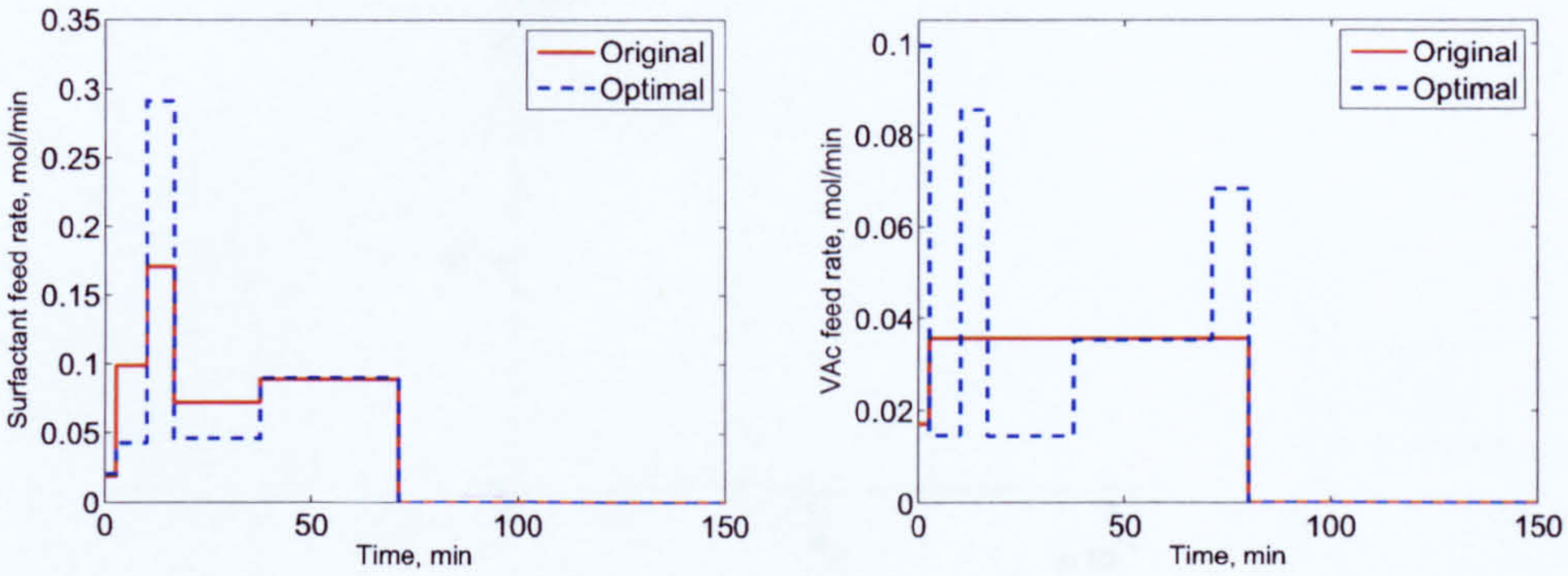
(c) Solids content.

Figure 3.9: Comparison between the weight-averaged PSD, total number of particles and solids content for a pareto optimisation based on formulation 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles).

aspect of the current routines.

3.2.3 Off-line computation of optimal recipes using a multi-objective approach

The results shown in figure 3.3 are good for a single-objective formulation implemented using gradient-based optimisation routines. This is even more true if this strategy is applied to such a complex and nonlinear problem as the PSD control in emulsion polymerisation and if results comparable to those obtained with the weighted sum and weighted min-max scheme



(a) Original and optimal feed rates of surfactant. (b) Original and optimal feed rates of VAc.

Figure 3.10: Comparison between original and optimal decision variables trajectories for a pareto optimisation based on formulation 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles).

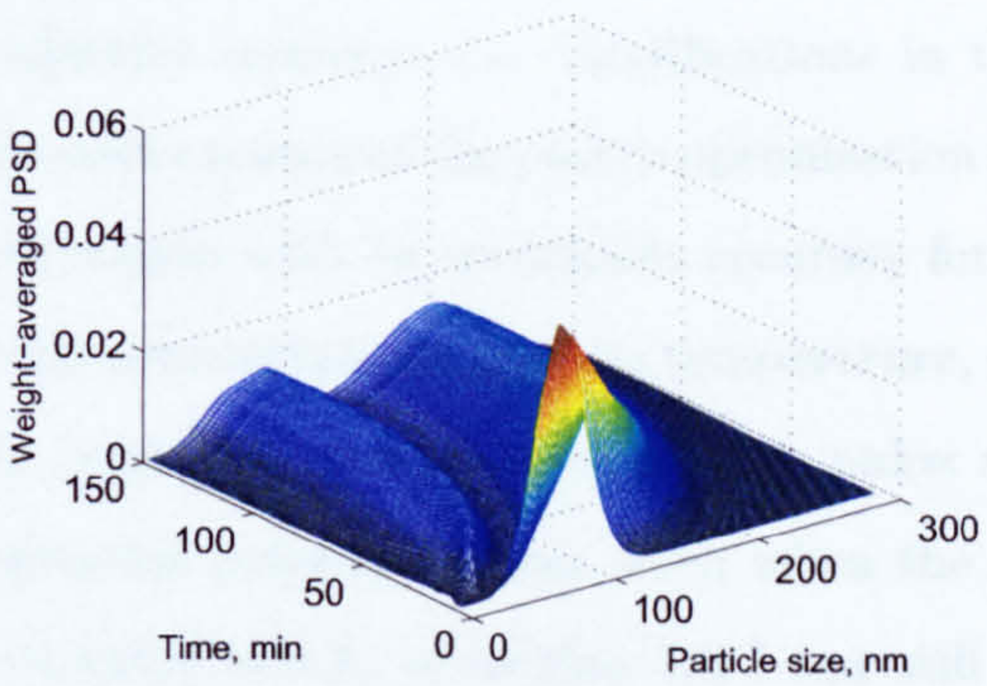


Figure 3.11: Weight-averaged PSD for a pareto optimisation based on formulation 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles).

(pseudo multi-objective scheme) are obtained with the single objective strategy tailored only on the PSD. This is probably a consequence of the accurate tuning of the optimiser on the system. It will be seen that the same accuracy in the match with the targets seen in figure 3.3 was rarely achieved when using the multi-objective strategy presented in this section. The main reason why studies have still been carried out on the pareto optimisation strategy is the greater reliability of this scheme. In cases where the single-objective strategies,

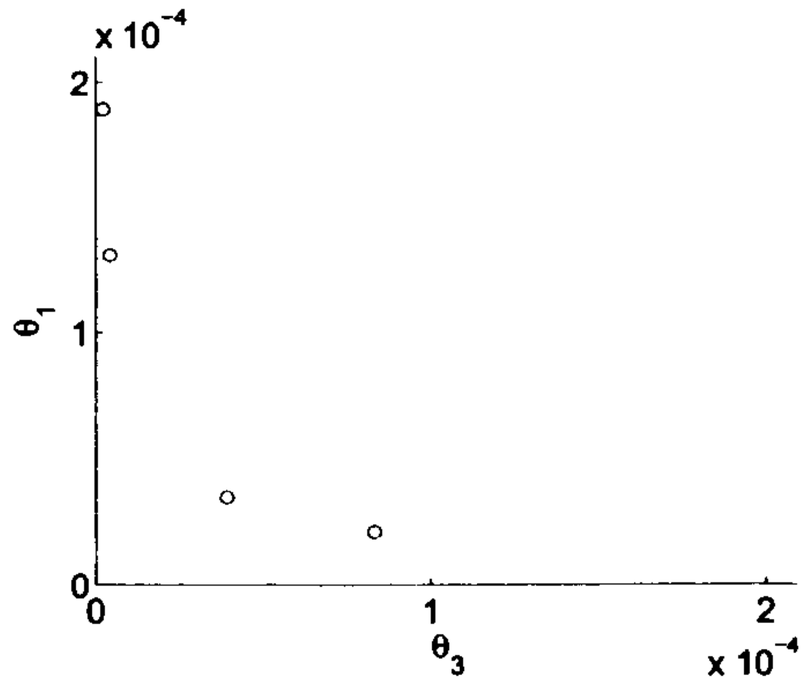
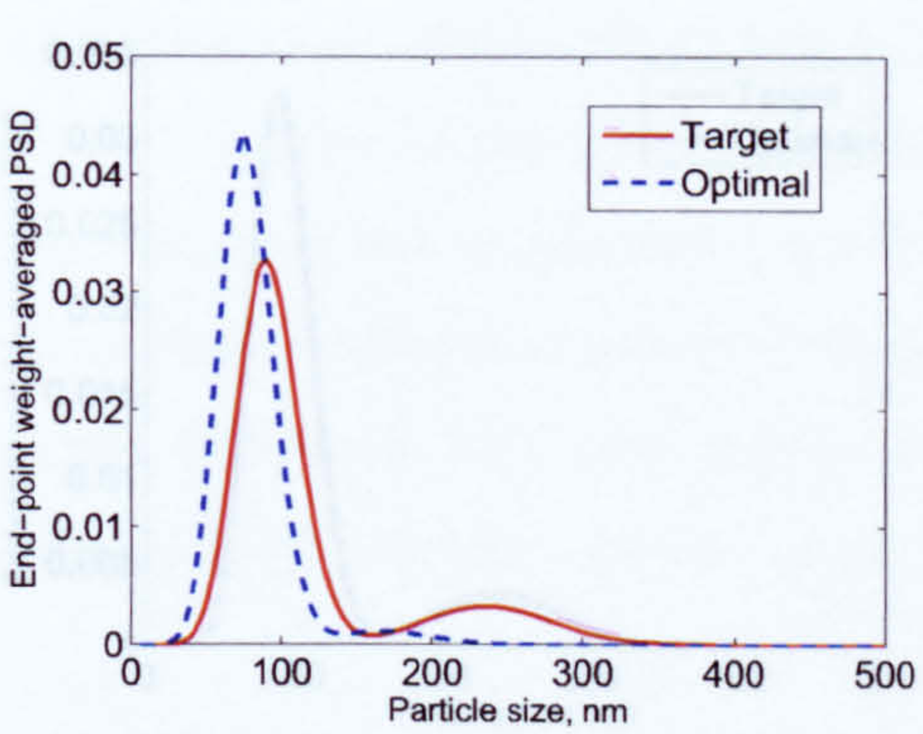


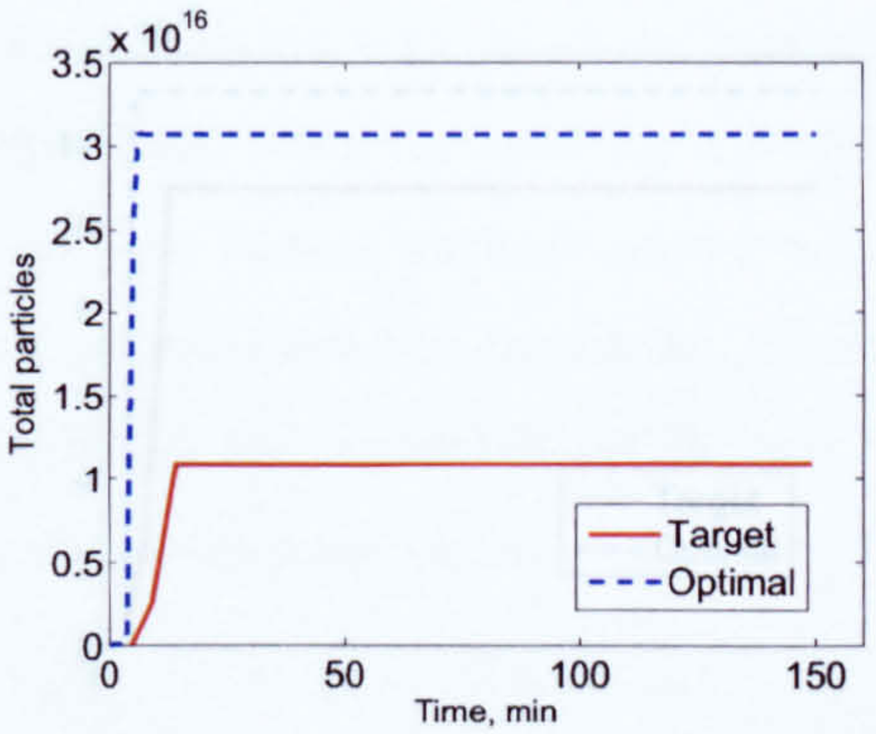
Figure 3.12: Set of pareto solutions obtained applying case 4(b) (two-objective optimisation, ϵ-constraint on the error of the number of particles profile).

weighted sum and weighted min-max included, failed to reach the desired profile, the multi-objective scheme was able to reach them with a good accuracy, offering enhanced robustness compared to the single-objective strategy, *i.e.* modifications in the system conditions had only a reduced effect on the performance of the pareto optimisation strategy. This routine was able to produce the desired targets with an acceptable accuracy for a wide range of operating conditions (different solution concentrations, system temperature, shear rate conditions, etc) and with different systems (ionic and non-ionic surfactant, redox and thermal initiator, and homogeneous and heterogeneous polymerisation), even when the single-objective strategies failed to do so. The encouraging results of section 3.2.2 can still and have to be exploited whenever possible. Single-objective strategies, when implementable with good accuracy, can be used as an alternative to the more robust, but also more computationally demanding, multi-objective strategy.

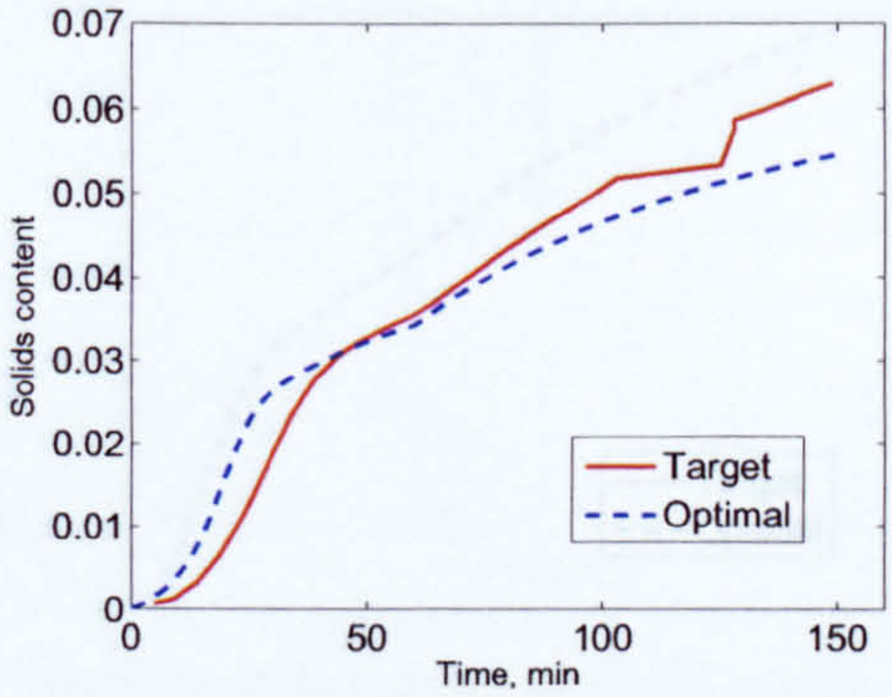
When implementing the multi-objective strategy to perform pareto optimisations, non-linear constraints are introduced. These are the inequality constraints imposed on θ_2 and θ_3 when using the formulations 4(a), 4(b) and 4(c) in section 3.1.3. Pareto solutions are a set of non-dominated solutions, *i.e.* each solution is better than every other solution in the set at least with respect to one of the objectives. Of all the pareto solutions in the set only the one closest to the utopia point is considered to be the optimal solution. The utopia point is where all the objective functions taken into account assume the corresponding smallest value



(a) End-point weight-averaged PSDs.



(b) Total number of particles.



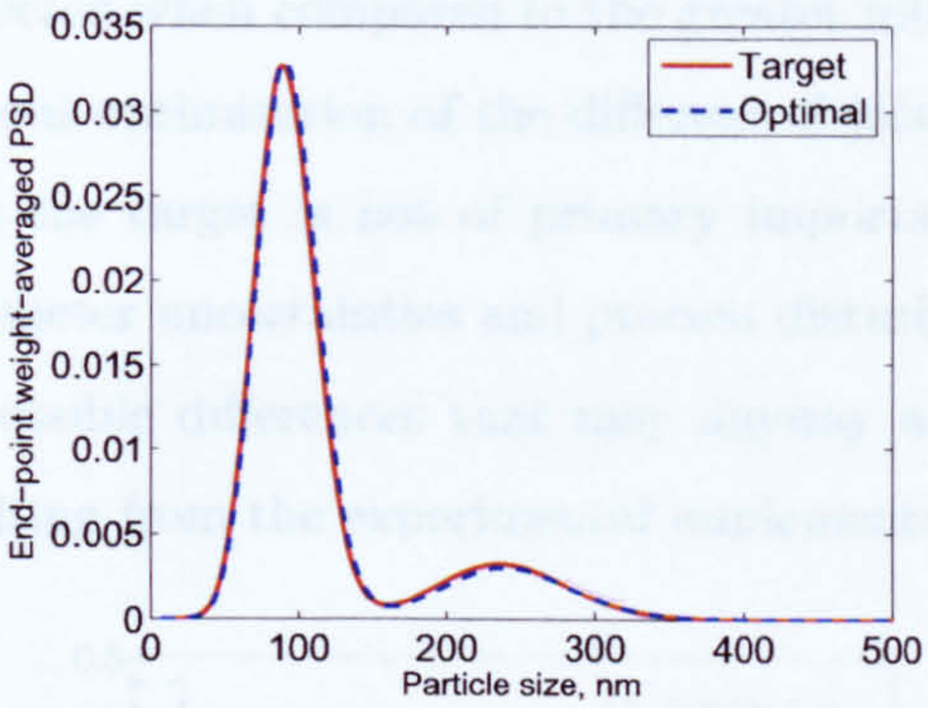
(c) Solids content.

Figure 3.13: Comparison between the weight-averaged PSD, total number of particles and solids content for a pareto optimisation based on formulation 4(a) (two-objective optimisation, ϵ-constraint on the error of the solids content profile).

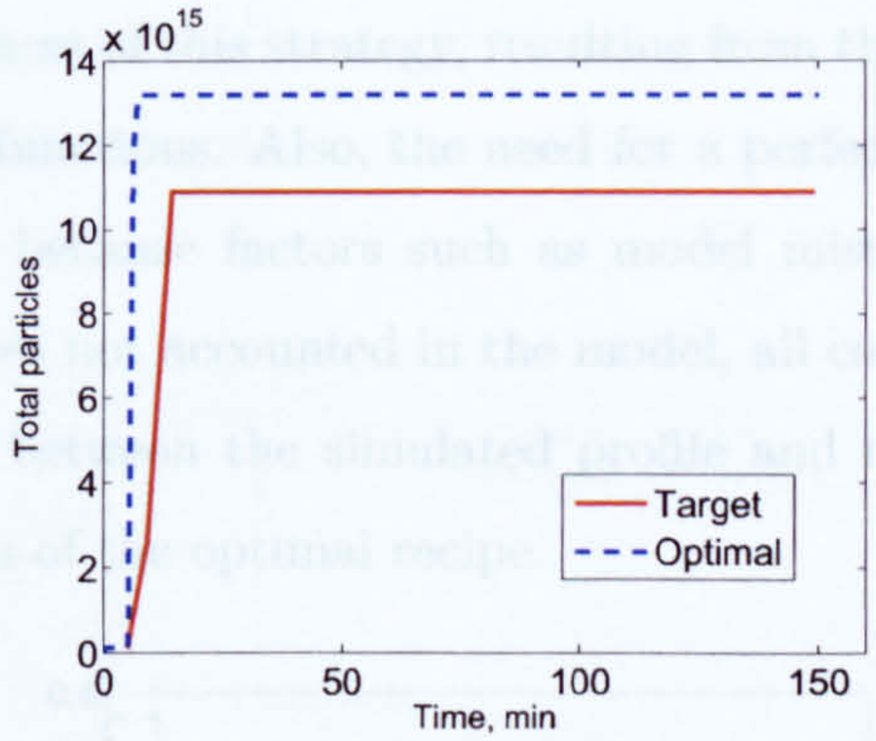
in the set. Because of the nonlinearity of the problem, only the routine based on SQP was implemented for the solution of these optimisation problems.

Figures 3.6, 3.7 and 3.8 show the results obtained implementing a two-objective formulation of the pareto optimisation, while figures 3.9, 3.10 and 3.11 show the results obtained from the implementation of a three-objective formulation of the problem. In figures 3.12 and table 3.2 the sets of pareto solutions to which the above solutions refer are presented. Surfactant and VAc feed rates were used as decision variables in these examples.

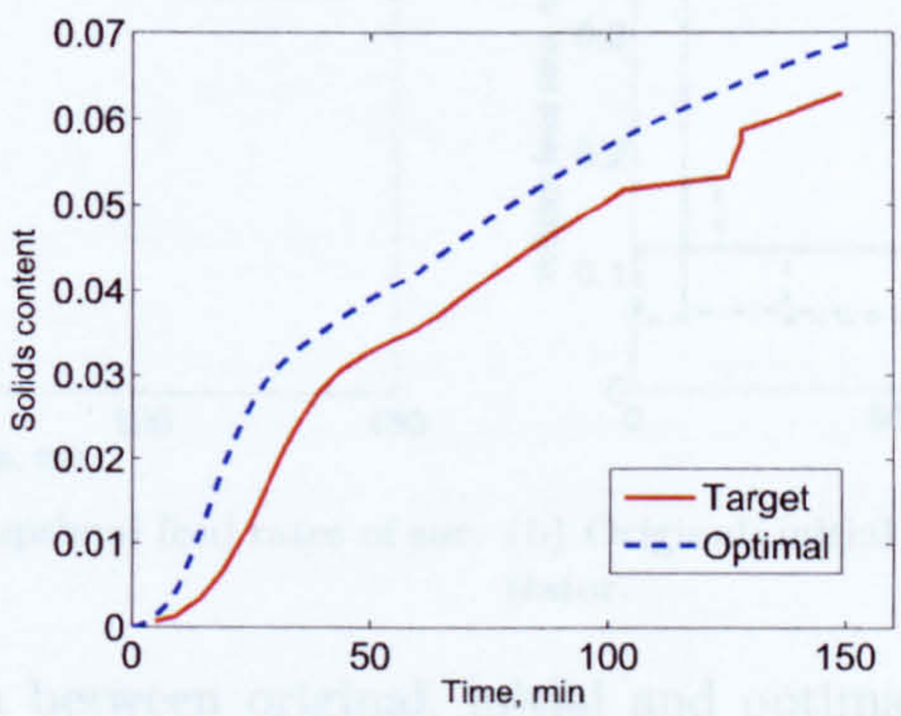
The study of the profiles obtained for PSD, number of particles and solids content confirms the strong bound between the different sub-processes in emulsion polymerisation. Slightly



(a) End-point weight-averaged PSDs.



(b) Total number of particles.

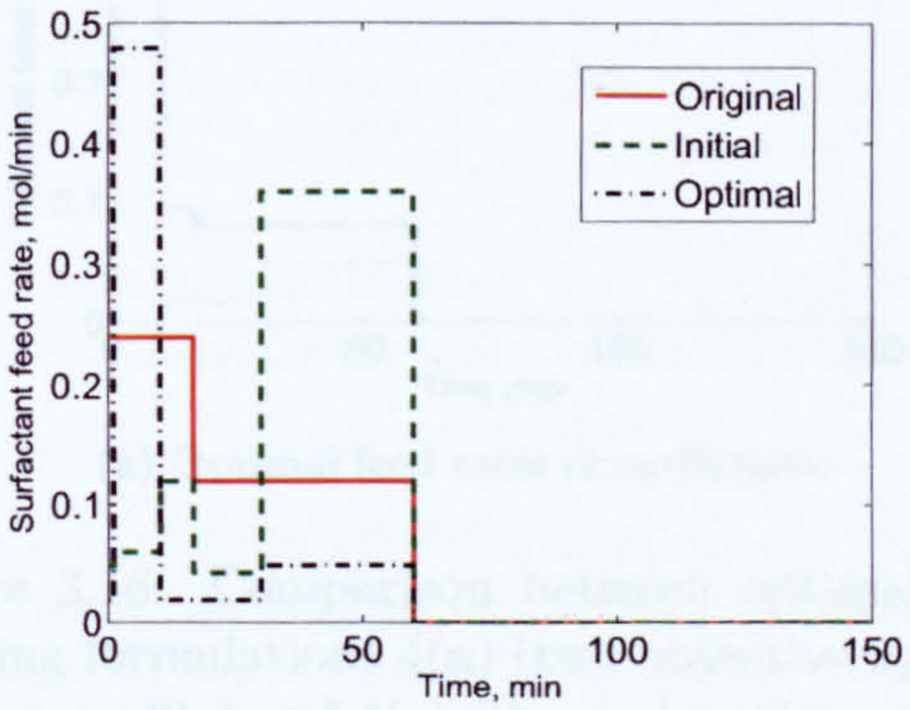


(c) Solids content.

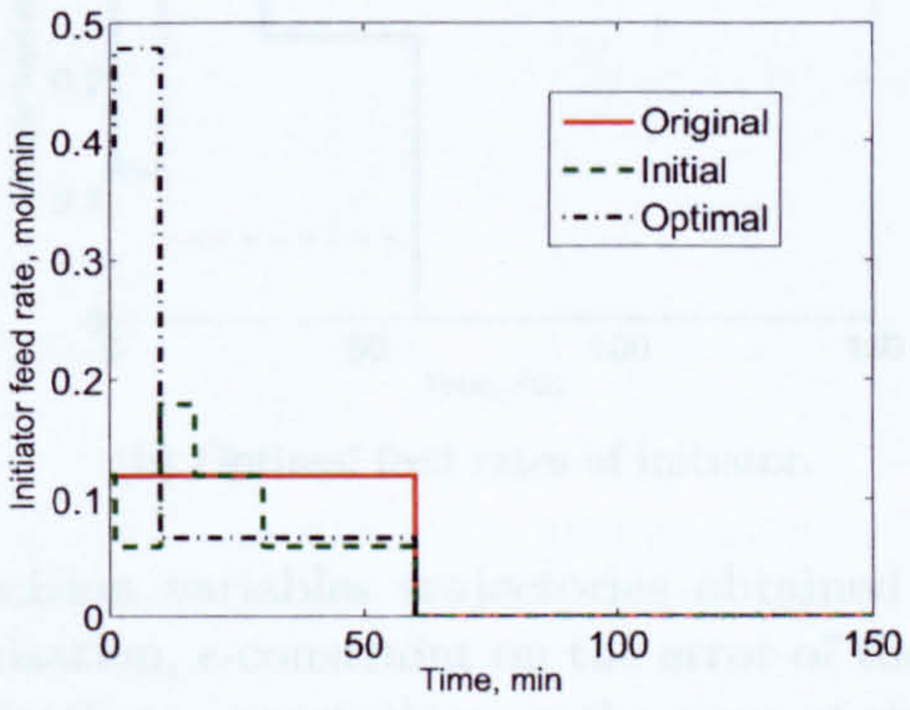
Figure 3.14: Comparison between the weight-averaged PSD, total number of particles and solids content for a pareto optimisation based on formulation 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles). The error is considerably corrected when including the third objective function to the problem formulation (refer to figure 3.13).

better results were in fact obtained when all three objective functions were optimised simultaneously. But, when optimising more than one objective function, the optimisation routine has to solve a problem of increased complexity due to the interaction between the rate processes and the integrated effect of the different inputs on the particle-level phenomena. Also, a larger number of constraints need to be satisfied. This is probably the cause of the slightly worse match with the targets observed when comparing the profiles in figures 3.6 and 3.9 with the results from the single-objective formulations in section 3.2.2. Still, this drawback can be

neglected when compared to the greater robustness of this strategy, resulting from the simultaneous optimisation of the different objective functions. Also, the need for a perfect match with the target is not of primary importance because factors such as model mismatches, parameter uncertainties and process disturbances not accounted in the model, all contribute to possible differences that may anyway arise between the simulated profile and the PSD resulting from the experimental implementation of the optimal recipe.



(a) Original, initial and optimal feed rates of surfactant.



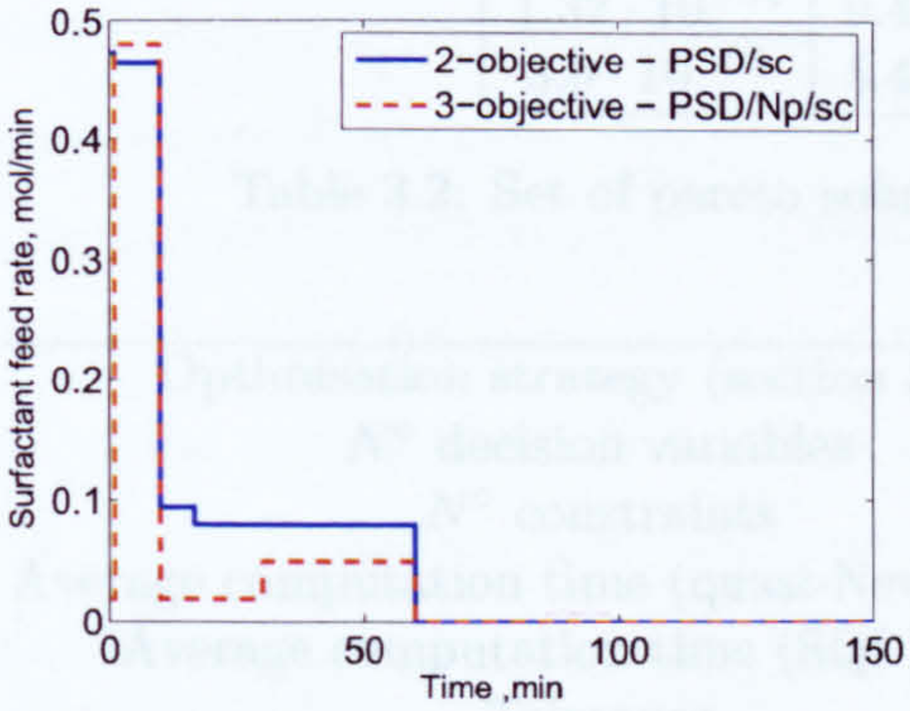
(b) Original, initial and optimal feed rates of initiator.

Figure 3.15: Comparison between original, initial and optimal decision variables trajectories for a pareto optimisation based on formulation 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles).

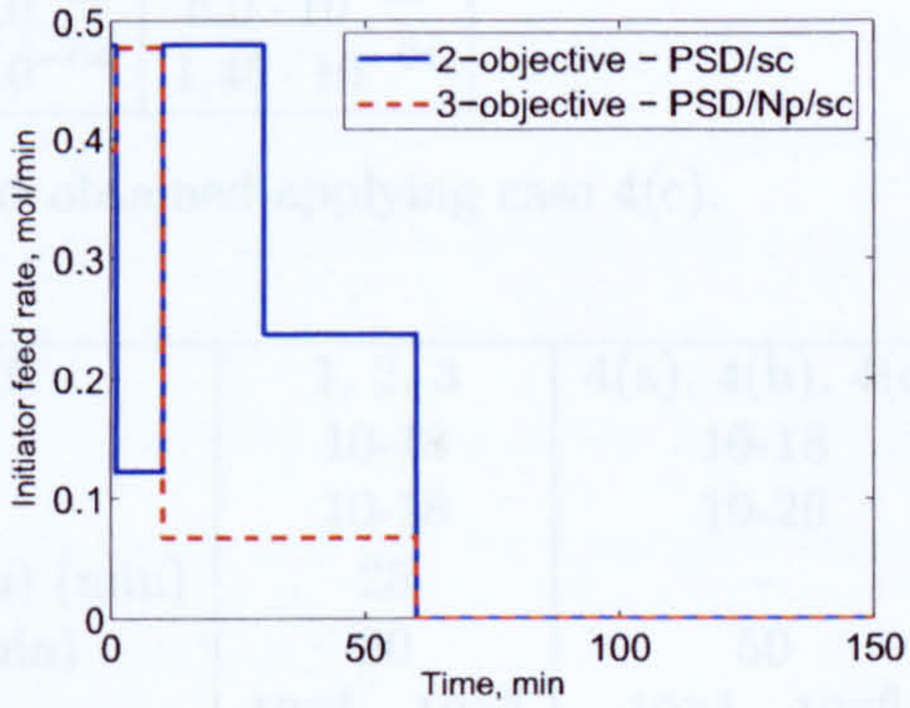
As observed in section 2.4.4, the end-use properties of the latex are often determined by the combination of more than one process variable. In a multi-objective strategy different process properties are optimised simultaneously, making the multi-objective optimisation in emulsion polymerisation often a requirement rather than an option.

The results presented in figures 3.13 and 3.14 confirm the ability of the multi-objective strategy to track the process evolution. The PSD, solids content and number of particles profile in figure 3.13 were obtained implementing a two objective formulation of the optimisation problem, with ϵ-constraint imposed on the error of the solids content profile. In this figure, a certain mismatch is observed between optimal and target profiles. The error is considerably corrected when including the third objective function to the problem formulation, as can be seen in figure 3.14. In this case, the optimal PSD overlap the target profile almost perfectly.

A worse match is obtained for the sc profile compared to the one obtained implementing the two-objective strategy, but this is balanced by a considerable improvement in the match with the number of particles (Np) profile.



(a) Optimal feed rates of surfactant.



(b) Optimal feed rates of initiator.

Figure 3.16: Comparison between optimal decision variables trajectories obtained implementing formulations 4(a) (two-objective optimisation, ϵ-constraint on the error of the solids content profile) and 4(c) (three-objective optimisation, ϵ-constraints on the error of the number of particles and solids content profiles).

The optimal feed trajectories resulting from the three-objective optimisation scheme are presented in figure 3.15. In this case a combination of surfactant and initiator feed rates are used as decision variables. In these last examples, a modified model accounting for the use of ionic surfactant and thermal initiator (Sweetman, 2008) was used to simulate the system.

Figure 3.16 compares the optimal feed trajectories obtained when implementing the two-objective and the three-objective formulations to the same problem (*i.e.* same operating conditions and initial input trajectory). These feed policies are those used to produce the profiles in figure 3.13 and 3.14, respectively. As already mentioned, the use of different formulations of the optimisation problem may lead to different optimal solutions. As it is possible to see from figure 3.16, starting from the same initial guess the optimal recipes, and consequently the match with the targets, are considerably different for the two formulations. This proves the importance of a careful formulation of the optimisation problem. Different optimal solutions are expected for the multi-objective formulations, for which both number

θ_1	θ_2	θ_3
$4.37 \cdot 10^{-04}$	$3.0 \cdot 10^{-06}$	$1.5 \cdot 10^{-05}$
$8.6 \cdot 10^{-05}$	$5.0 \cdot 10^{-06}$	$1.32 \cdot 10^{-04}$
$8.0 \cdot 10^{-05}$	$8.0 \cdot 10^{-06}$	$1.5 \cdot 10^{-05}$
$6.6 \cdot 10^{-05}$	$9.0 \cdot 10^{-06}$	$8.0 \cdot 10^{-06}$
$1.32 \cdot 10^{-04}$	$9.49 \cdot 10^{-04}$	$5.0 \cdot 10^{-06}$
$3.0 \cdot 10^{-05}$	$5.48 \cdot 10^{-04}$	$1.45 \cdot 10^{-04}$

Table 3.2: Set of pareto solutions obtained applying case 4(c).

Optimisation strategy (section 3.1.3)	1, 2, 3	4(a), 4(b), 4(c)
$N°$ decision variables	10-18	10-18
$N°$ constraints	10-18	10-26
Average computation time (quasi-Newton) (min)	25	-
Average computation time (SQP) (min)	30	50
Tolerance	10^{-4} - 10^{-6}	10^{-4} - 10^{-6}

Table 3.3: Average computation time associated with the different optimisation strategies. Constraints are simple bounds for cases 1, 2 and 3, and simple bounds, linear and nonlinear penalties for cases 4(a), 4(b) and 4(c).

and type of the objective functions change from case to case.

The two optimisation routines implemented in these studies, based on quasi-Newton method and SQP, showed comparable performances. The implementation of both routines resulted in a good match with the different targets for most of the operating conditions considered. The major difference between the two routines was that the SQP algorithm was able to handle linear and nonlinear constraints, while the quasi-Newton algorithm only simple bound penalties. Then, between the two routines, the one based on SQP was the only one that could be applied to the multi-objective optimisation problem (nonlinear constraints imposed on the objective functions) and to problems where the duration of the feed injections was included as decision variable (linear constraints relating the time intervals). A comparison of the SQP and quasi-Newton algorithms, and of the different optimisation strategies implemented, in terms of computation time, is presented in table 3.3.

3.3 Summary

Studies were carried out on the open-lop control of emulsion latex PSD. A model-based strategy was implemented as the most suitable to meet the complex and multi-modal PSD objectives required by industrial practice. The optimal recipes were computed via optimisation routines based on single-objective and multi-objective hierarchical cost functions.

A hierarchical control strategy can drive a property towards a specific target through the inferential control of other related variables. The PSD dynamics can be indirectly controlled regulating the evolution of solids content and number of particles of the latex. These are directly related to particle nucleation and growth rates, and can be controlled through the manipulation of initiator, monomers and surfactant feed rates.

The optimisation problems associated with the computation of optimal input trajectories to be used for the production of target PSDs are highly non-convex and characterised by discontinuities. These problems were solved using gradient-based optimisation routines, which gave excellent results in terms of the match between targets and simulated distributions. These optimisation strategies were used as an alternative to global optimisation techniques with the aim of reducing the computation time and because of the greater accuracy of gradient-based optimisation strategies in identifying local minima when proper boundaries are supplied.

Open-loop control studies were carried out exploiting the features of the population balance model developed by Immanuel and co-workers (Immanuel et al., 2002, 2003). The effectiveness of different optimisation strategies in finding the optimal feed trajectories towards multi-modal and complex target PSDs was tested. The copolymerisation of Vinyl Acetate (VAc) and Butyl Acrylate (BuA) under non-ionic surfactant and redox initiator in a semi-batch reactor was first considered. A modified model (Sweetman, 2008) accounting for the use of ionic surfactant and thermal initiator was also employed.

Three objective functions were considered in the present study, θ_1, θ_2 and θ_3, accounting for the error on the end-point weight-averaged PSD, solids content and number of particle profiles, respectively. They were used in different formulations of the optimisation problem: direct single objective, weighted sum, weighted min-max and multi-objective ϵ-constrained

pareto optimisation. The optimisation problems were solved subject to simple bounds penalties applied to each decision variable, linear constraints relating the time intervals and nonlinear inequality constraints imposed on θ_2 and θ_3 in the pareto optimisation.

Monomers, surfactant and initiator feed rates, together with the duration of the time interval for the injection of these reactants, were used as manipulated variables. The batch was divided in time intervals, and the feed rates were defined as piece-wise constants within each time interval. The decision variables used for optimisation were the duration of the time intervals and the piece-wise constant values of the flow rate of reactants. Different combinations of these decision variables were tested. For a batch spanning 150 minutes, generally the feed rates in the first 80 minutes of the batch were used as manipulated variables. The reactant feed rates were set equal to 0 towards the end of the batch to prevent the distribution to evolve behind the end-batch point.

Two different gradient-based optimisation strategies were implemented using routines from NAG in FORTRAN (NAG, 2005). The first routine implements a quasi-Newton algorithm, while the second in designed to minimise an arbitrary smooth function subject to constraints using a sequential quadratic programming (SQP) method.

The analysis of the results confirmed the non-convexity of the optimisation problem under study. This analysis also showed that working with a sufficiently large number of carefully selected manipulated variables the optimality criteria set by the implemented routines are satisfied by a number of local minima. Sensitivity of the system to the chosen decision variables and an adequate range of search directions both contribute to the excellent performance of the optimiser. When testing the single-objective, weighted min-max and weighted sum formulation of the objective function, an almost perfect match between target and simulated PSD, solids content and number of particles profiles was observed for the majority of the targets and operating conditions tested.

From the various cases analysed it was observed that the use of a combination of two different feed rates, limited to the first time intervals, as decision variables is sufficient to drive the optimiser towards the desired target with a satisfactory accuracy. The use of feed rates of more than two reactants did not result in considerable improvement. At the

same time, to limit the search vector to the feed rates of only one reactant does not always give an acceptable match with the desired target. From the different studies, it emerged that surfactant feed rates need always to be included in the control vector for the open-loop scheme to be effective. This is understandable when realising that all three major phenomena that drive the evolution of the PSD depends on the surfactant concentration.

The same accuracy in the match with the targets obtained when implementing the single-objective strategies was rarely achieved when using the multi-objective strategy. On the other hand, the pareto optimisation strategy showed greater reliability. In cases where the single-objective strategies failed to reach the desired PSD profile, the multi-objective scheme was able to reach it with a good accuracy, offering enhanced robustness compared to the single-objective strategy. When implementing the multi-objective strategy to perform pareto optimisation, nonlinear constraints were introduced. Because of the nonlinearity of the problem, only the routine based on SQP was implemented for the solution of these optimisation problems. Single-objective strategies, when implementable with good accuracy, can still be used as an alternative to the more robust, but also more computationally demanding, multi-objective strategy.

The end-use properties of the latex are often determined by the combination of more than one process variable. In a multi-objective strategy different process properties are optimised simultaneously, making the multi-objective optimisation in emulsion polymerisation often a requirement rather than an option. When optimising more than one objective function, the optimisation routine has to solve a problem of increased complexity due to the interaction between the rate processes and the integrated effect of the different inputs on the particle-level phenomena. Also, a larger number of constraints need to be satisfied. This is probably the cause of the slightly worse match with the targets observed when comparing the results obtained implementing the multi-objective strategy with the results obtained implementing the single-objective formulations.

Chapter 4

Controllability Issues, Inferential Control of Rheology and Batch-to-Batch Control Simulations

A strategy for the inferential control of the latex rheology through a knowledge-based optimisation approach is proposed. Different PSD profiles are characterised in terms of their controllability and a strategy for the batch-to-batch feedback control to be implemented in those cases where in-batch feedback control is not applicable is proposed. An example is presented where the batch-to-batch strategy is applied to the feedback control of the PSD in a semi-batch emulsion polymerisation process (Immanuel, Wang and Bianco, 2008).

4.1 Inferential control studies on the rheology of emulsion polymers

4.1.1 Rheology of emulsion polymers

The rheology of emulsion polymers is strongly influenced by the PSD of the latex (Choi and Krieger, 1986; Chang and Powell, 1994; Luckham and Ukeje, 1999; Parkinson et al., 1970). Mathematical relations linking rheological properties with the PSD have been formulated by

different authors (do Amaral et al., 2004; Sudduth, 1993a). Schneider et al. (2002) highlighted the importance of

- polymer content (*i.e.* solids content) of the latex
- maximum packing factor
- particle-particle interaction parameter

in determining the rheological properties of the emulsion polymers.

Based on previous models by Mooney (1951); Sudduth (1993b) and Luckham and Ukeje (1999), Arevalillo et al. (2006) recently developed a comprehensive formulation that quantitatively describes the relation between the viscosity of the latex and the PSD, accounting also for the influence on the final viscosity of the solids content

$$\phi_n = \frac{\int_0^\infty r^3 F(r)dr}{\int_0^\infty max(0,(r-\bar{r})^3)F(r)dr + \frac{1}{\beta}\int_0^\infty [(r+\bar{r})^3 - max(0,(r-\bar{r})^3]F(r)dr} \tag{4.1}$$

$$\ln(\eta_r) = \left(\frac{[\eta]\phi_n}{\sigma-1}\right)\left(\left(\frac{\phi_n-\phi}{\phi_n}\right)^{1-\sigma} - 1\right) \tag{4.2}$$

A schematic of the integrated nature of the process and the relation between the rheology of the system and the latex properties are illustrated in figure 4.1. The PSD is influenced by the dynamics of nucleation, growth and coagulation, while at the same time it also controls these phenomena through an integrated feedback mechanism, as can be seen from figure 4.1, making the control problem highly nonlinear.

Equation 4.1 is used to compute the maximum packing factor ϕ_n. $\bar{r}$ is the average particle radius and β is a model parameter. The maximum packing factor is then used to compute the relative viscosity η_r through equation 4.2. ϕ is the solids content of the latex, $[\eta]$ is a model parameter called intrinsic viscosity and σ is the particle-particle interaction parameter

$$\sigma = k_1 \exp[-k_2(\phi_n - \phi)^{1/3}\gamma^{k_3}] \tag{4.3}$$

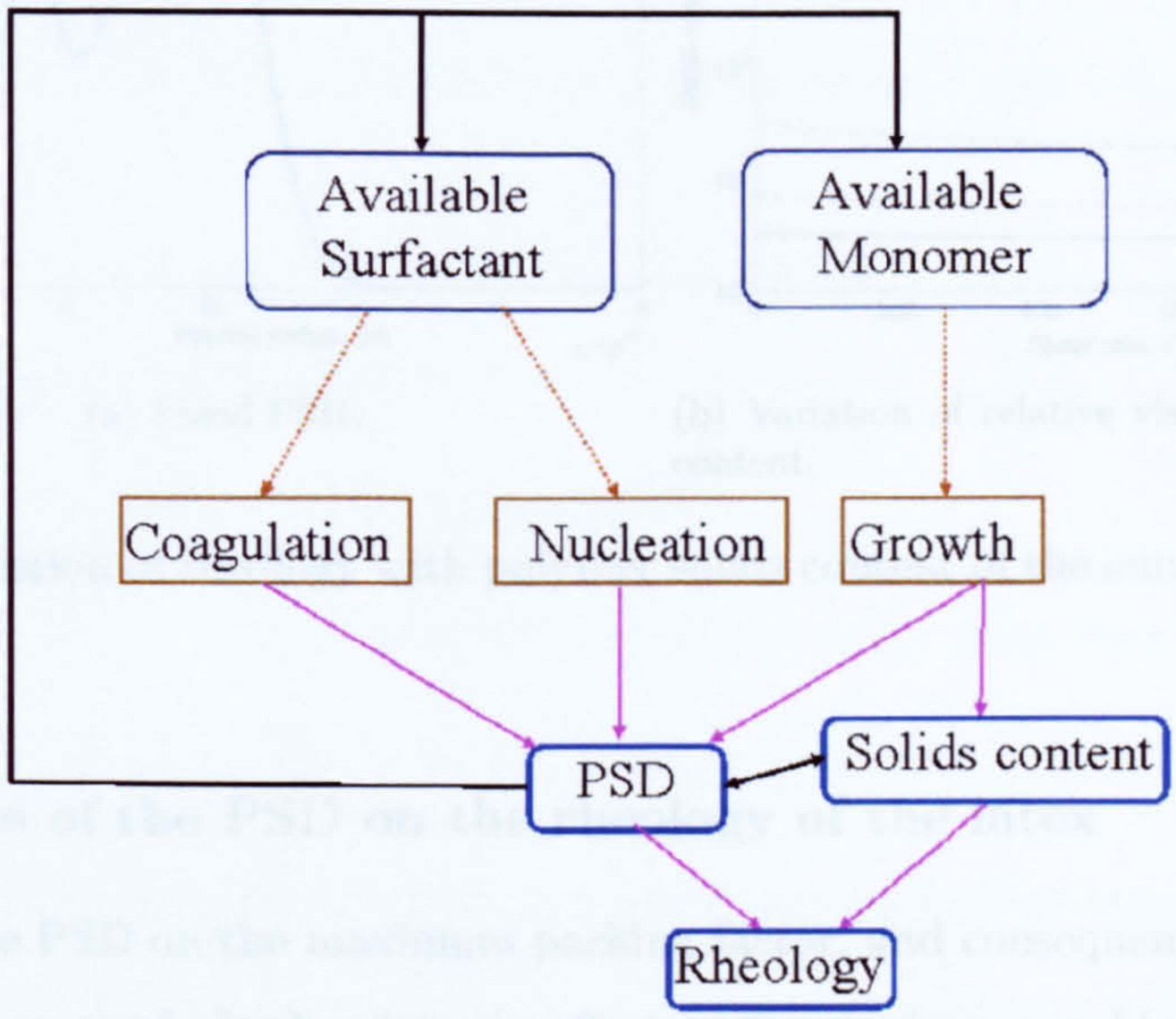
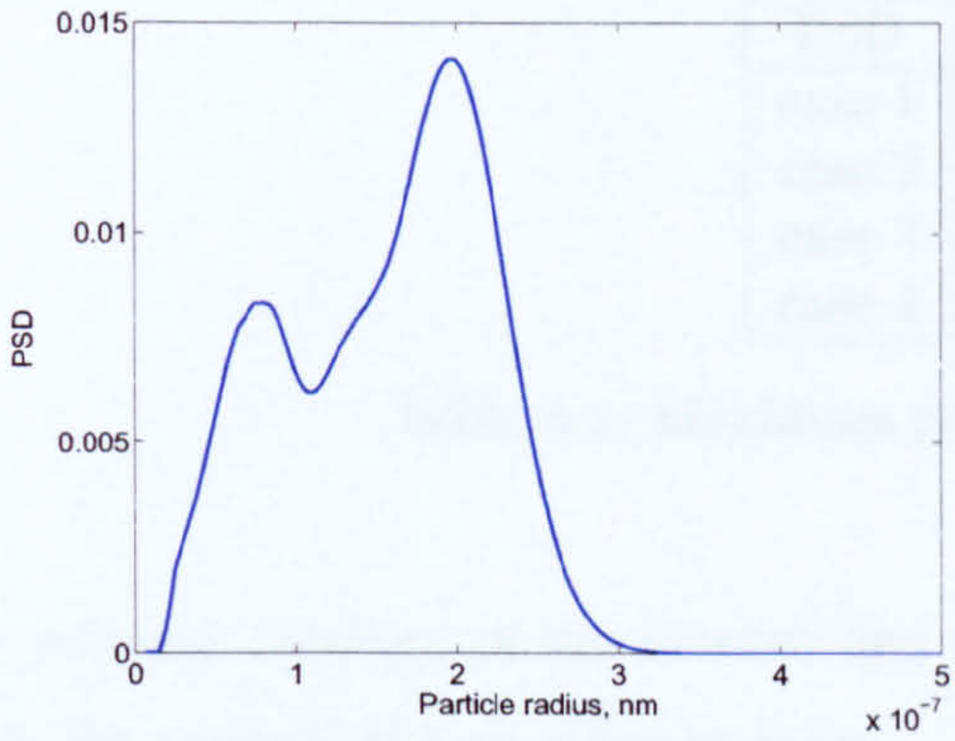


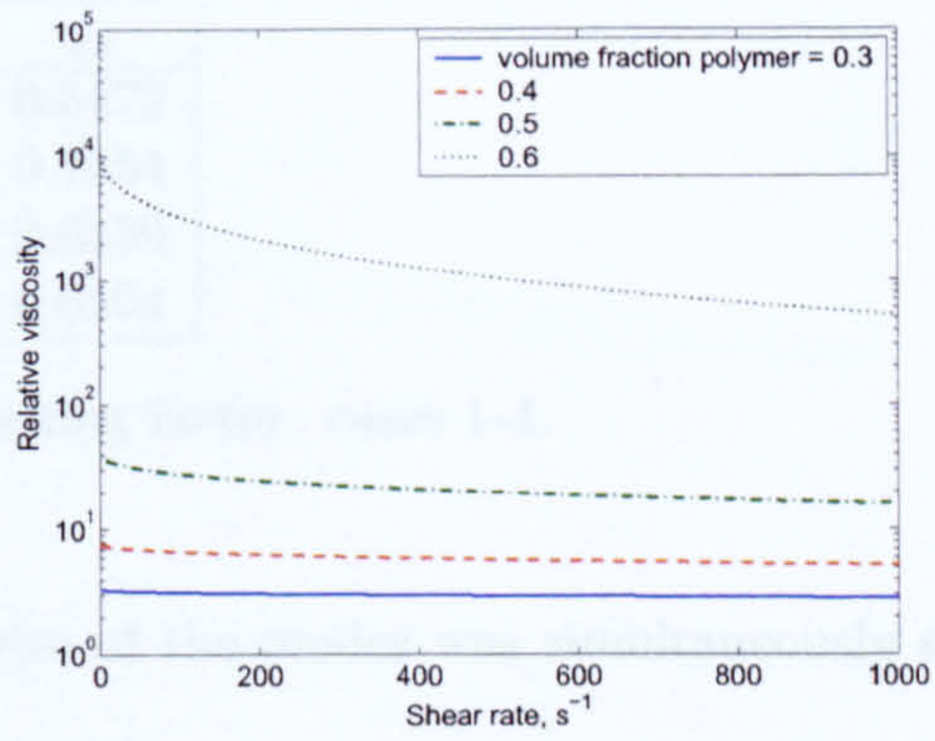
Figure 4.1: Integrated systems representation of the emulsion polymerisation process and of the evolution of rheology in the emulsion polymer.

The effect of the shear stress γ is included in this expression together with that of solids content and maximum packing factor of the latex. More details on the model and its formulation can be found in Arevalillo et al. (2006).

The maximum packing factor of the system is directly related to the number density PSD. Thus, the PSD influences the relative viscosity η_r through both its interrelation with the solids content ϕ via the polymerisation mechanisms and the maximum packing factor. The integrated nature of the relation between PSD and rheology of emulsion polymers, the interaction between the particle-level phenomena of nucleation, growth and coagulation, and their dependence from the evolution of the PSD through the feedback mechanism illustrated in figure 4.1, all contribute in making the relation between rheology and available control variables complex and highly nonlinear.



(a) Fixed PSD.



(b) Variation of relative viscosity with solids content.

Figure 4.2: Variation of rheology with polymer solids content of the emulsion for a fixed PSD.

4.1.2 Effects of the PSD on the rheology of the latex

The effect of the PSD on the maximum packing factor, and consequently on the rheology of the emulsion latex, can be broken into the effect on the maximum packing factor of the number of modes of the PSD, the size of these modes and the magnitude (number of particles) of each mode. An initial test was performed to show the effect of the solids content on the relative viscosity of the latex. A fixed PSD was considered and used to compute the maximum packing factor. Different arbitrary values of the solids content were then chosen and substituted in equations 4.3 and 4.2. The comparison between the different relative viscosities resulting from these calculations is presented in figure 4.2.

The solids content (volume fraction of polymer) ϕ was increased from 0.3 to 0.6, with the maximum packing factor for the current PSD equal to 0.65. It is possible to notice from figure 4.2(b) that as the solids content approaches the maximum packing factor the relative viscosity increases rapidly, thereby illustrating the effect of the polymer solids content on rheology.

The rheology model implemented was of reduced validity for low solids content systems, due to differences in the mechanisms that influence the rheology of dilute emulsions. For this reason, the subsequent tests focused on systems with high polymer content. The influence

PSD	ϕ_n
case 1	0.6472
case 2	0.7654
case 3	0.6439
case 4	0.6504

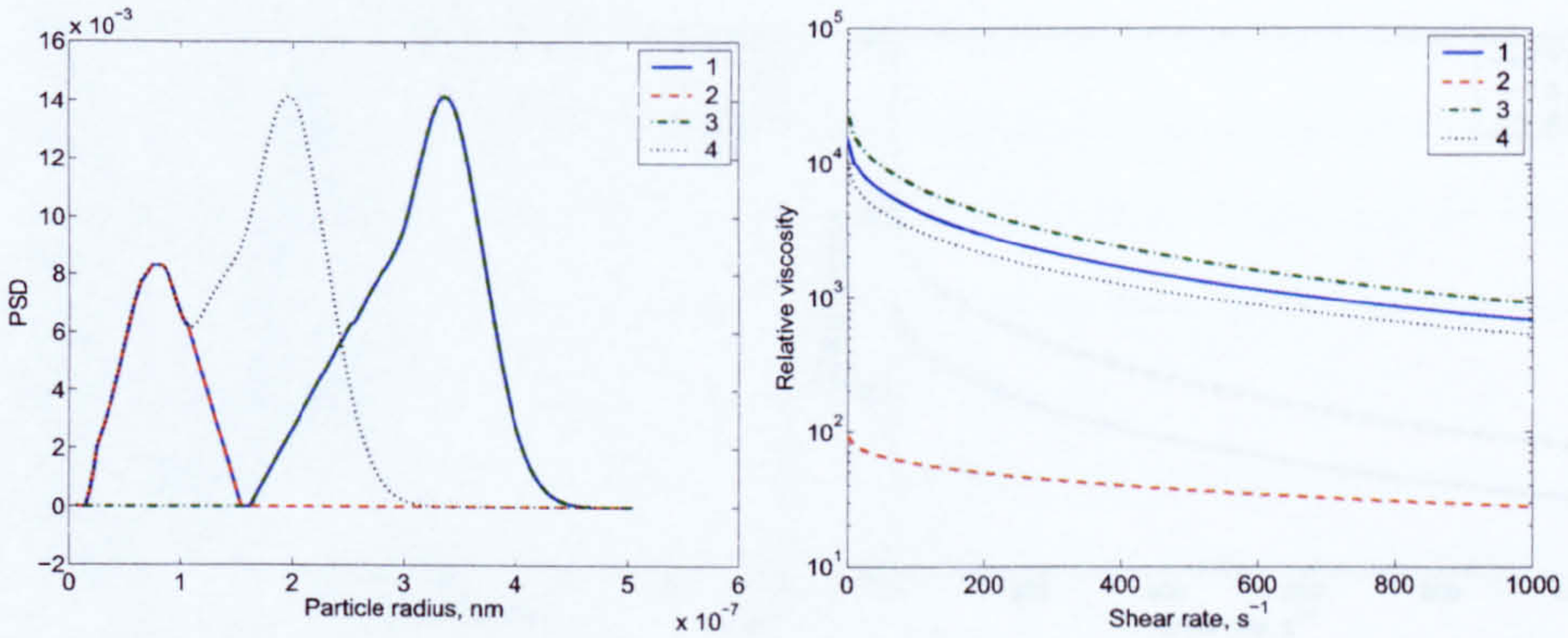
Table 4.1: Maximum packing factor: cases 1-4.

on the polymer rheology of the number and size of the modes was simultaneously studied through the analysis of four different cases

1. bi-modal PSD with clearly separated modes
2. unimodal PSD with only the small particle size mode from case 1
3. unimodal PSD with only the large particle size mode from case 1
4. bi-modal PSD with the two modes merging into each other (same as figure 4.2(a))

These four cases are illustrated in figure 4.3(a) and the relative viscosity associated to them are presented in figure 4.3(b). The PSDs considered are characterised by different maximum packing factors, which are listed in table 4.1. The strong dependence on the packing factor of the relative viscosity results in a large difference between the relative viscosity for case 2, characterised by the highest packing factor, and for the other cases analysed. The small unimodal particles of case 2 have the largest packing factor, resulting in a considerably reduced viscosity for the same polymer content. The other three cases present smaller and comparable values of the maximum packing factor and the associated relative viscosity are then relatively close to each other, with lower packing factors corresponding to higher viscosities. The smaller values of the packing factor for cases 1 and 4 compared to case 3 derives from the ability of the smaller particles in the bi-modal distributions to pack between the larger ones. The change in ϕ_n is small between cases 1, 3 and 4 because of the particular relative magnitude of particles in the two modes.

Finally, the effect on the rheology of the relative amounts of particles in the two modes was analysed. Figure 4.4(a) illustrates the three PSDs simulated



(a) Different PSDs: cases 1-4.

(b) Variation of relative viscosity with number and size of modes.

Figure 4.3: Effect of number and size of the modes on the rheology of emulsions.

PSD	ϕ_n
case 1	0.6678
case 2	0.6512
case 3	0.6504

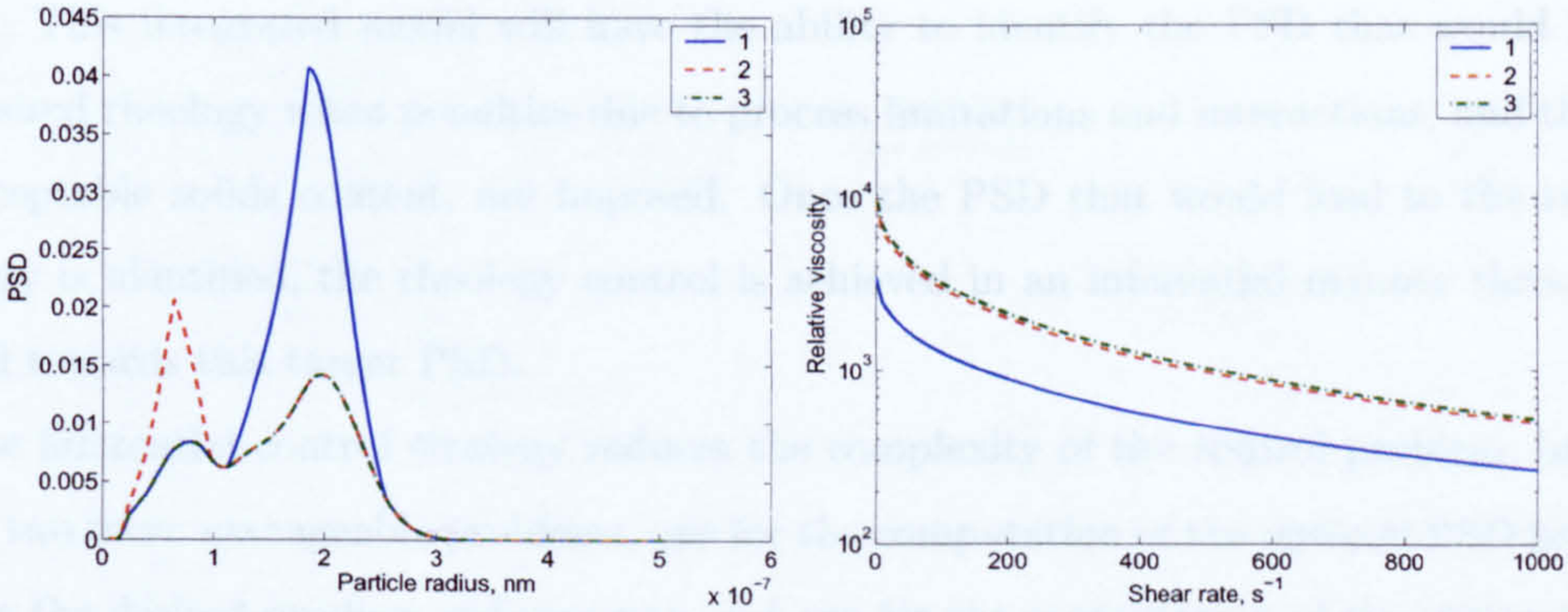
Table 4.2: Maximum packing factor: cases 1-3.

1. bi-modal PSD of figure 4.2(a) with higher magnitude of the large particle size mode

2. bi-modal PSD of figure 4.2(a) with higher magnitude of the small particle size mode

3. bi-modal PSD of figure 4.2(a)

The relative viscosity associated to each one of these cases in shown in figure 4.4(b). An increase in the relative amount of the larger particles (case 1) results in an increase of the packing factor and a consequent drop in the viscosity. A much smaller increase in ϕ_n is observed when a larger first mode is considered (case 2), which results in a considerable smaller decrease of the viscosity. The values of the maximum packing factor for the different cases analysed is presented in table 4.2.



(a) Different PSDs: cases 1-3.

(b) Variation of relative viscosity with magnitude of the modes.

Figure 4.4: Effect of the relative amounts of particles in the two modes on the rheology of emulsions.

4.1.3 Inferential control considerations

In the different studies carried out in section 4.1.2 the solids content was chosen arbitrarily and used for computation. This raises the issue of whether the solids content implemented in equations 4.2 and 4.3 would actually result from the process when trying to achieve the particular PSD selected.

From the considerations in section 4.1.2 it is evident that a wide range of PSD could potentially lead to the desired rheology, but not only rheological properties are important in the emulsion polymer. The solids content (conversion) by itself constitute a valuable controlled variable, especially from the economical point of view. Therefore, when selecting the PSD for inferential rheology control it is important to simultaneously explicitly account for the interrelation with the solids content so that the optimal recipe computed drive the system towards the targeted rheology as well as the desired solids content. Also a third constraint needs to be accounted for when selecting the optimal PSD. This is the one resulting from process limitations, input constraints and inherent interactions/regulations in the system that limit the range of achievable PSD.

The need to account for these limitations and interactions and, at the same time, to relate the rheological properties with the PSD call for a combined process model and rheology

model. This integrated model will have the ability to identify the PSD that would lead to the desired rheology when penalties due to process limitations and interactions, and the need for acceptable solids content, are imposed. Once the PSD that would lead to the targeted rheology is identified, the rheology control is achieved in an inferential manner through the control towards this target PSD.

The inferential control strategy reduces the complexity of the control problem, breaking it into two more manageable problems, one for the computation of the optimal PSD profile to achieve the desired product end-property and one for the computation of the optimal recipe towards this target PSD. It provides with a strategy to identify control moves that would lead to the desired rheology and facilitates the complex and non-linear rheology control problem.

4.2 Feedback controllability of PSD in emulsion polymerisation

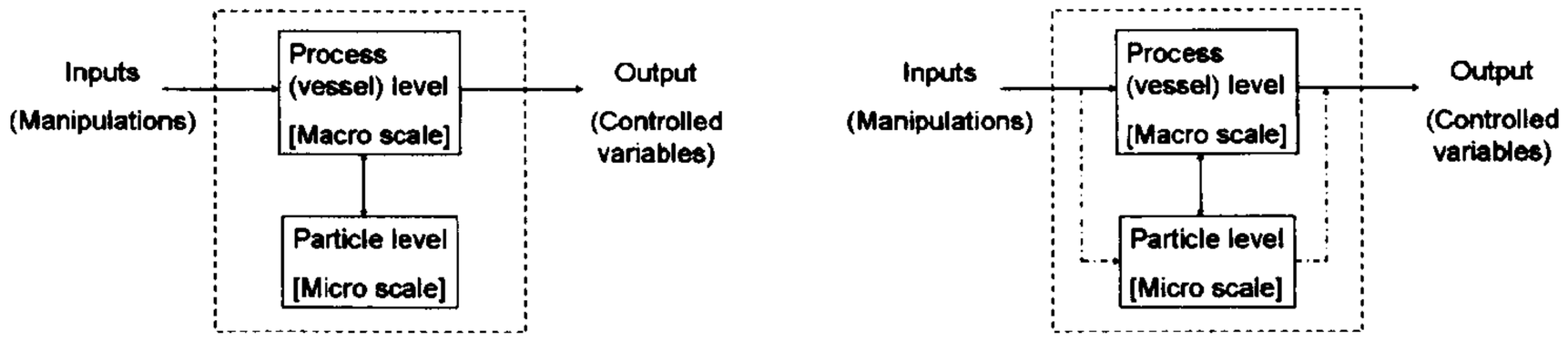
4.2.1 Control strategy development

Because of the need to account for the influence of micro-scale phenomena (*i.e.* nucleation, growth and coagulation) when controlling the PSD at the macro-scale level, the controlled system under study is characterised by a multi-scale structure, schematically represented in figure 4.5.

The multi-scale PSD modelling approach required in emulsion polymerisation also calls for a multi-objective control approach, of the kind presented in section 3.2 and schematically depicted in figure 4.5(b). In this approach the process inputs are directly linked to the particle-level rate processes. A multi-objective optimisation problem, subject to actuator limitations and process constraints, is solved to attain the desired PSD while providing a decoupling of the underlying particle processes of nucleation and growth (Immanuel and Doyle III, 2003c).

When building a control system the strategy followed is usually composed of two stages

- open-loop determination of operating conditions
- closed-loop feedback control



(a) Multi-scale structure of the emulsion polymerisation process.

(b) Hierarchical control strategy.

Figure 4.5: Depiction of the multi-scale modelling and control problems that underlie the emulsion polymerisation process and hierarchical control strategy proposed for PSD control.

This is especially true for semi-batch processes. An initial dynamic optimisation for the computation of the optimal recipe and operating conditions to guide the system towards the desired PSD and other controlled variables, has to be followed in a second stage by the formulation of a closed-loop strategy accounting for model mismatches and process disturbances. An advanced control scheme such as MPC typically acts over open-loop optimal control trajectories to account for these model and process uncertainties.

4.2.2 In-batch feedback control limitations

For a feedback control to be applicable to a system two are the requirements. These are that a control action to counter the errors introduced in the process exists, *i.e.* controllability (Kailath, 1980), and that sufficiently frequent measurements of the output are available. This last information is fed back to the controller and used to evaluate the extent of the deviation from the desired target, and to decide on the correction to implement to counter the detected error.

In emulsion polymerisation, control actions to compensate for mismatches with desired targets may not exist. This is especially true when the PSD is the variable that needs to be controlled, *i.e.* in-batch controllability is not always guaranteed for all the possible PSDs

that may want to be produced.

Controllability issues also arise from the implementation of the different available techniques for the measurement of the PSD (Kammona et al., 1999). The different technologies available, such as light scattering and capillary hydrodynamic fractionation, all have a measurement delay attached to them. Moreover, these methods usually require a certain solids content to be reached before a reliable measurement is provided. For the capillary hydrodynamic fractionator (CHDF) a solids content of 3-4% is needed for reliable PSD measurements. For a typical *ab initio* process, this level of conversion is reached usually after 8-10 minutes. The time required for the CHDF to process the sample is about 10-12 minutes and this time adds up to the one needed to reach the required solids content to a factored time delay of approximately 20 minutes. So, a first feedback from the process is available only after approximately 20 minutes, with a second measurement not available before 30 minutes into the batch.

The purpose of an in-batch feedback control is to correct the open-loop identified operating conditions and feed policies, should the need for it arise from errors introduced in the process. The limitations associated with the on-line feedback control of the process under study call for a critical assessment of feedback controllability in an in-batch sense. These controllability considerations are presented in sections 4.2.4 and 4.2.5.

4.2.3 Modified model for real-process simulation

When implementing a specified input trajectory to a model and to the corresponding process, from the observation of the mismatch between the two resulting output profiles, control actions can be taken to correct the process dynamics and achieve the end-point profile predicted by the model. Before embarking on expensive and time-demanding experimental simulations, a more straightforward and practical approach to test the performance of the control system is to simulate the real process through available models. In the case under study, the original model (Immanuel et al., 2002, 2003) was modified to produce model mismatches and reconstruct process disturbances. Specific modifications were implemented to the rate of nucleation, growth and coagulation. The terms modified in the original model were those

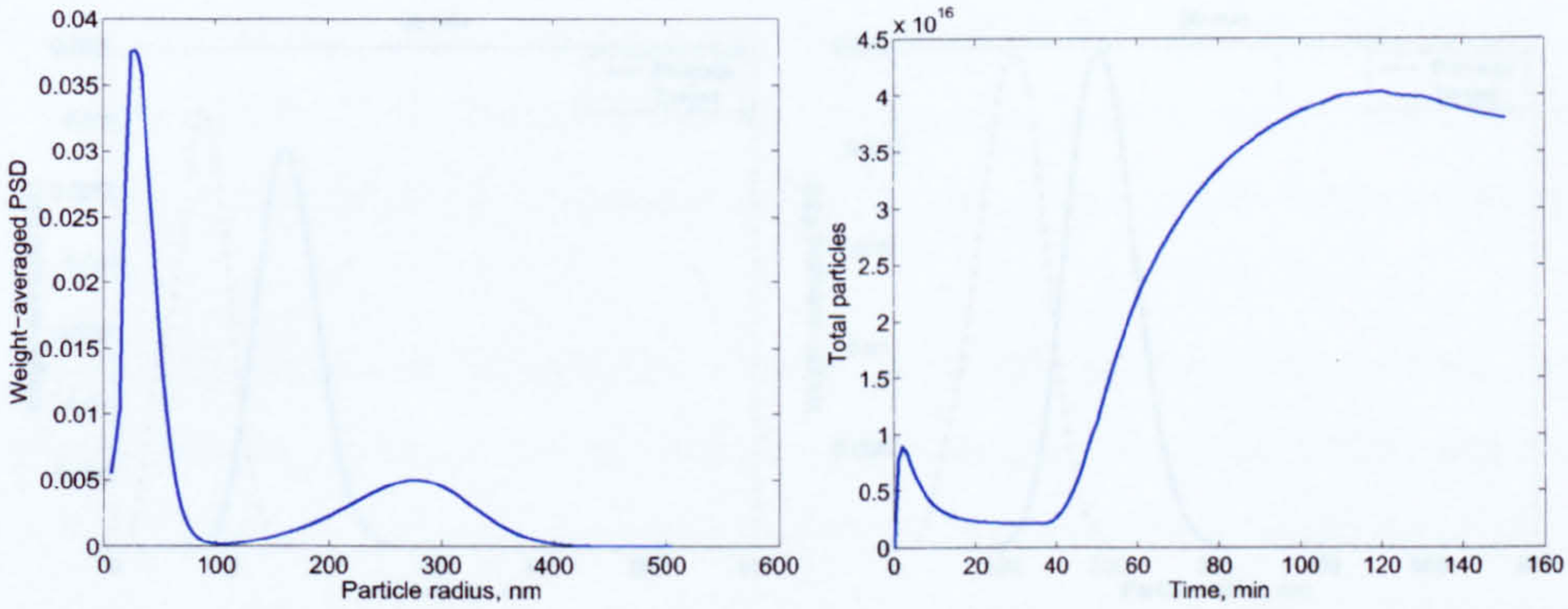
deemed to be uncertain and believed to be a possible cause of mismatch between model and real process.

The critical micelle concentration (cmc) defines the concentration above which micelles form. The cmc value was decreased from 2×10^{-5} mol/l to 1.01×10^{-5} mol/l. This produces an increase in the number of micelles in the reaction bulk when the same amount of surfactant is used and a consequent larger formation of particles by micellar nucleation. The radius of the nuclei (smallest particles) was also modified from 5 to 15 nm. The growth rate was modified using two factors. The rate expression was multiplied for a constant factor, 0.85, to produce an overall decrease in the size of the particles, and for a factor varying linearly with the particle size from 1.2 (nucleated particles) to 1.26 (particles of 500 nm), to modify the size dependence of the growth rates and generate a broadening of the PSD. Only one modification was applied to the coagulation term. The range of the particles able to coagulate was increased using a larger value for the size of the unstable particles.

While simpler formulations for the viscosity of the latex were used in the original model, the more complex and comprehensive model formulated by Arevalillo et al. (2006) was implemented in the modified model to account for the dynamic variation of the viscosity in the real process. The carryover of trace amount of latex from previous batches was accounted for in the modified model as one of the possible disturbances to the process responsible for the mismatch with the model predictions. The latex carryover was found to be a key process disturbance with a large influence on the process dynamics (Immanuel and Doyle III, 2002). A simple model description of this disturbance that characterise the carryover in terms of amount (total number or mass of particles), mean size and standard deviation, is used in the modified model. A comparison between the PSD produced by this hypothetical process and the one produced by the original model when implementing the same input trajectory is provided in figure 4.9(a)

4.2.4 A potentially in-batch feedback controllable PSD class

The bi-modal PSD in figure 4.6(a) was produced implementing a pre-determined recipe in the original model and presents two clearly separated modes. The solids content profile in



(a) PSD profile.

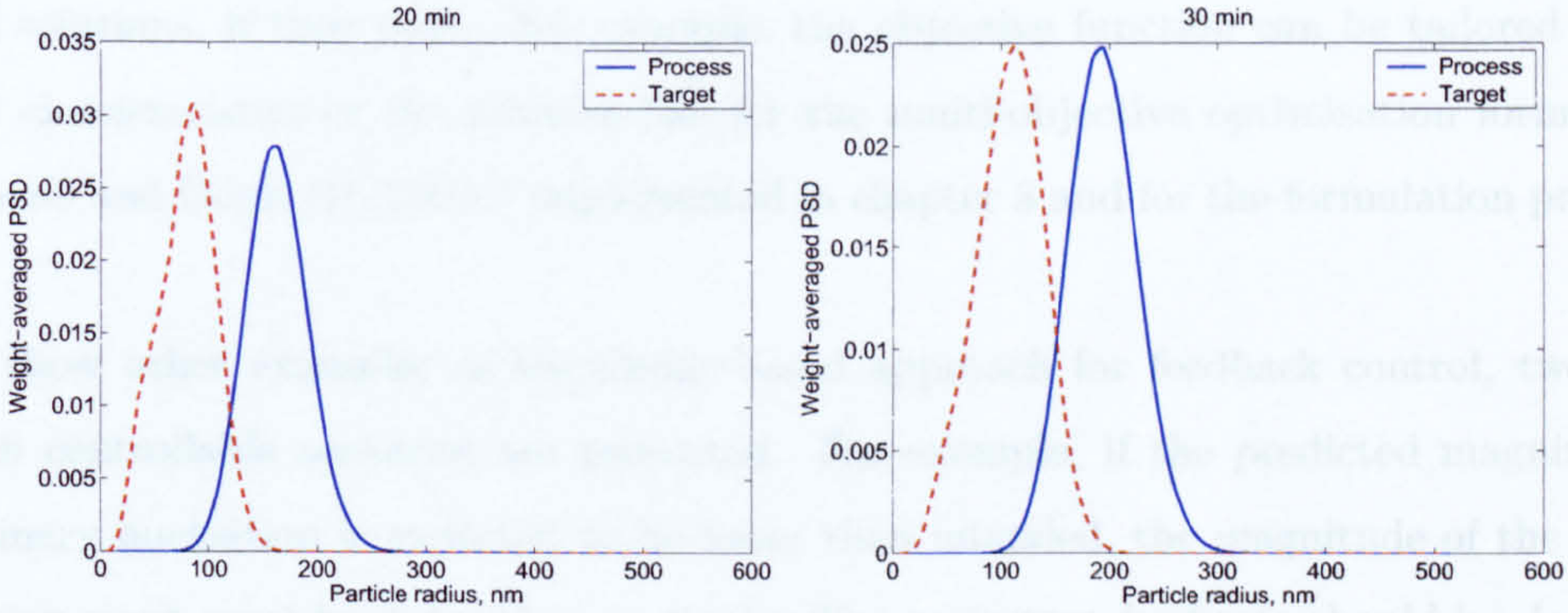
(b) Total particles profile.

Figure 4.6: A PSD target and the corresponding profile of total particles.

figure 4.6(b) is the one expected to lead to this target PSD for open-loop implementation of the input trajectory. From the observation of this profile it may be evinced that a second nucleation event commences only after about 40 minutes into the batch. This means that 2-3 PSD measurements may be available by the time the second nucleation starts. These characteristics make the profile in figure 4.6(a) a potentially controllable PSD. For this profile the information fed back to the controller after the first nucleation can be used to re-size the modes of the distribution and to regulate the relative magnitude of the two nucleation events.

From the open-loop implementation of the input trajectory in the model and in the process (see section 4.2.3) different profiles are obtained (see figure 4.7). In this figure the PSDs available from the process at 20 and 30 minutes, corresponding to the PSDs in the reactor at 10 and 20 minutes, are compared with the profiles predicted by the model. The PSD measurement at 30 minutes shows that a single nucleation event occurred in the reactor after 20 minutes into the batch. This makes a feedback control of the PSD through the regulation of the second nucleation event possible. As illustrated in section 4.1.2 the PSD control problem can be broken into different sub-problems for the regulation of the number and size of the modes, and the relative number of particles in each mode.

The target profiles in figure 4.7 are expected to lead to the bi-modal end-time PSD of figure 4.6(a), with the size of the mode produced by the process being larger compared to the one in the target profiles. A control action may then be devised to re-size the modes of



(a) PSD at 20 minutes.

(b) PSD at 30 minutes.

Figure 4.7: Measurements of PSD at 20 and 30 minutes into the batch resulting from process and model simulation.

the distribution, through modulation of the growth rate.

From the PSD and density measurements (when the process is implemented on a real plant) it is possible to infer the number of particles. Thus, this value is known for each PSD and the number of particles nucleated during the first nucleation event can be used to decide on a control action that would lead to the relative, if not the absolute, magnitude (number of particles) of the two modes to be retained through the regulation of the upcoming second nucleation event. Eventually, control of the water flow may be used to adjust the magnitude of the modes and attain a closer match with the absolute profile.

The control actions have to be tailored also to ensure that the required solids content is achieved, both for economical reasons and due to its direct influence on the rheological properties. So, solids content, size of the modes and number of particles in each mode all have to be considered as objectives when formulating the optimal control strategy for the process.

A careful formulation of the optimisation problem still appears to be a key factor in the optimal control of the PSD in emulsion polymerisation. In many complex applications the straightforward implementation of optimisation algorithms such as gradient-based techniques for the direct optimisation of the PSD may be less effective. A knowledge-based formulation of the objective function in these cases may lead to the identification of better feedback

control solutions, if they exist. For example, the objective function can be tailored on the desired characteristics of the solution like for the multi-objective optimisation formulation (Immanuel and Doyle III, 2003c) implemented in chapter 3 and for the formulation proposed here.

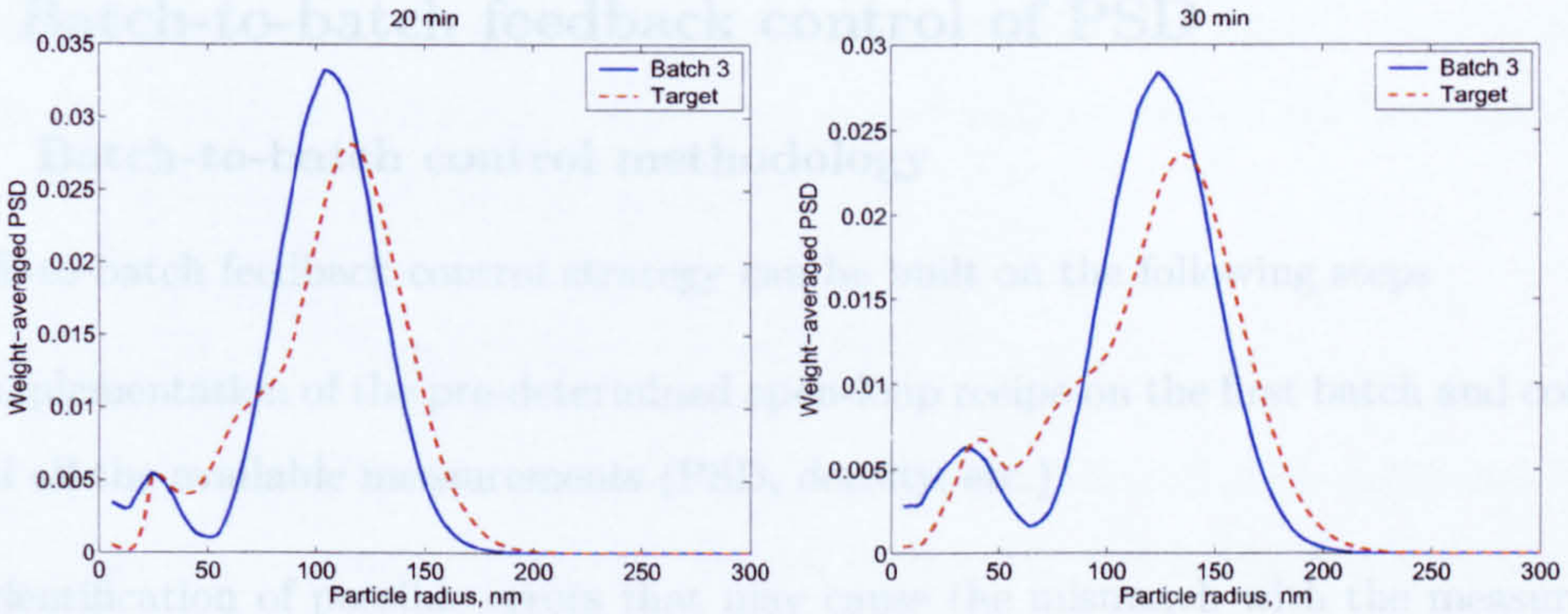
To show other examples of knowledge-based approach for feedback control, two more in-batch controllable scenarios are presented. For example, if the predicted magnitude of the primary nucleation is expected to be lower than intended, the magnitude of the second nucleation event must be reduced accordingly. The surfactant feed rate should be decreased to have a smaller number of particles formed by micellar nucleation in the second mode and preserve the relative number of particles in the two modes. But modifications in the PSD result in a feedback regulation on the available surfactant and monomers (see figure 4.1) and a modification of the monomer feed rate may then also be needed to compensate for the effect on the growth rate.

In a different scenario the expected number of particles from the primary nucleation event is formed, but a higher growth rate is registered, resulting in a larger size of the mode. If the system is unsaturated with respect to the monomer, a reduction in the feed rate of monomer may be effective in this case. The regulation of the growth rate may again alter the free surfactant concentration and result in the modification of the second nucleation event. Thus, the manipulation of the monomer feed rate may need to be followed by the modulation of the surfactant feed rate.

4.2.5 An in-batch feedback uncontrollable PSD class

A different PSD is presented in figure 4.8. In this case the two modes merge into each other and after 10 minutes into the batch both the nucleation events have either been completed or have begun. These two aspects make this profile likely to be uncontrollable.

Actions performed on the control variables to regulate the relative number of particles in the two modes may be not effective because by the time they are implemented both nucleation have already occurred or begun. The control action is shared by the two modes and their individual re-shaping may not be possible. Also the correction of the initial growth rates to



(a) PSD at 20 minutes.

(b) PSD at 30 minutes.

Figure 4.8: Comparison of the PSD from the process with the target PSD at 20 and 30 minutes of semi-batch operation.

correct the sizes of the two modes may be unproductive.

Control actions to counter errors on the PSD have to be implemented while keeping to a minimum the possible negative effect that these control moves may have on the latex solids content (Dokucu et al., 2008a). The need to simultaneously control the PSD and the solids content makes the uncontrollability of the process even more likely.

A batch-to-batch feedback strategy seems to be for all the uncontrollable cases the only resort. The information from previous batches can be used for the open-loop re-computation of optimal recipes to implement in subsequent batches. The feed policy re-computation is used to compensate in a feed-forward mode for causes of mismatch between process and model outputs. A batch-to-batch approach for the control of the PSD in a semi-batch process is presented in section 4.3. Figure 4.8 was obtained via implementation of input trajectories computed through a batch-to-batch optimisation. The PSD profiles labelled as Batch 3 in figures 4.8(a) and 4.8(b) are those leading to the optimal match with the target profile that will be presented in figure 4.9(c).

4.3 Batch-to-batch feedback control of PSD

4.3.1 Batch-to-batch control methodology

A batch-to-batch feedback control strategy can be built on the following steps

1. implementation of the pre-determined open-loop recipe on the first batch and collection of all the available measurements (PSD, density, etc.)

2. identification of possible errors that may cause the mismatch with the measurements and correction of these errors in the model used to compute the recipe for the first batch

3. use of the corrected model to re-optimise the recipe for the next batch

Usually step 2 takes the form of a parameter identification/update, often performed after sensitivity studies on the model parameters. The second and third steps are repeated iteratively till the errors on the objective functions are within the allowable tolerances.

Steps 1 and 3 involve the solution of a dynamic optimisation. In the case presented here the integral of the squared error between end-point simulated and target PSD was minimised

$$\theta_{recipe} = \int_{r_{nuc}}^{r_{max}} \Big(W(r,t_f) - W_{ref}(r)\Big)^2 dr \tag{4.4}$$

In this equation $W(r,t_f)$ is the weight-averaged PSD at the end-time t_f and $W_{ref}(r)$ is the target weight-averaged PSD. A single-objective optimisation strategy of the type described in section 3.2.2 was implemented in this example. The batch was discretised into time intervals and piece-wise constant values were used for the surfactant and monomers feed rates in each interval. The feed rates and the duration of the time intervals were used as control variables. This optimisation problem was solved using the sequential quadratic programming (SQP) algorithm described in section 3.1.4. More rigorous optimisation strategies that implement mixed-integer algorithms may also be used to include the number of intervals as decision variable, and feed rate addition policies different from the zero-order holds can eventually be considered. More robust optimisation formulations accounting for potential model uncertainties can also be implemented.

In step 2 a dynamic optimisation problem also needs to be solved. In this case the objective function was formulated as the sum of the squared differences between the PSD produced by the model and the one measured

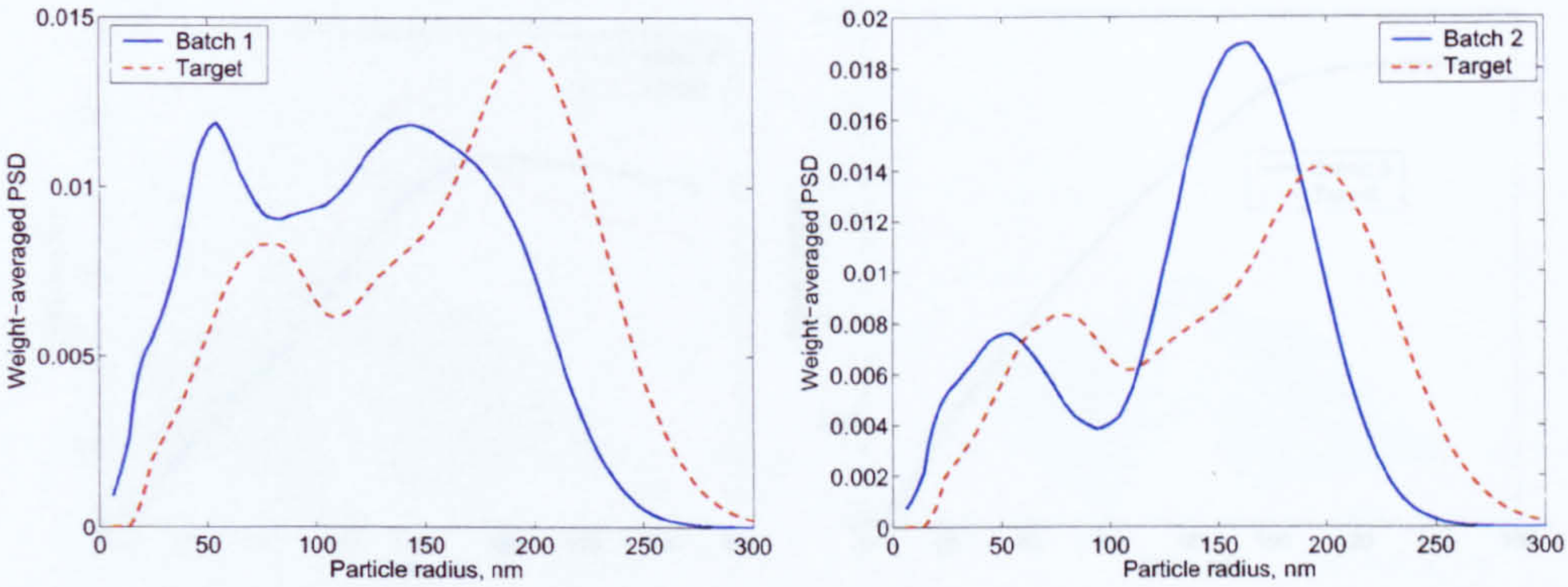
$$\theta_{update} = \int_{r_{nuc}}^{r_{max}} \Big(W_{model}(r, t_f) - W_{meas}(r, t_f)\Big)^2 dr \tag{4.5}$$

$W_{model}(r, t_f)$ is the model-predicted weight-averaged PSD at the end of the batch and $W_{meas}(r, t_f)$ is the experimentally measured weight-averaged PSD at the end of the batch. It was important to first consider a simpler framework for control, consisting of dynamic optimisation and model update, due to the implementation of an already rigorous non-linear population balance model. The modified model in section 4.2.3 was used to simulate the experiment.

The decision variables used for the optimisation in step 2 include uncertain and sensitive model parameters. The variables chosen for feedback correction/update of the model were identified as the most sensitive based on simulation-based sensitivity analysis performed using the detailed population balance model available. These parameters/aspects are listed below

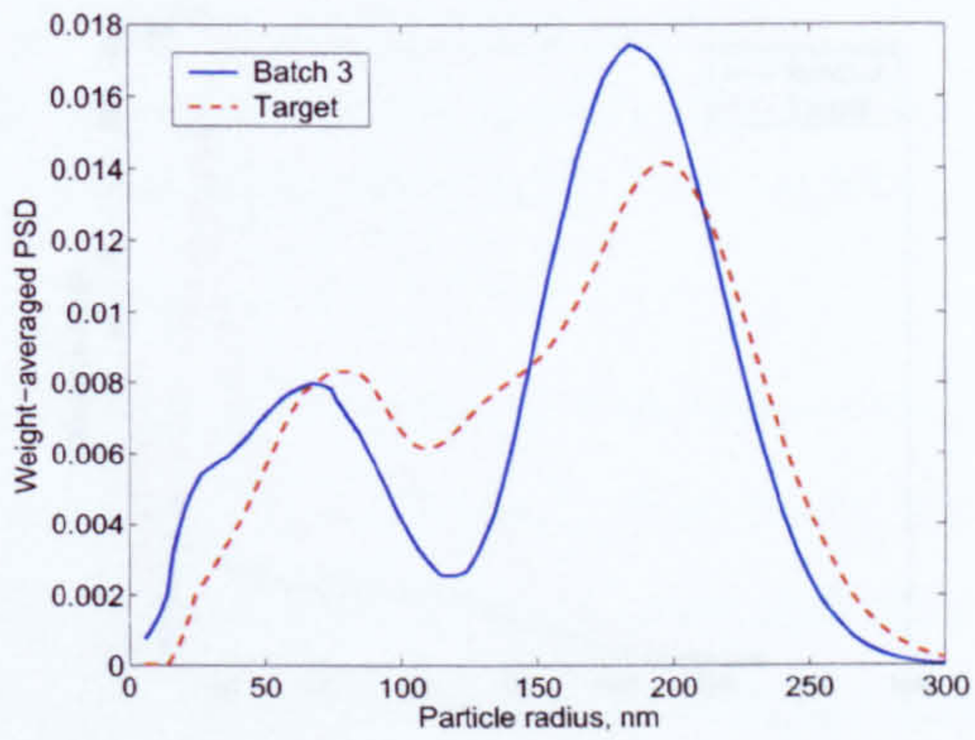
- critical micelle concentration
- additive correction for the propagation rate constant
- multiplicative correction factor for the coagulation rate
- multiplicative correction factor for the size-dependent growth rate
- particle (latex) carryover

The cmc primarily affects the micellar nucleation, while the additive correction factor for the propagation rate constant affects both homogeneous nucleation and growth. These terms were estimated on the first iteration using the measured end-point PSD from the first batch (first run of the process). The model updated with the new parameters was used to re-compute the optimal input trajectory to implement in the second batch. When also the data from this run were available, the new parameters/model update was performed using the data from both batch 1 and 2. The same strategy may be followed for different target PSD and the number of batch used may be increased till a satisfactory convergence with



(a) Batch 1.

(b) Batch 2.



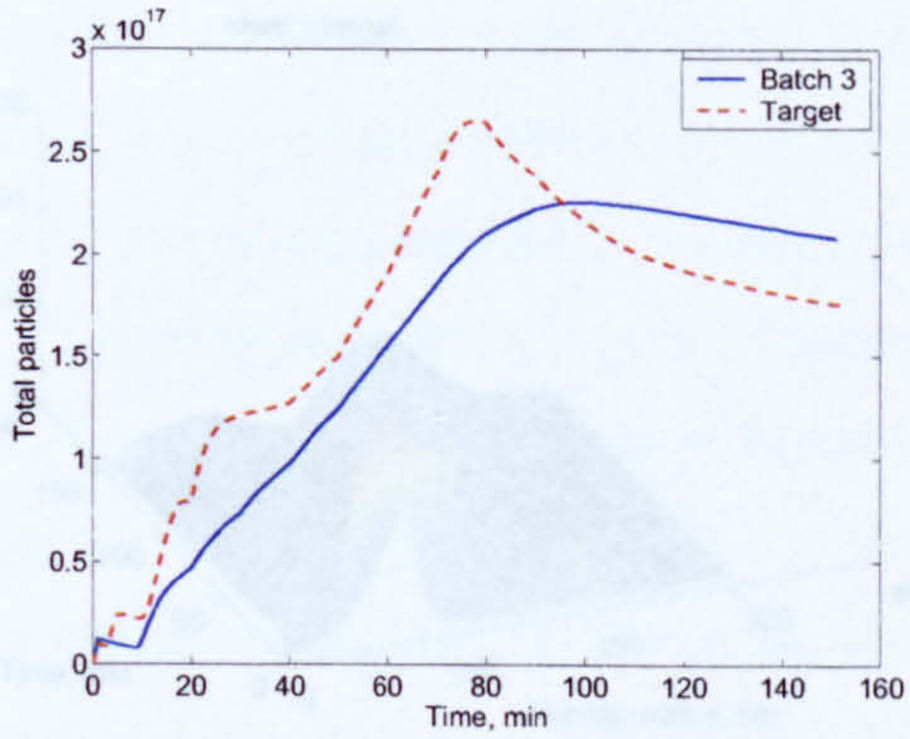
(c) Batch 3.

Figure 4.9: Batch-to-batch improvement in the match of the target PSD.

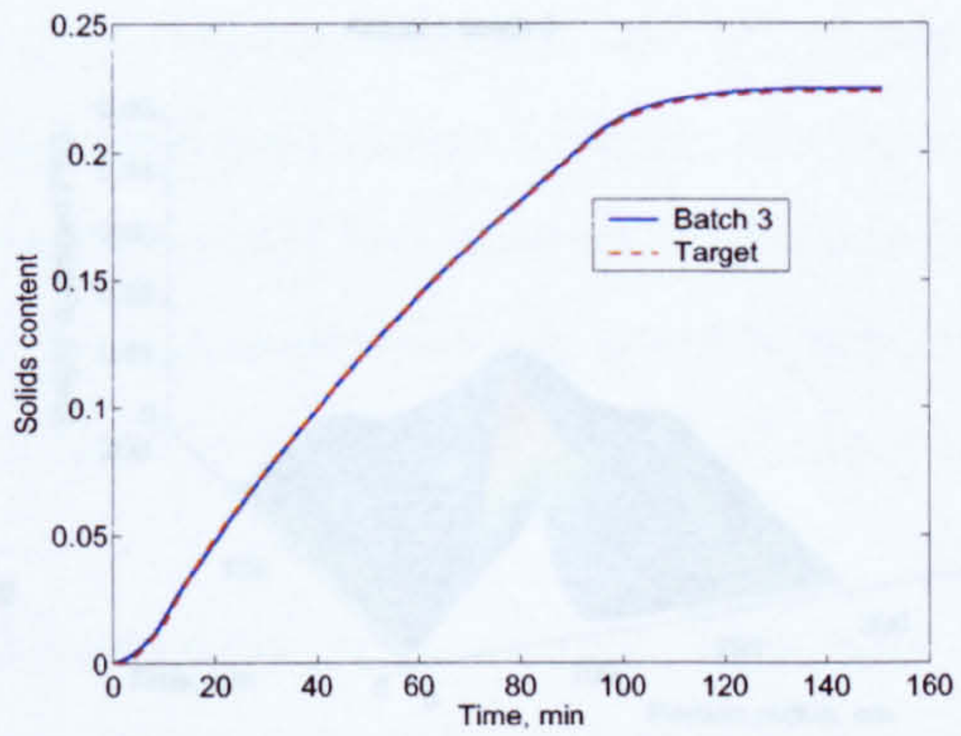
the target is achieved. Results from the application of this batch-to-batch strategy for the control of a specific PSD in a semi-batch emulsion polymerisation process are presented in the next section.

4.3.2 Implementation of batch-to-batch feedback control to emulsion polymerisation

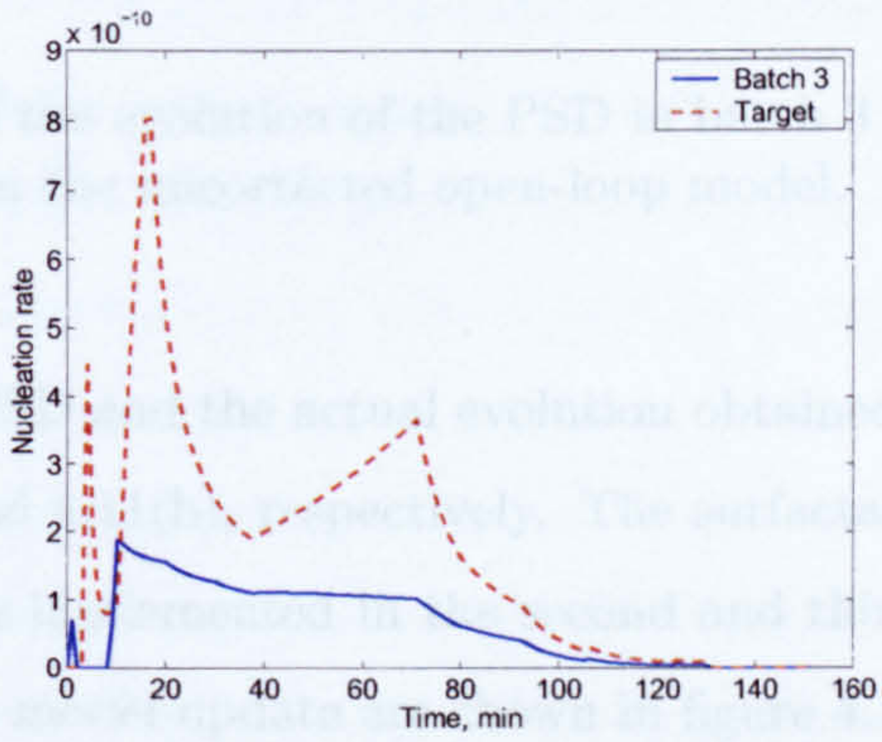
In figure 4.9 the dashed line represents the target PSD and the solid lines are the profiles obtained from the hypothetical process in batches 1, 2 and 3, and resulting from the implementation of the batch-to-batch optimisation strategy described in section 4.3.1. After the first batch both size and magnitude of the two modes of the distribution do not reproduce



(a) Total particles.



(b) Solids content.

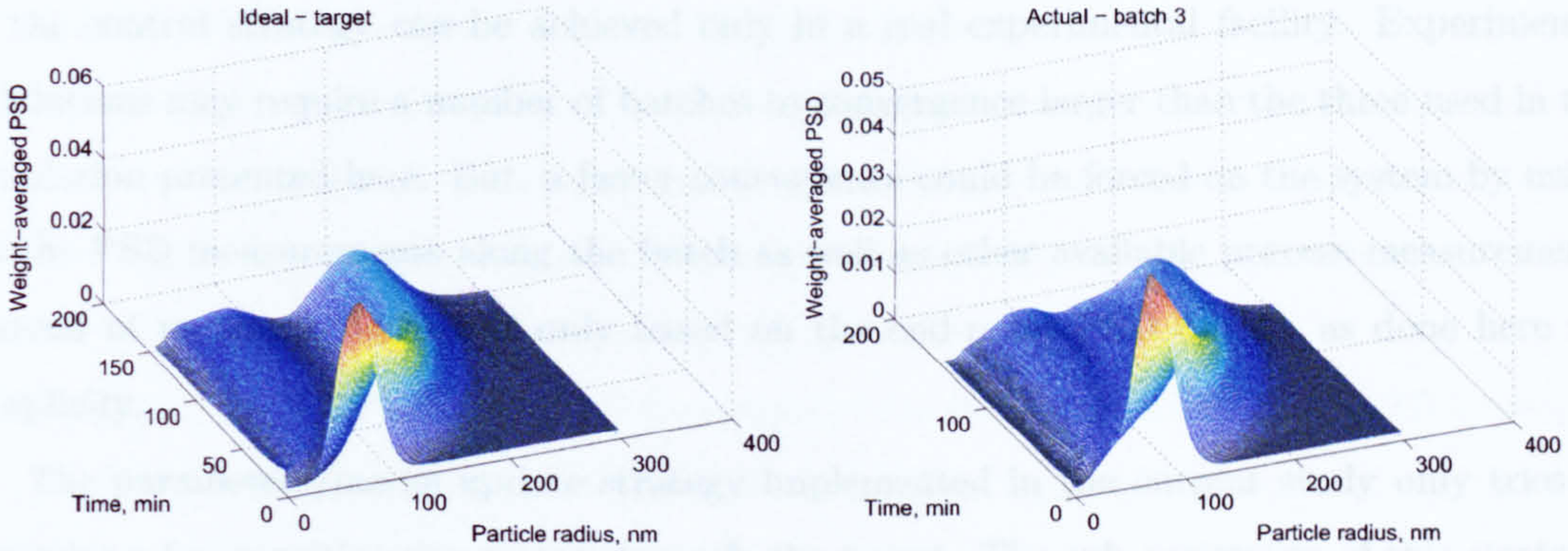


(c) Nucleation rate.

Figure 4.10: Comparison of the profiles of key process variables in batch 3 with the profiles originally expected based on the uncorrected open-loop model.

accurately those of the target PSD. The implementation of the updated model in the second batch improves the match with the target, particularly in terms of the relative number of particles (magnitude) in the two modes. The error in terms of both size and magnitude of the modes is considerably improved after the third batch. Even if the match is not extremely accurate a further improvement would be eventually unnecessary in view of measurements errors, and bearing also in mind that the final goal may eventually not be the control of the PSD, but the inferential control of rheology or of a different end-use property via PSD.

A comparison of the target profiles for the number of particles, solids content and nucleation rate with the same profiles from the solution obtained in the third batch is shown in figure 4.10. A positive close match with the solids content profile is observed. The original



(a) PSD evolution from uncorrected open-loop model.

(b) PSD evolution in batch 3.

Figure 4.11: Comparison of the evolution of the PSD in batch 3 with the evolution that was originally expected based on the uncorrected open-loop model.

expected evolution of the PSD and the actual evolution obtained in the third batch are presented in figures 4.11(a) and 4.11(b), respectively. The surfactant feed rate trajectory used in the first batch and those implemented in the second and third batch and resulting from recipe re-optimisation after model update are shown in figure 4.12.

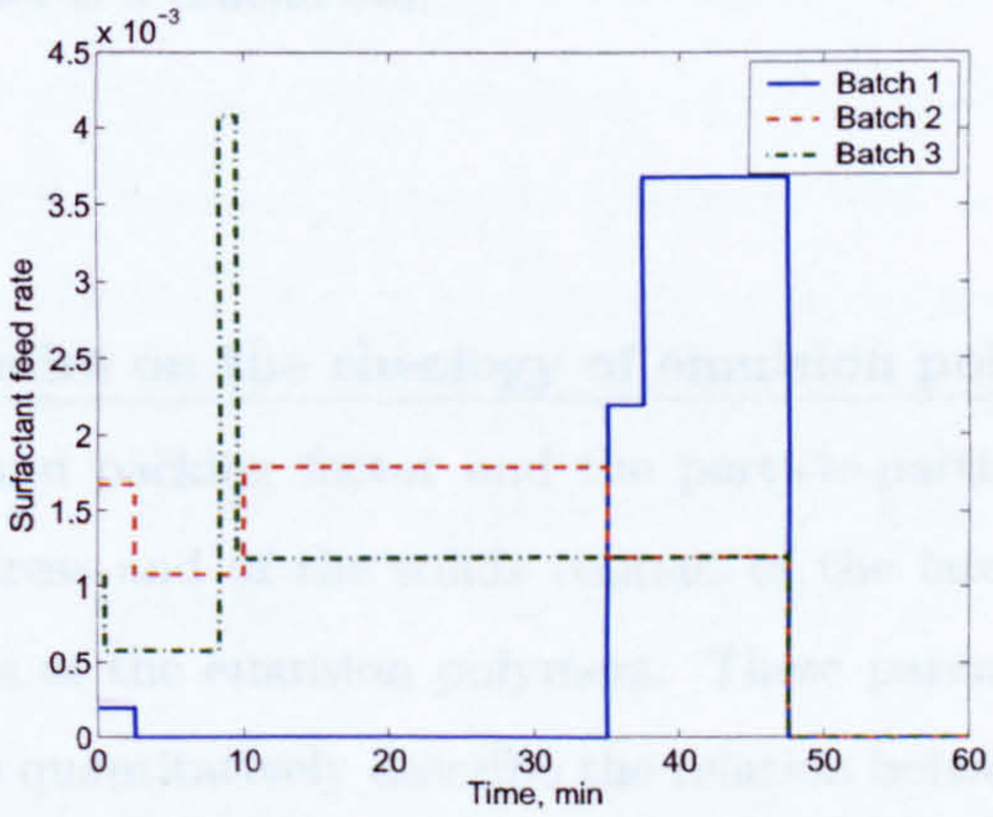


Figure 4.12: Variation of the feed profiles during the three batches for a representative reagent.

The batch-to-batch feedback control strategy has been implemented using a modified model as surrogate of the actual process. Even if this hypothetical process model provides a good representation of a real experimental process (Immanuel et al., 2003) a true validation

of the control strategy can be achieved only in a real experimental facility. Experimental validations may require a number of batches to convergence larger than the three used in the simulation presented here. But, a faster convergence could be forced on the system by using all the PSD measurements along the batch as well as other available process measurements instead of updating the model only based on the end-point PSD profile, as done here for simplicity.

The parameters/model update strategy implemented in the current study only tries to optimise a few sensitive parameters towards the target. The sub-optimality of this strategy, coupled with the lumped nature of the model parameters makes the updated model valid primarily in the vicinity of the current operating conditions. A way to render this batch-to-batch strategy more robust would be, for example, to use data from the feedback update towards a first PSD to update the model with respect to a second target PSD. This would increase the range of validity of the model and, as a consequence, reduce the number of batches required to the batch-to-batch feedback control to converge on the optimal recipe. To repeat this batch-to-batch scheme on a range of PSDs would eventually lead to the identification of a globally valid model despite the lumped update policy employed. From this prospective, the use of a detailed model is a crucial aid.

4.4 Summary

Inferential control studies on the rheology of emulsion polymers The solids content of the latex, the maximum packing factor and the particle-particle interaction parameter (function of the shear stress and of the solids content of the latex), all strongly influence the rheological properties of the emulsion polymers. These parameters have been used by Arevalillo et al. (2006) to quantitatively describe the relation between the viscosity of the latex and the PSD. The PSD influences the relative viscosity through both its interrelation with the solids content via the polymerisation mechanisms and its direct relation to the maximum packing factor.

The effect of the PSD on the maximum packing factor, and consequently on the rheology of the emulsion latex, can be broken into the effect on the maximum packing factor of

the number of modes of the PSD, the size of these modes and the magnitude (number of particles) of each mode. Tests were performed and showed that larger packing factors result in smaller viscosity of the correspondent latexes. These tests also demonstrated that the relative viscosity increases rapidly as the solids content approaches the maximum packing factor.

A combined process model and rheology model can be used to identify the PSD leading to the desired rheology when penalties due to process limitations and interactions, and the need for acceptable solids content, are imposed. Once the PSD that would lead to the targeted rheology is identified, the rheology control can be achieved in an inferential manner through the control towards this target PSD.

Feedback controllability of PSD in emulsion polymerisation The purpose of an in-batch feedback control is to correct the open-loop identified operating conditions and feed policies, should the need for it arise from errors introduced in the process. Limitations in the in-batch feedback control of the PSD in emulsion polymerisation were identified. This called for a critical assessment of feedback controllability of the process in an in-batch sense.

Controllability issues arise from the implementation of the different available techniques for the measurement of the PSD. The different technologies available all have a measurement delay attached to them. Moreover, these methods usually require a certain solids content to be reached before a reliable measurement is provided. For the capillary hydrodynamic fractionator (CHDF) the time required to process the sample adds us to the one needed to reach the required solids content to a factored time delay of approximately 20 minutes. In emulsion polymerisation, control actions to compensate for mismatches with desired targets may also not exist. This is especially true when the PSD is the variable that needs to be controlled.

If a PSD presents clearly separated modes and a sufficient number of measurements can be recorded between the different nucleation events and used for the calculation of feedback control actions, the correspondent PSD profile is likely to be controllable. It is necessary to remember that control actions have to be tailored also to ensure that the required solids content is achieved. So, solids content, size of the modes and number of particles in each mode

may all need to be considered as objectives when formulating the optimal control strategy for the process. A careful formulation of the optimisation problem still appears to be a key factor in the optimal control of the PSD in emulsion polymerisation. As for the hierarchical multi-objective formulation, a knowledge-based formulation of the objective function in these cases may lead to the identification of better feedback control solutions.

If the modes of the distribution merge into each other and the nucleation events take place in a period of time too short to allow to feed back to the controller a sufficient number of measurement, then the correspondent PSD profile is likely to be uncontrollable. A batch-to-batch feedback strategy for all the uncontrollable cases become then the only resort.

Batch-to-batch feedback control of PSD A simpler framework for batch-to-batch control, consisting of dynamic optimisation and model update, was considered due to the implementation of an already rigorous non-linear population balance model. The batch-to-batch strategy consisted in the implementation of a pre-determined open-loop recipe on the first batch and the collection of all the available measurements. This was followed by the identification of the errors that may have caused the mismatch between the simulated profile and the measured values, and the correction of these errors in the model used to compute the recipe for the first batch. This last step took the form of a parameter identification/update, which was performed after sensitivity studies on the model parameters. Final step was the use of the corrected model to re-optimise the recipe for the next batch. The last two steps were repeated iteratively till the errors on the objective functions were within the allowable tolerances. All these steps involved the solution of dynamic optimisations.

The batch-to-batch feedback control strategy has been implemented using a modified model as surrogate of the actual process. A true validation of the control strategy can be achieved only in a real experimental facility. Experimental validations may require a larger number of batches to converge, but a faster convergence could be forced on the system by using all the available process measurements.

Chapter 5

Experimentally Aided Sensitivity Studies and Parameter Identification

The process of identification and selection of uncertain/sensitive model parameters for model update is presented in this chapter. This selection is performed based on the analysis of experimental data obtained from the validation of an optimal simulated recipe.

5.1 Emulsion polymerisation small-scale reaction plant

5.1.1 Experimental facility

The experimental validation of an optimal recipe computed using the pareto multi-objective optimisation strategy presented in section 3.2.3 was performed. The experimental facility was comprised of a 0.7 litres stainless steel reactor for the implementation of emulsion polymerisation reactions, of which a picture is shown in figure 5.1. The reaction bulk is mixed continuously to create and maintain the homogeneous dispersion of the polymer particles in the latex. An electrical impeller attached to the top of the reaction vessel is used for mixing. A picture of the impeller is also shown in figure 5.1. A schematic representation of the experimental apparatus is presented in figure 5.2.

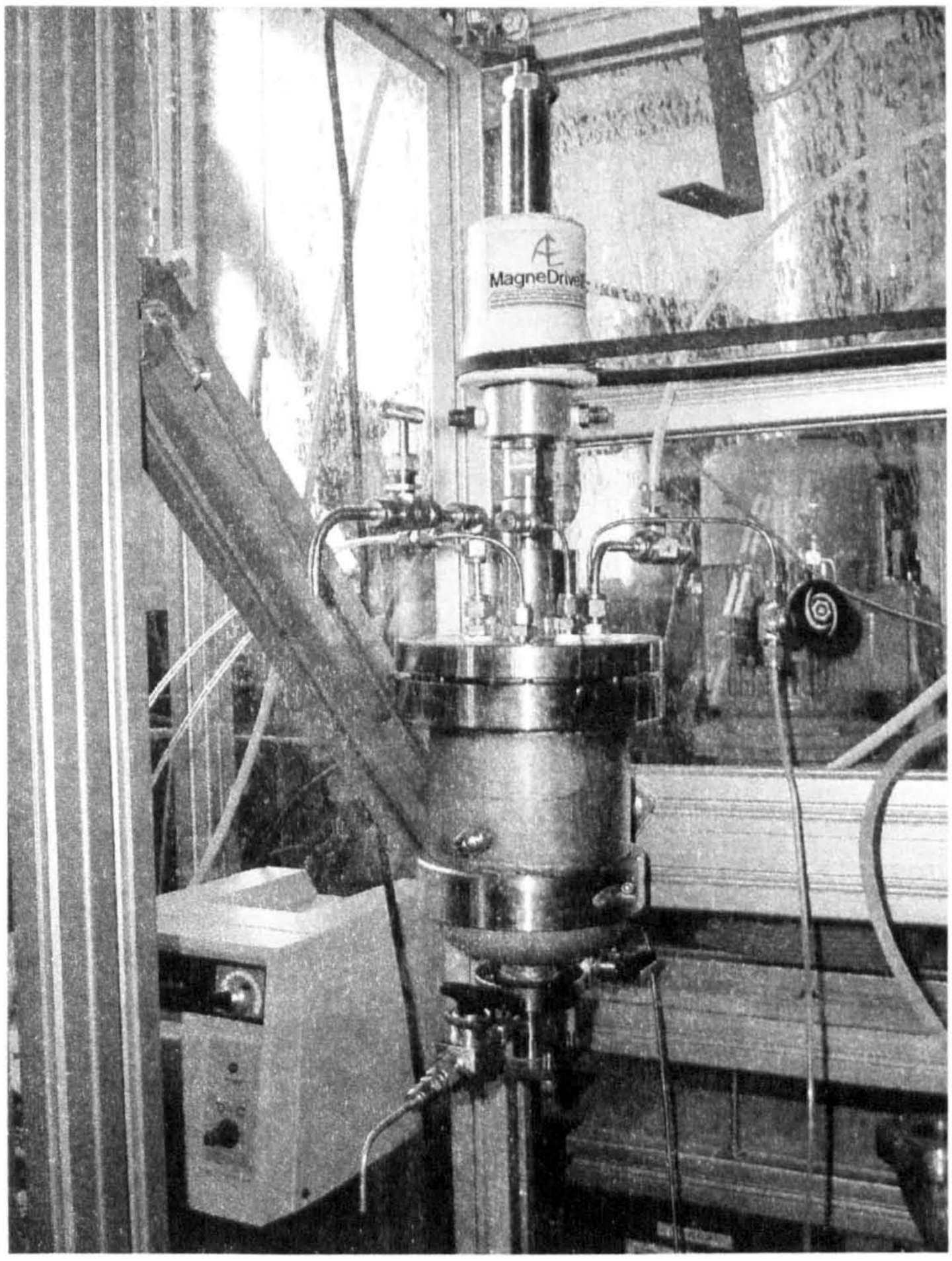


Figure 5.1: Emulsion polymerisation reactor - 0.7 litres stainless steel jacketed vessel with impeller.

The reactor was operated isothermally. The vessel was maintained at an approximately constant temperature through the regulation of the temperature of a thermal oil circulated in the reaction vessel jacket. Temperature control and circulation of the oil (heat transfer medium) was realised through a heat exchanger unit. The temperature of the reactor was controlled manually (no control loop) via regulation of the thermal oil set point temperature, with its flow maintained constant by the heat exchanger. Variation in the reactor temperature was registered during the process operation as a consequence of the heat of reaction produced during the polymerisation, of the addition of cold feed of reactants in the vessel, of the

extraction of samples and due to the oscillation resulting from the implementation of the manual adjustments of the thermal oil set point. Oscillations of $\pm$ 3 – 4 °C around the required set point of 70 °C were observed. A thermocouple placed into the reactor was used for temperature measurements. The temperature of the reaction bulk was displayed by a digital thermometer connected to the thermocouple.

To avoid the formation of pressure gradients that would have impeded the reagents flow, the vessel had to be opened to the atmosphere. A hole was opened on top of the reactor, with a condenser fitted on the hole to avoid any reagent evaporating out of the reactor. A borosilicate glass coil reflux condenser was used to condense the vapours formed from the reactor. Water from the main was used as cooling medium for the condenser.

The reagent feed rates were supplied using peristaltic pumps. Two of them were used to supply the two feed rates used to control in open-loop mode the system. Samples were extracted from the reactor through a sampling port in the bottom part of the reaction vessel, which was opened and closed through a manual ball valve. For safety reasons, the pilot plant was operated in an extraction cabinet.

5.1.2 Plant operation

The same policy used in the simulated process was implemented experimentally. This resulted in the introduction in the reaction vessel of the total amount of the two monomers and of the water needed to produce the desired latex, all at the beginning of the batch. This was followed by the feed of the aqueous solution of initiator and surfactant, used as control variables. The formulation components used were VAc (>99%), BuA (>99%) and aqueous solutions of sodium dodecyl sulfate (SDS) and sodium persulfate. To quench any reaction in the samples withdrawn from the reactor, two drops of 2 wt% hydroquinone solution were pipetted into each sample right after their collection from the reactor. The water used as reaction media and to prepare the aqueous solution of initiator and emulsifier was deionised.

An initial purging of the plant with nitrogen was carried out. This was done to eliminate possible traces of oxygen, which may cause the inhibition of the polymerisation reaction. The use, in the current experiment, of a condenser open to the air may still have induced

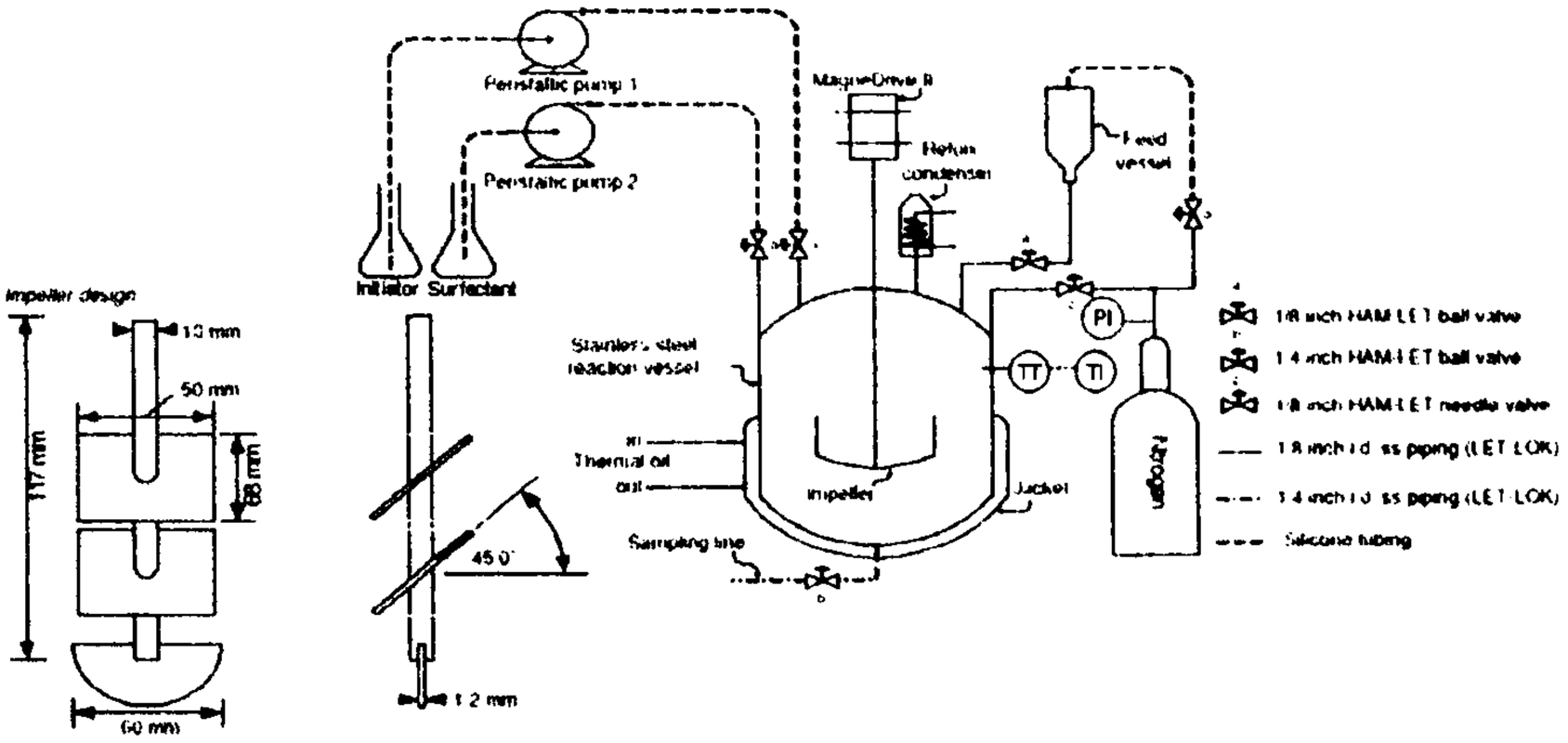


Figure 5.2: Schematic of experimental facility and impeller design (Sweetman, 2008).

contamination of the reaction bulk by oxygen. For this reason the inhibition of the reaction was still considered as a possible disturbance to the system in the model sensitivity studies of section 5.3.1.

The purging was followed by the heating of the initial formulation components in the reactor via thermal oil circulated in the reactor jacket. A thorough mixing of the reaction bulk was achieved setting the rotational speed of the agitator to 15 rpm, which was used throughout the heating and reaction stage. Time 0 is defined as the time of the first control feed injection into the reactor, which was made after the temperature in the reactor reached an approximate value of 70 $^{\circ}C$, optimal temperature for thermal decomposition of the sodium persulfate. Initiator and surfactant aqueous solutions were fed into the reactor using the two available peristaltic pumps.

Latex samples of 1-2 ml were withdrawn from the reactor at specified times. These

sampling times were selected to attain a satisfactory resolution of the output profiles. The polymerisation reaction was quenched in the samples as soon as withdrawn from the vessel. This was done to avoid the polymerisation reaction to progress and to have a sample representative of the system at the time of its collection. A total batch time of 150 minutes was used in the experiment.

5.1.3 Samples characterisation

The PSD was measured using a capillary hydrodynamic fractionator (CHDF) from Matec Applied Sciences (model: CHDF 2000), which uses the principle of capillary hydrodynamic fractionation to measure particles sizes in the range of 15 nm to 1.1 μm. An eluent continuously pumped into the fractionation cartridge is used as transport medium for the sample. A 0.1wt% solution of sodium benzoate is used as marker. Sample and marker injection, and elution are all controlled via computer. A residence time of approximately 11 minutes is required for the sample to be completely processed.

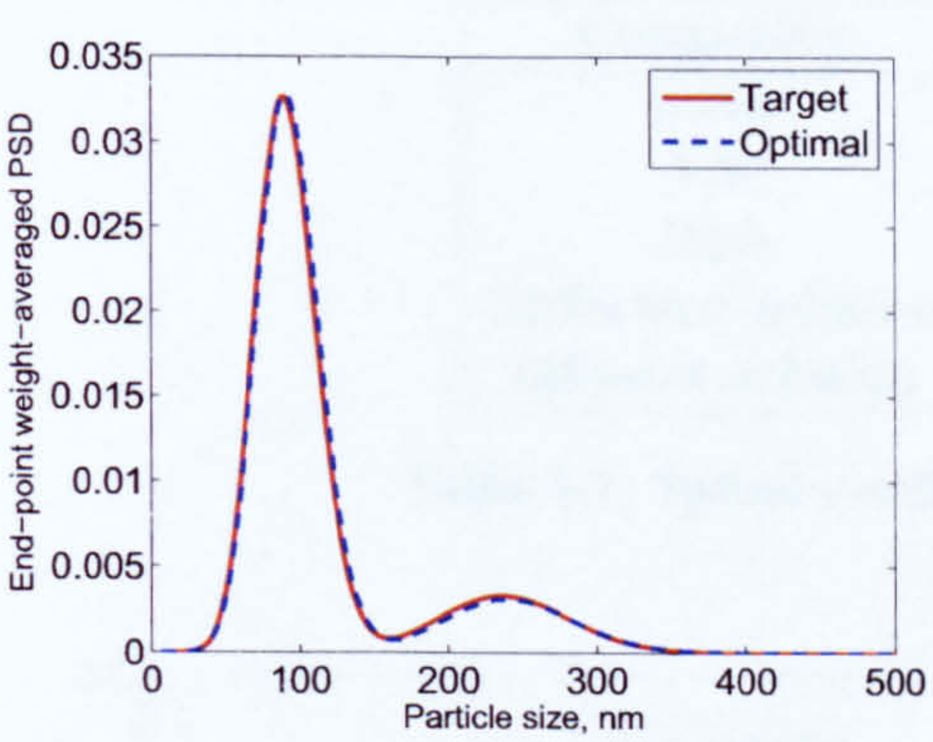
For reliable PSD measurements the samples are usually required to have a solids content between 0.1-5% in volume. Samples with higher solids content were diluted using deionised (DI) water. Gravimetric analysis was used for the determination of the solids content of each sample. PSD and solids content data were used to compute the total number of particles.

5.2 Experimental validation of a simulated optimal recipe

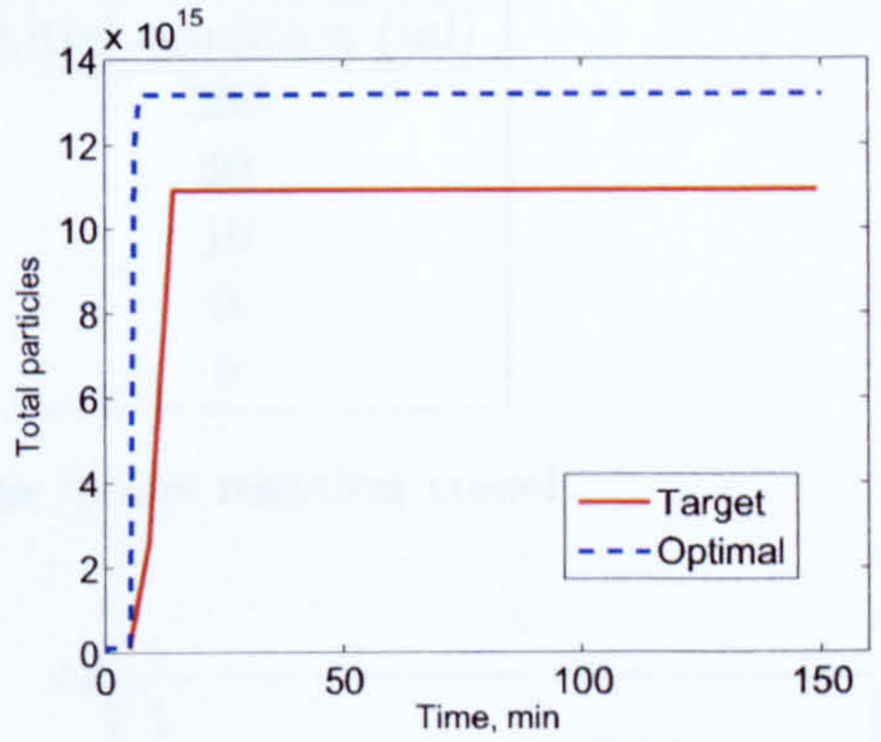
5.2.1 Experimental procedure

An experiment was carried out to validate the optimal open-loop recipe used to attain the targets in figure 5.3. In this figure, the simulated profiles resulting from the implementation of the optimal recipe in the model are also provided. The target and simulated PSD profiles overlap almost perfectly and makes the selected case suitable for validation.

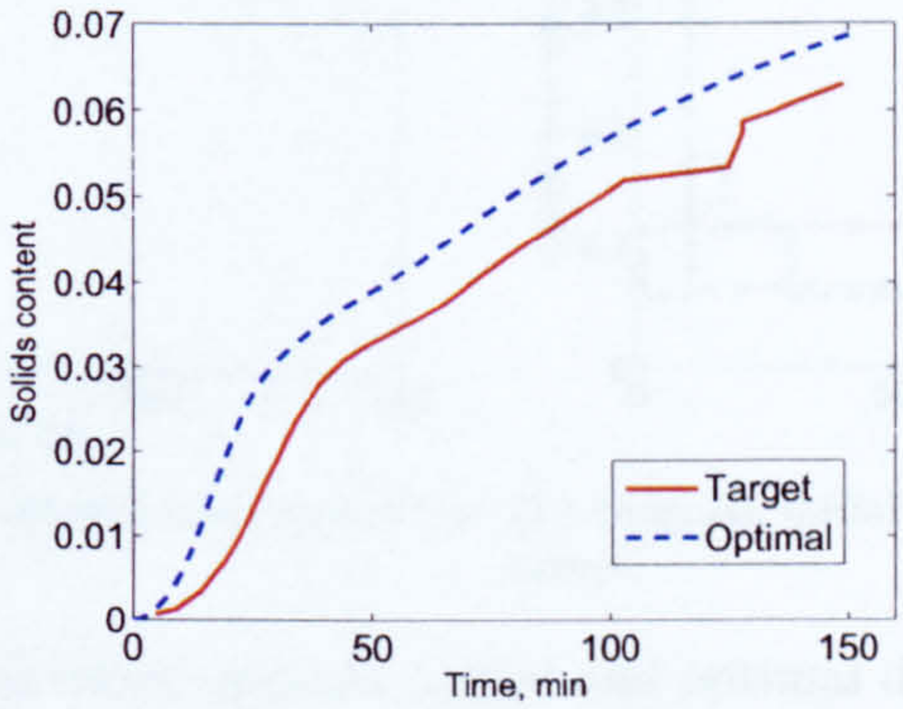
The initial conditions used in the simulation of these profiles are reported in table 5.1. The same conditions were implemented experimentally, with 300 ml of water, 50 ml of VAc and 10 ml of BuA introduced in the reactor at time 0. During the experiment no more water,



(a) End-point weight-averaged PSDs.



(b) Total number of particles.



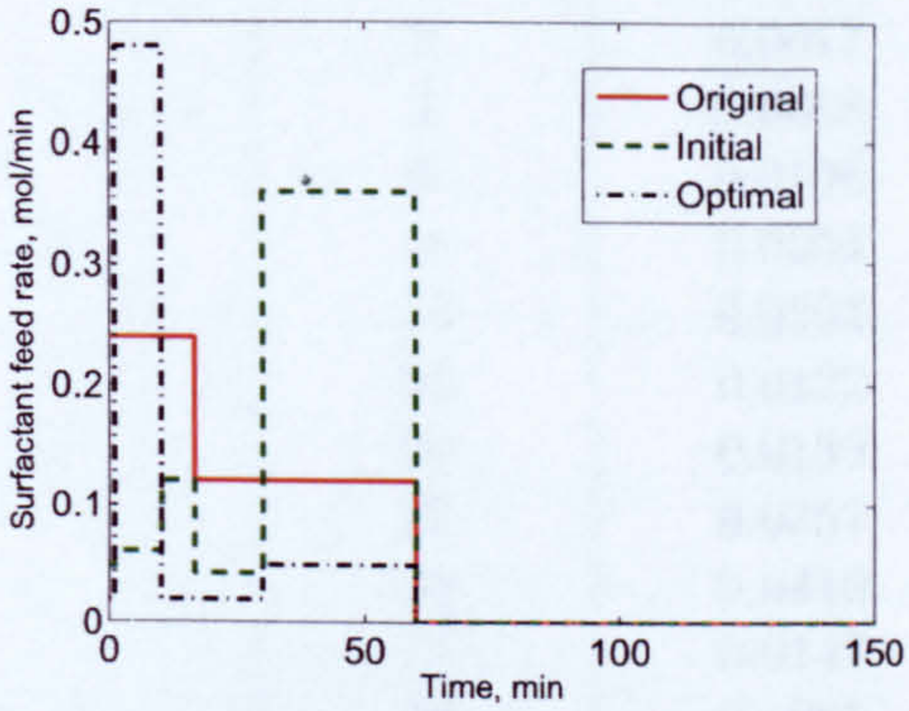
(c) Solids content.

Figure 5.3: Comparison between target and optimal simulated weight-averaged PSD, total number of particles and solids content.

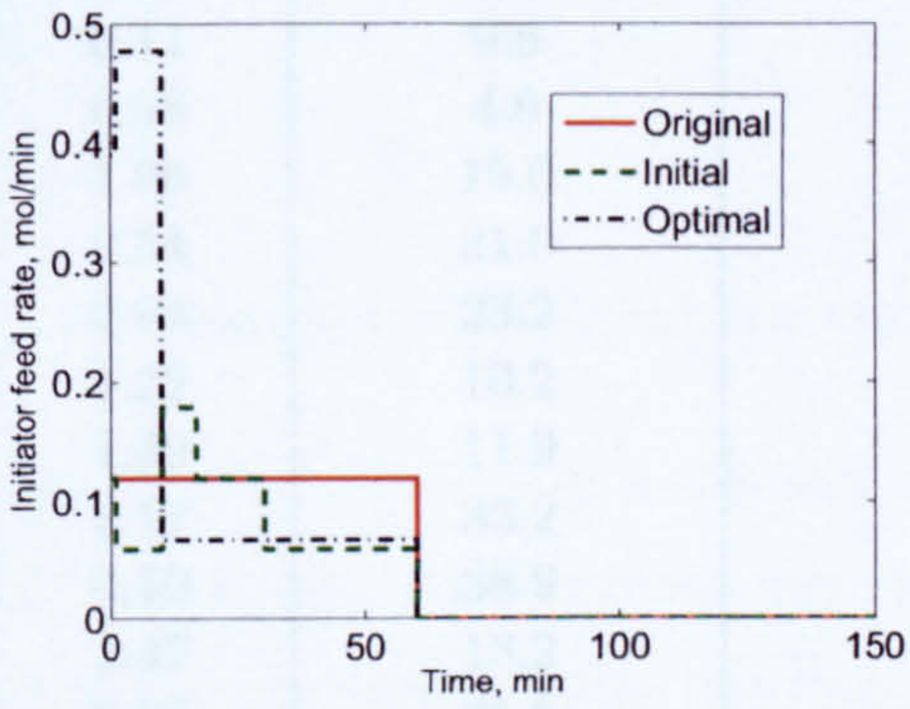
VAc or BuA was added and the two available peristaltic pumps were used to supply initiator and surfactant solutions. The surfactant solution was prepared dissolving 10 grams of SDS in 1 litre of water, while the initiator solution was prepared dissolving 15 grams of sodium persulfate in 1 litre of water. The optimal feed policies of these two solutions are shown in figure 5.4. The other two profiles in this figure are the original feed policy used to produce the target PSD and the initial guess used in the optimisation routine.

Component	Initial condition (ml)
water	300
VAc	50
BuA	10
surfactant solution	0
initiator solution	0

Table 5.1: Initial conditions in the reaction vessel.



(a) Original, initial and optimal feed rates of surfactant.



(b) Original, initial and optimal feed rates of initiator.

Figure 5.4: Comparison between original, initial and optimal decision variable trajectories.

5.2.2 Data analysis

The final gravimetric results are shown in table 5.2. The solids content for each sample was calculated as

$$sc = \frac{dry(g)}{wet(g)} \tag{5.1}$$

where *dry* is the weight in grams of the polymer particles in each sample and *wet* is the weight in grams of the sample (*i.e.* polymer particles, water and unreacted monomers). A comparison between optimal simulated solids contents profile and the profile obtained from the gravimetric analysis is presented in figure 5.5.

The low solids content, which is a consequence of the low conversion achieved in the process, probably introduced inaccuracy in the gravimetric measurements. This could have

Time (min)	Solids content	Solids (%)	Conversion (%)
0	0.0000	0.00	0.0
2	0.0011	0.11	0.6
4	0.0068	0.68	4.6
6	0.0196	1.96	15.0
8	0.0254	2.54	21.0
10	0.0264	2.64	23.2
15	0.0122	1.22	10.2
20	0.0139	1.39	11.9
25	0.0357	3.57	33.2
30	0.0410	4.10	38.9
35	0.0147	1.47	13.2
40	0.0265	2.65	25.5
45	0.0197	1.97	18.8
50	0.0178	1.78	17.1
55	0.0134	1.34	12.6
60	0.0230	2.30	23.3
70	0.0220	2.20	22.2
80	0.0135	1.35	12.9
90	0.0283	2.83	29.2
100	0.0283	2.83	29.1
110	0.0267	2.67	27.4
120	0.0383	3.83	40.2
130	0.0241	2.41	24.5
140	0.0240	2.40	24.4
150	0.0365	3.65	38.1

Table 5.2: Data from gravimetric analysis: solids content, % of solids and conversion.

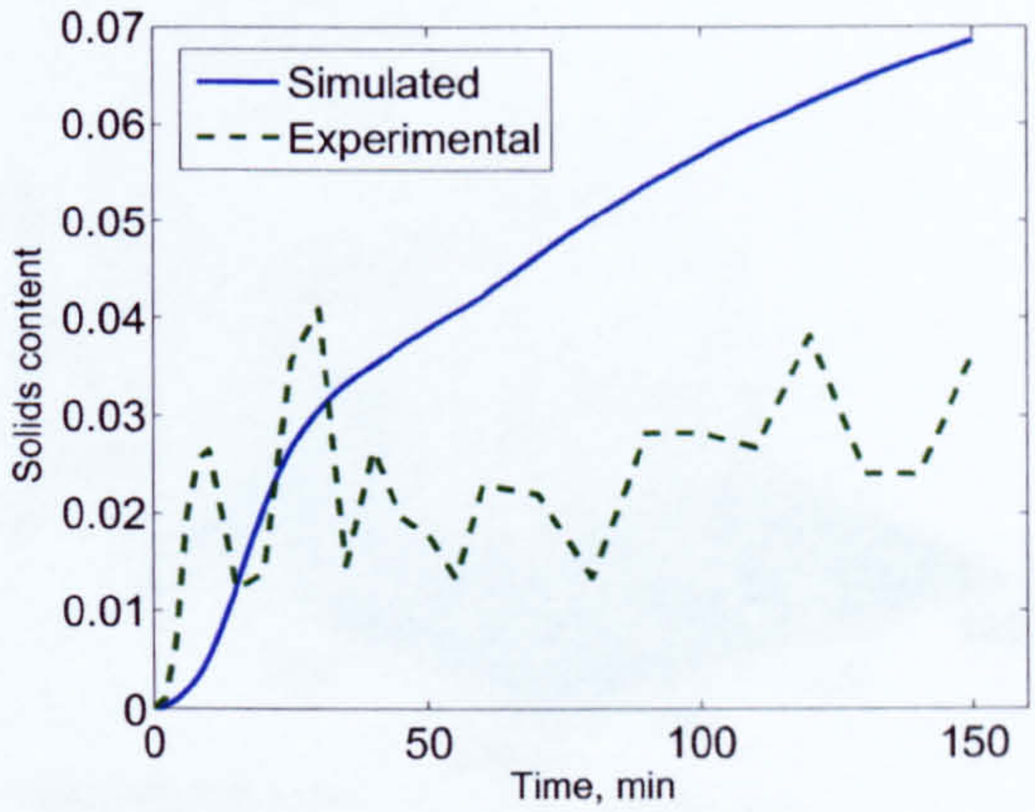


Figure 5.5: Comparison between simulated and experimental solids content profile.

resulted in the large fluctuation of the gravimetric data. The use of a different method, such as the inference of the solids content profile from density measurements, may have lead to more reliable data. The solids content predicted by the model is also relatively low. A final 7% solids content is predicted by the model against an approximately 4% obtained experimentally at the end of the batch.

The actual weighted PSD ($W(r)$) was computed from the normalised weighted PSD ($N(r)$) produced by the CHDF using the following relation (Immanuel and Doyle III, 2003b)

$$W(r) = \frac{W_{max}}{100} N(r) \tag{5.2}$$

where W_{max} is the highest value of the actual weight average distribution over the entire particle size range. The experimental PSD evolution is shown in figure 5.6. The comparison of some of the PSD profiles obtained experimentally with those simulated by the model is provided in figure 5.7. The mismatch between simulated and experimental profiles is considerably large. A single nucleation event occurs experimentally, probably resulting from micellar nucleation, while the model produces a bi-modal distribution as a result of two predicted nucleation events, one of them homogeneous. The peak obtained from the experiment is much larger than either of the two modes in the simulated profile, with the size of the particles in this mode considerably smaller compared to those of the simulated profile. This

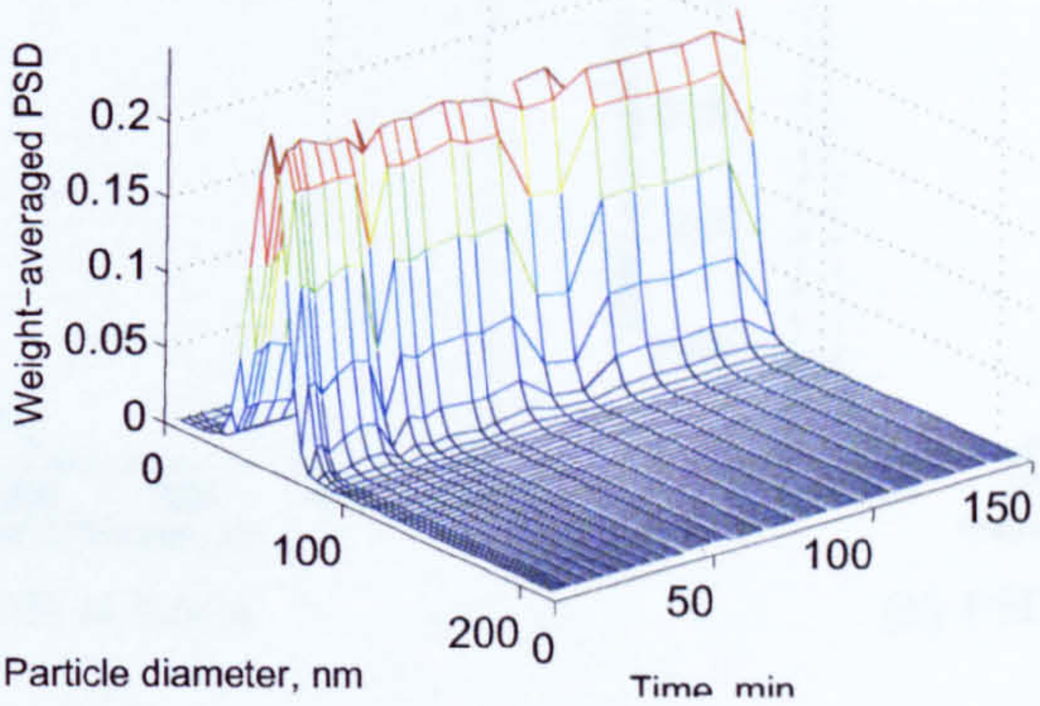
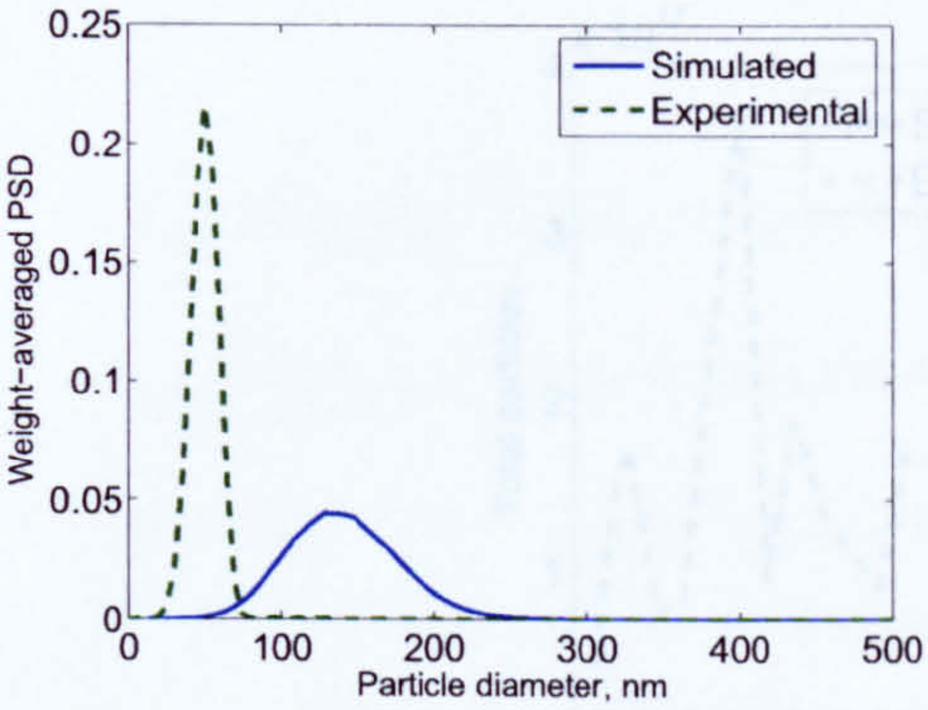


Figure 5.6: Experimental PSD.

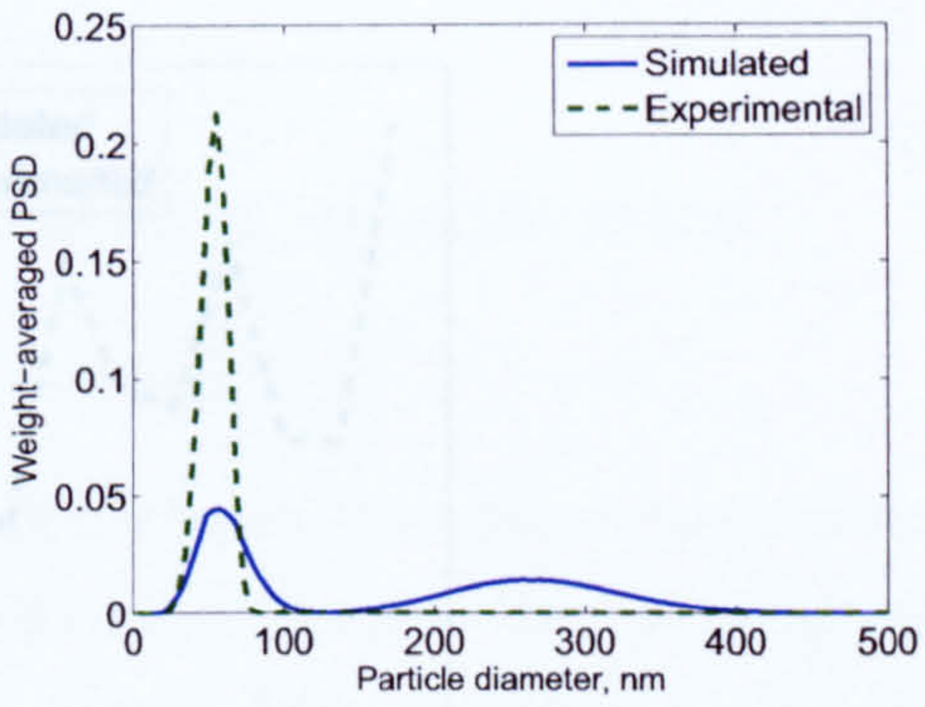
may suggest, in the hypothesis of the experimental results being correct, that the nucleation rate expressions in the model have to be modified to account for the absence of one of the nucleation event and for the much larger extent of the one event that occurs.

From the experimental profiles it seems that particles are formed in one single shot after 4-6 minutes and once formed they remain in the same status for the rest of the batch, without undertaking almost any further growth or coagulation. This could be explained as the result of the use of an excessive amount of surfactant, which does not allow particles to coagulate further after the early-stage coagulation phenomena. Also, this could be explained as the result of a lack of initiator to start new nucleations. From the observation of the optimal recipe implemented experimentally (figure 5.4) it seems that these two hypothesis are actually both feasible explanation of the results obtained experimentally. In fact, an initial large shot of both surfactant and initiator was supplied right after 1 minute and their feed rates were then drastically reduced after 10 minutes into the batch. This may have resulted in saturation of the system with surfactant in the early-stage of the process and caused most of the initiator to be consumed right at the beginning of the batch. Also loss of monomer and inhibition of the reaction by oxygen fit well with the experimental results.

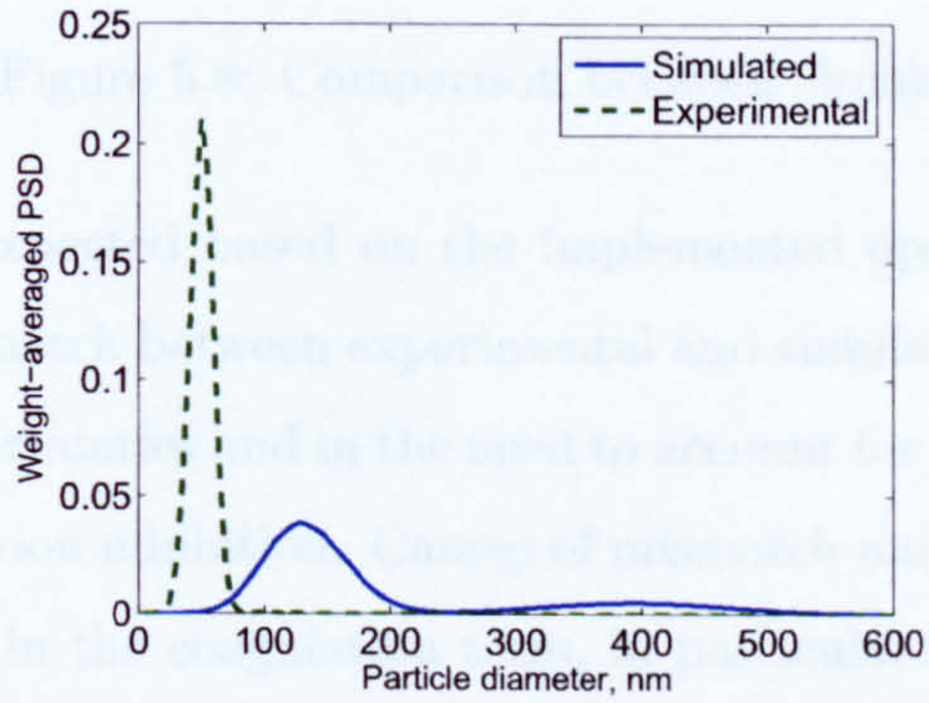
These two disturbances were both deemed to be possible in the current experiment due to plant design and operating procedures implemented. The open-air condenser was a possible



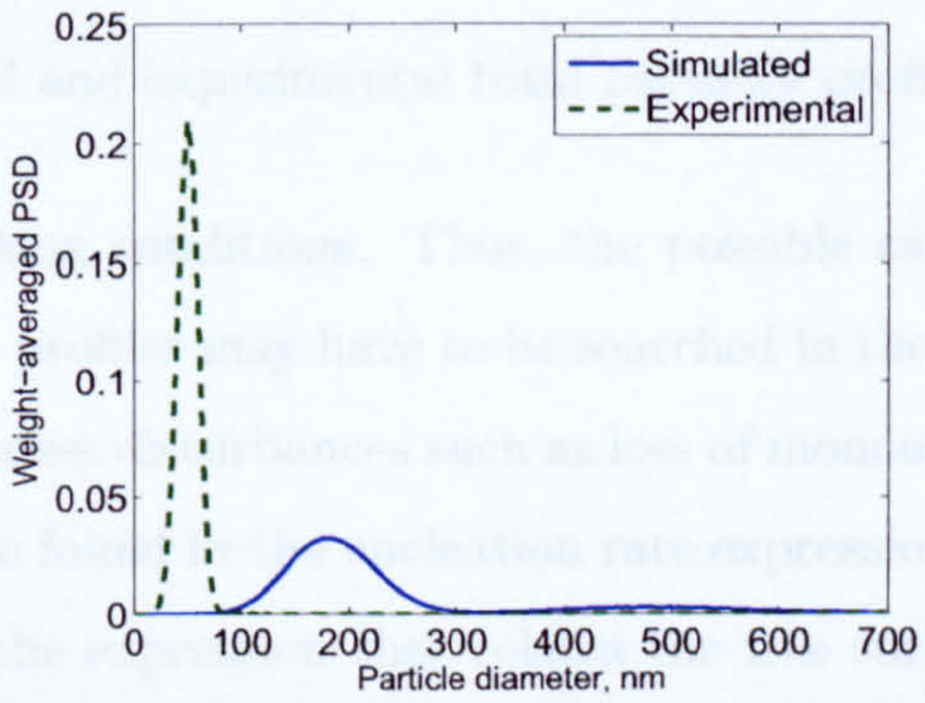
(a) PSD at 4 min.



(b) PSD at 10 min.



(c) PSD at 30 min.



(d) PSD at 150 min.

Figure 5.7: Comparison between experimental and simulated PSD at different times into the batch.

route for the oxygen into the reaction bulk via atmospheric air. The withdrawal of 25 samples of 1-2 ml each was a considerable source of monomer loss, together with the loss deriving from the purging strategy implemented. The purging with nitrogen was carried out during the heating of the reaction bulk from ambient temperature to 70 $^{\circ}C$ and interrupted before feeding initiator and surfactant solutions to start the reaction. The purging was interrupted because the gas flow was forcing volatile monomer and liquid particles out of the reactor through the condenser. This phenomena was promoted by the high temperatures and the stirring of the latex.

From these considerations it seems that the profile obtained experimentally is the one to

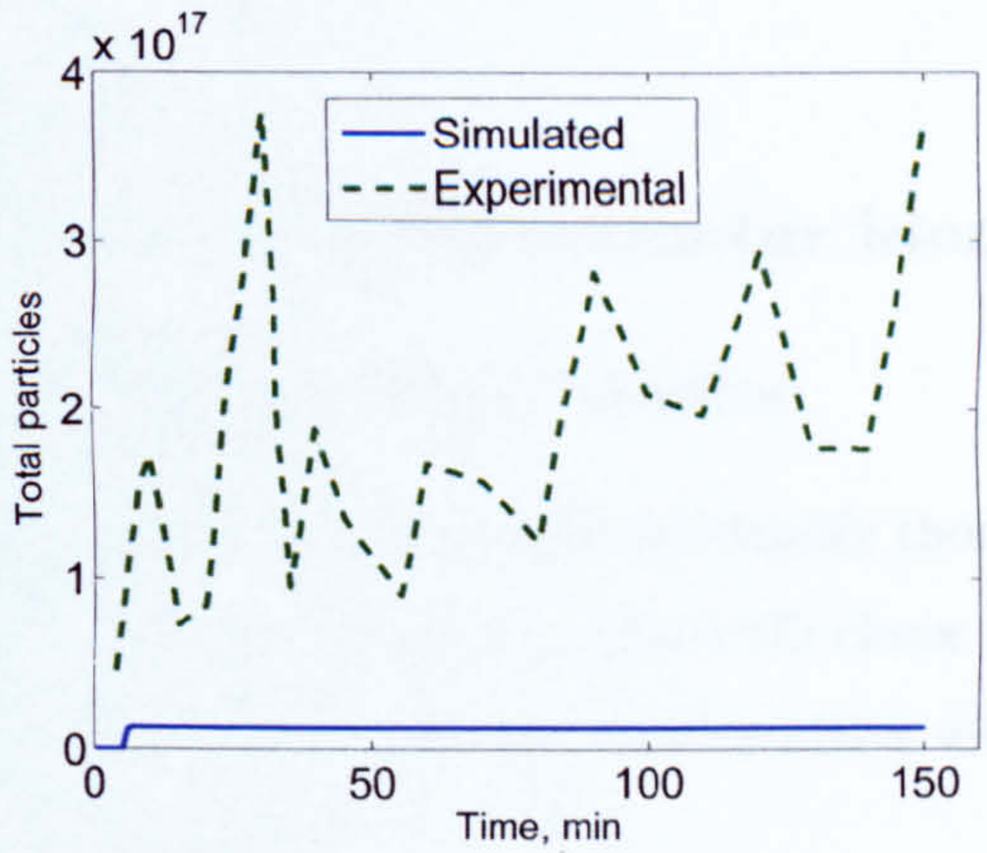


Figure 5.8: Comparison between simulated and experimental total particles profile.

be expected based on the implemented operating conditions. Thus, the possible causes of mismatch between experimental and simulated profiles may have to be searched in the model uncertainties and in the need to account for process disturbances such as loss of monomer and reaction inhibition. Causes of mismatch may be found in the nucleation rate expressions, but also in the coagulation term, in particular in the expression that relates the free surfactant concentration and the coagulation kernel, and in the growth rate.

The temperature oscillations around the required set point may be seen as another disturbance, due to the large sensitivity of the system to this parameter. Its oscillations may be responsible for the fluctuation of the solids content profile. Temperature variations were not anyway considered as one of the possible causes of mismatch because the model used to simulate the reactor (Immanuel et al., 2002, 2003) was built for isothermal systems and did not explicitly account for the relation between the temperature and the different process mechanisms.

The profile of the number of particles can be computed from the available solids content and PSD data. The comparison of the total particles profiles in figure 5.8 confirms that the number of particles produced experimentally is much larger than the one predicted by the model. The large fluctuation in the experimental profile is a direct consequence of the implementation of the solids content from the gravimetric analysis to compute the number

of particles.

5.3 Sensitivity studies and parameter identification

5.3.1 Experimental aided sensitivity studies

Sensitivity studies were performed on the system to identify those parameters and aspects to be added/modified in the model to produce a final PSD closer to the distribution obtained experimentally. Between these parameters the most sensitive were selected and used for the subsequent parameter identification.

Different parameters were selected or included into the model based on previous simulation-based sensitivity studies and on the observations from the experimental results in section 5.2.2. Two possible disturbances were considered to be

- loss of monomers
- inhibition of the reaction by oxygen

From the comparison with the simulated optimal profile, adjustments to the model were suggested by the following observations on the experimental profile

- absence of the homogeneous nucleation event
- larger micellar nucleation event
- reduced growth
- reduced particle coagulation

Some of the uncertain/sensitive terms taken into account in this analysis to correct for the model uncertainties/disturbancies listed above were

- rate of homogeneous nucleation
- total amount of monomer in the reactor
- critical micelle concentration

- relation between free surfactant concentration and coagulation kernel (surface charge and adsorption equilibrium constant for the surfactant)
- coagulation kernel
- micellar nucleation rate
- termination rate (average rate constant for termination)

A trial and error strategy was initially implemented to test the sensitivity of the model to the modifications applied on these terms. The modulation of the parameters and correction factors included in the model all influenced number, size and magnitude of the modes to a certain extent and with a specific force. A large sensitivity, and the ability to obtain through their modulation a progressive and considerable improvement in the match with the experimental target, was observed in particular for three parameters. These were

- correction factors for the total amount of VAc and BuA in the reactor
- multiplicative correction factor for critical micelle concentration (cmc)
- multiplicative correction factor for the micellar nucleation rate

The correction factors for the initial amount of VAc and BuA in the reactor were selected to account for the possible loss of these monomers from the reactor. They were chosen based on different considerations, such as for example the relative volatility of the two molecules. The value of the cmc was reduced to simulate a larger particle formation via micellar nucleation and the same was done through the modulation of the corrective factor for the micellar nucleation rate. The new values for the cmc and the micellar nucleation rate were computed using the following expressions

$$cmc_{corrected} = factor_1 \cdot cmc \tag{5.3}$$

$$\Re_{micellarcorrected} = factor_2 \cdot \Re_{micellar} \tag{5.4}$$

Case	Correction factor (VAc)	Correction factor (BuA)
1	0.73	0.99
2	0.70	0.70
3	0.90	0.90
4	0.50	0.50
5	0.95	0.75
6	0.80	0.60

Table 5.3: Multiplicative correction factors for the initial amount of VAc and BuA in the reactor.

Some of the results obtained from the tuning of these parameters are presented in figure 5.9. The cases 1 to 6 in figure 5.9(b) represent different combinations of the multiplicative correction factors used for the initial amount of the two monomers, when these amounts are expressed in moles. The values of these correction factors for the different cases are reported in table 5.3.

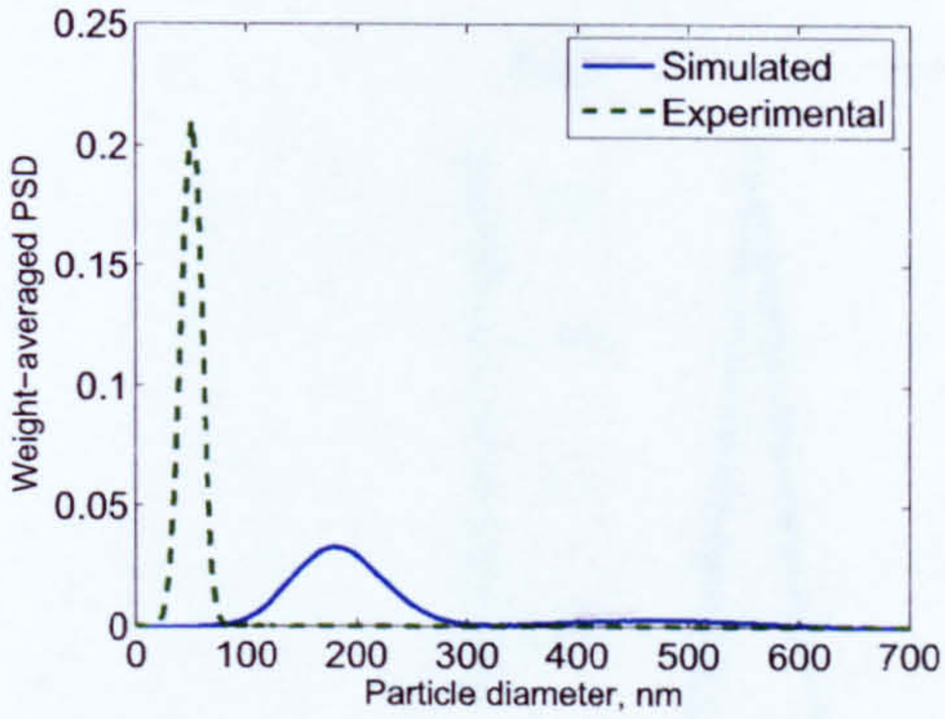
The importance of the micellar nucleation in driving the evolution of the PSD is confirmed by these results. In fact, the cmc primarily influences the micellar nucleation phenomenon and the use of a correction factor for the micellar nucleation rate speeds up and improve the match with the experimental profile.

5.3.2 Parameter identification

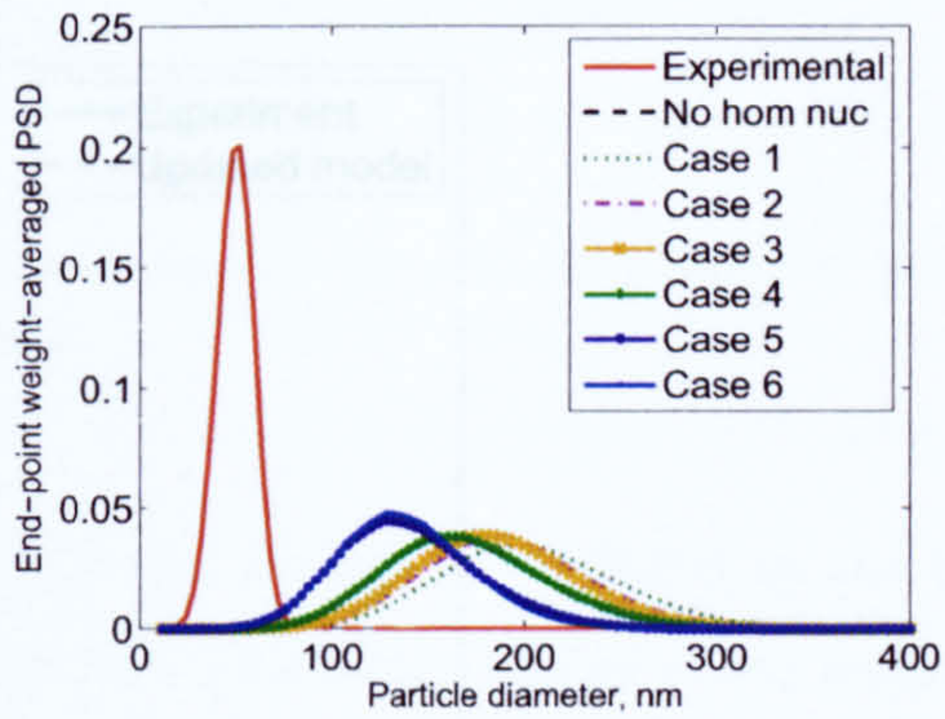
The sensitivity studies of section 5.3.1 highlighted the importance of tuning aspects of the model such as cmc, termination rate constants, micellar nucleation rate, total amount of monomer and coagulation kernel to shape the PSD produced by the model. In particular, the correction factors on

- total amount of monomer
- cmc
- micellar nucleation rate

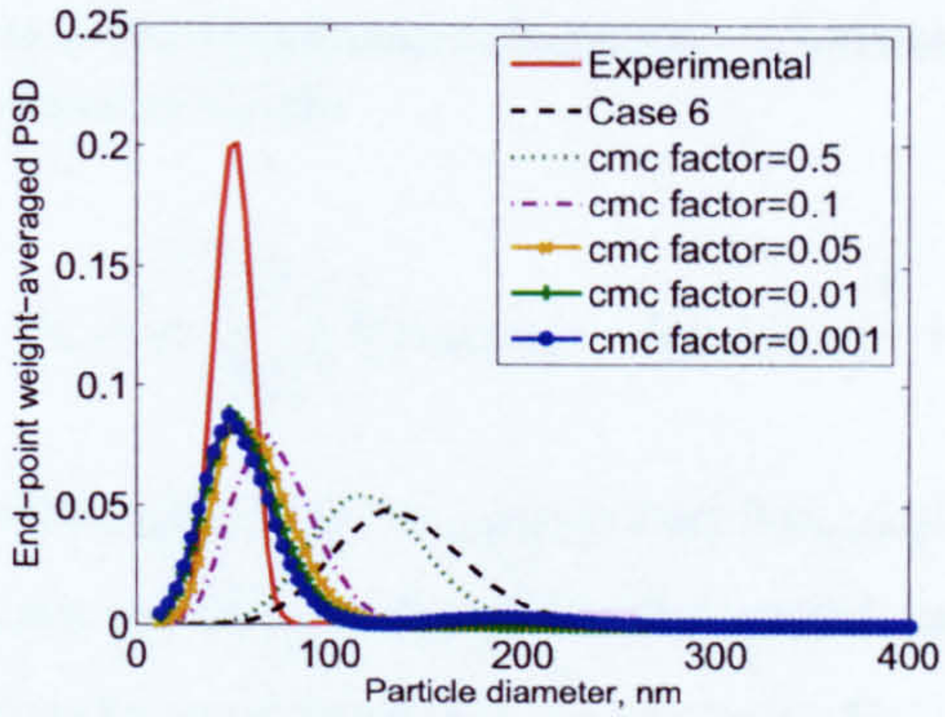
were particularly effective in driving the system towards the expected experimental PSD.



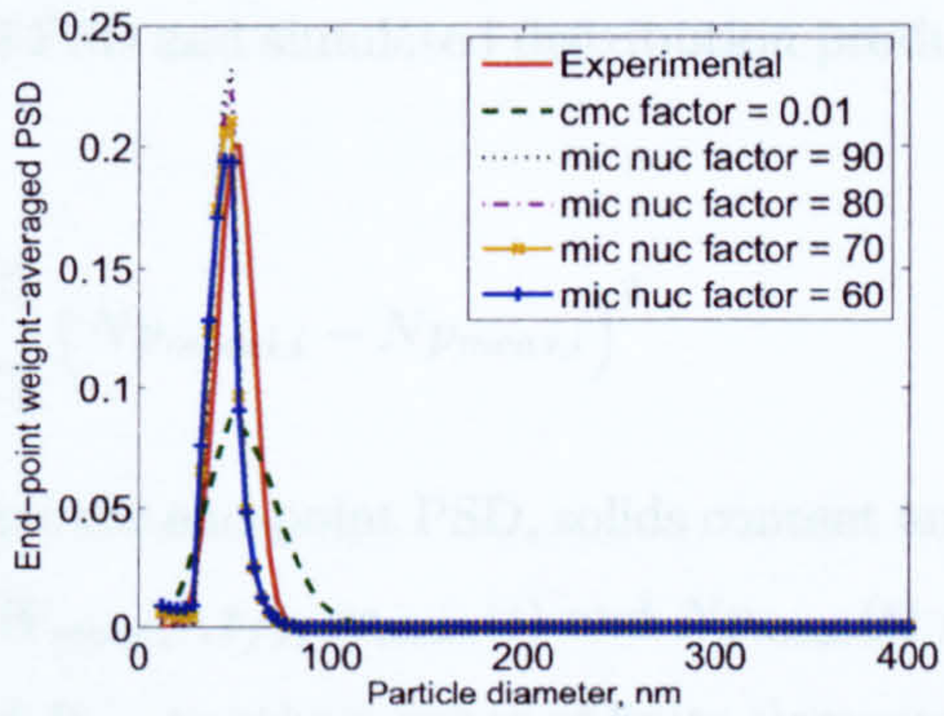
(a) Experimental and simulated end-point PSD.



(b) Modulation of monomer loss correction factors.



(c) Modulation of cmc.



(d) Modulation of micellar nucleation rate.

Figure 5.9: Sensitivity of the model to loss of monomer from the reactor, cmc and micellar nucleation rate and ability to modulate these uncertain parameters to produce a closer match with the experimental PSD.

Parameter identification was performed using single and multi-objective optimisation formulations of the type described in chapter 3. The objective functions were formulated as follows

$$\theta_1 = \sum_{i=1}^{N_{bin}} \left(W_{model,i}(t_f) - W_{meas,i}(t_f) \right)^2 \tag{5.5}$$

$$\theta_2 = \sum_{i=1}^{N_{exp}} \left(sc_{model,i} - sc_{meas,i} \right)^2 \tag{5.6}$$

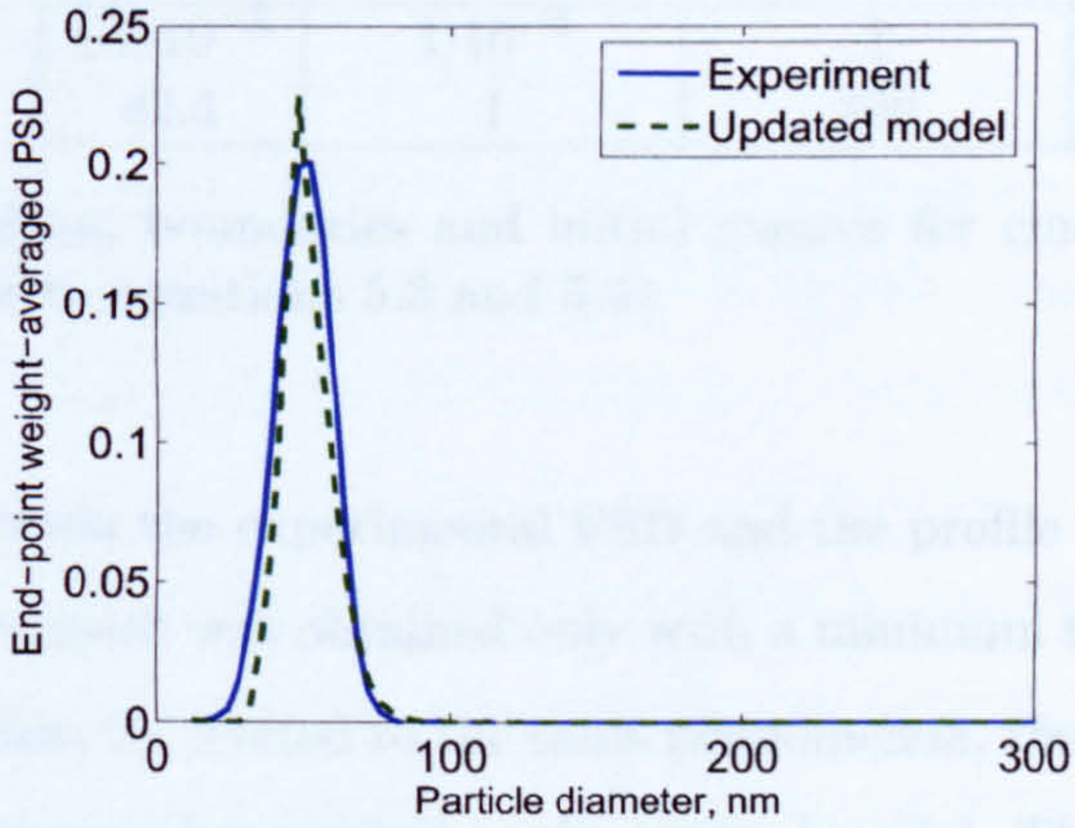


Figure 5.10: Comparison between experimental PSD and simulated distribution produced by the updated model.

$$\theta_3 = w \sum_{i=1}^{N_{exp}} \left(Np_{model,i} - Np_{meas,i} \right)^2 + \sum_{i=1}^{N_{exp}} \left(Np_{model,i} - Np_{meas,i} \right)^2 \tag{5.7}$$

where $W_{model}(r, t_f)$, $sc_{model}(t)$ and $Np_{model}(t)$ are the end-point PSD, solids content and total particles profiles produced by the model, and $W_{meas}(r, t_f)$, $sc_{meas}(t)$ and $Np_{meas}(t)$ are the profiles obtained from the experiment. N_{bin} and N_{exp} are the number of finite elements (bins) in which the particle size domain is discretised and the number of experimental readings taken for each variable, respectively.

Different combinations of the identified sensitive parameters were used as control variables. The best set of these variables, as expected, was found to be the one constituted by the correction factors for the total amount of monomer, cmc and micellar nucleation rate. From subsequent studies was also observed that the first of these parameters may also be excluded without considerable alteration of the final outcome. The use of the only cmc and micellar nucleation rate correction factors as decision variables and the implementation of a single-objective strategy (more suitable in this case due to the strong fluctuation in the solids content and total particles profile) produced the match with the PSD target showed in figure 5.10. Optimised values for these two parameters, together with boundaries imposed on them and initial guesses are provided in table 5.4.

Parameter	Optimal	Lower bound	Upper bound	Initial guess
$factor_1$	$1.2{\cdot}10^{-3}$	$1{\cdot}10^{-4}$	1	$1{\cdot}10^{-2}$
$factor_2$	42.4	1	100	50

Table 5.4: Optimal values, boundaries and initial guesses for cmc and micellar nucleation correction factors (refer to equations 5.3 and 5.4).

The agreement between the experimental PSD and the profile produced by the updated model is accurate. This result was obtained only with a minimum tuning of the model. Only two parameters, both directly related to the same phenomenon, the micellar nucleation, were modified in the updated model compared to the original model. This result highlight the importance of a detailed mechanistic model for model update in a feedback control strategy. To validate and confirm the conclusions derived from this study, more experiments are required.

5.4 Summary

An experiment was performed on a bench-scale emulsion polymerisation reactor to validate an optimal recipe computed using the pareto multi-objective optimisation strategy. The aim of the experiment was also to to identify and select uncertain and sensitive parameters for model update. The experimental facility was comprised of a 0.7 litres stainless steel reactor. Homogeneous dispersion of the polymer particles in the latex was achieved through an electrical impeller attached to the top of the reaction vessel.

The reactor was operated isothermally. The vessel was maintained at an approximately constant temperature through the manual regulation of the temperature of a thermal oil circulated in the reaction vessel jacket. The temperature of the reaction bulk was displayed by a digital thermometer connected to a thermocouple placed into the reactor. Variations of the reaction temperature around the set point value of 70 °C were registered during the process operation.

A hole was opened on top of the reactor, with a condenser fitted on the hole to avoid any reagent evaporating out of the reactor. The reagent feed rates were supplied using peristaltic pumps. Samples were extracted from the reactor through a sampling port in the bottom part

of the reaction vessel. Time 0 was defined as the time of the first control feed injection into the reactor, which was made after the temperature in the reactor reached an approximate value of 70 $^{\circ}C$, optimal temperature for thermal decomposition of the sodium persulfate. Latex samples were withdrawn from the reactor at specific times, which were selected to attain a satisfactory resolution of the output profiles. A total batch time of 150 minutes was used in the experiment.

The PSD was measured using a capillary hydrodynamic fractionator (CHDF), which uses the principle of capillary hydrodynamic fractionation to measure particle size. Gravimetric analysis was used for the determination of the solids content of the samples. PSD and solids content data were used to compute the total number of particles.

The open-loop recipe to validate was used to attain a specified bi-modal target PSD. The introduction in the reactor of the total amount of the two monomers (liquid VAc and BuA with purity >99%) and of the water, at the beginning of the batch, was followed by the feed of the aqueous solution of initiator (sodium persulfate) and surfactant (SDS), used as control variables. An initial purging of the bench-scale plant was carried out to eliminate possible traces of oxygen, which may have caused the inhibition of the polymerisation reaction.

From the analysis of the experimental results it was possible to observe how the experimental solids content was low and only reached the value 4% at the end of the batch, with its profile not matching the one predicted by the model. The mismatch between simulated and experimental PSD was also considerably large. A single nucleation event occurred experimentally, probably resulting from micellar nucleation, while the model produced a bi-modal distribution as a result of two nucleation events, one of them homogeneous. The comparison of the total particles profiles also showed that the number of particles produced experimentally was much larger than the one predicted by the model.

From considerations on the process evolution, it seemed that the profile obtained experimentally was the one to be expected based on the implemented operating conditions. Thus, the possible causes of mismatch between experimental and simulated profiles were searched between the possible model uncertainties and the process disturbances, such as loss of monomer and reaction inhibition.

Sensitivity studies were performed on the system to identify those parameters and aspects to be added/modified in the model to produce a final PSD closer to the distribution obtained experimentally. Between these parameters the most sensitive were selected and used for the subsequent parameter identification. Correction factors and parameters were used in the model to modify the rate of homogeneous nucleation, the total amount of monomer in the reactor, the critical micelle concentration, the coagulation kernel, the micellar nucleation rate and the termination rate. These were used to correct model uncertainties and process disturbances deemed to be responsible for the mismatch between experimental and optimal simulated profiles. The multiplicative correction factors for total amount of monomer, cmc and micellar nucleation rate were particularly effective in driving the system towards the expected experimental PSD.

Parameter identification was performed using single and multi-objective optimisation formulations of the type described in chapter 3, with the objective functions formulated as the error between the PSD, solids content and number of particles produced by the model and obtained from the experiment. The best set of control variables was found to be a vector of only two elements, namely the correction factors for the critical micelle concentration and for the micellar nucleation rate. When using these control variables and a single-objective optimisation strategy, the agreement between the experimental PSD and the profile produced by the updated model was accurate.

Chapter 6

Conclusions and Future Work

In this final chapter the outcomes of the current research project are summarised and the major contributions highlighted. A path for future work is also suggested for further advancements in the area.

6.1 Conclusions

6.1.1 Open-loop control studies

The aims of these initial studies were essentially to

- test the accuracy and efficiency of different optimisation problem formulations
- confirm the suitability of these formulations for different operating conditions
- select the best set of decision variables to use for optimisation

Gradient-based strategies were implemented successfully. The different optimisation strategies tested proved to be effective in matching the target distributions. Single-objective and multi-objective strategies were implemented. The multi-objective scheme proved to be more robust, *i.e.* valid for a larger range of targets and operating conditions. Good results were obtained with the single-objective strategies, which can then be used as a valid alternative to multi-objective formulations every time this is feasible as a means to reduce the computation time.

Optimal sets of decision variables to be used for open-loop control of the PSD were identified. Feed rates and duration of the injection were considered as control variables. The use, as decision variables, of the feed rates in the first time intervals of two different reagents proved to be effective in controlling the system towards the desired targets. The importance of surfactant feed rates as control variables was highlighted and derives from the strong influence of the surfactant concentration on all the major phenomena that drive the evolution of the PSD, namely nucleation, growth and coagulation.

6.1.2 Inferential control of end-use latex properties

The inferential control strategy can be used as a means to control those variables that are not measurable in real time or cannot be characterised in a reasonable short time. End-use properties of emulsion latexes often fall in this category. The inferential control of these properties via available process variables would be a simpler and valid alternative to the direct control of these properties. The inferential control of the rheology of emulsion polymers through the combined regulation of PSD and solids content profiles is an example of inferential control strategy of end-use latex properties and was presented in chapter 4.

This strategy effectively decomposes the rheology control problem from the process variable control problem, and breaks the complex non-convex problem that underlies the end-use product property control into relatively simpler sub-problems. The computation of the PSD leading to the desired rheology needs an integrated model accounting for the following aspects

- combined influences of PSD and solids content on the rheology
- interactions between PSD and solids content, the latter by itself being an important controlled variable
- process imposed limitations on the ranges of attainability of PSD

The results presented in section 4.1 clearly illustrate that the PSD can influence the rheology of the emulsion polymers. In particular, the number of modes, the size of the modes and the relative amounts of particles in the different modes directly influence the maximum

packing factor. The PSD also affects the solids content via the polymerisation mechanisms, with PSD and solids content having together an integrated effect on the rheology of the latex.

There is a non-unique relation between PSD and rheology of the emulsion polymer, in the form of non-convexity of the problem for the computation of the optimal PSD that lead to the desired rheological properties. This may allow selection of the PSD for recipe optimisation so that is also likely to be in-batch feedback controllable. This could be a further criterion/constraint in the process of identification of the optimal PSD that would lead to the desired rheology.

6.1.3 Feedback controllability and batch-to-batch feedback control strategy

Controllability issues caused by the sparse and delayed nature of the PSD measurements limits the classes of PSD that are controllable. Only classes of PSD with clearly separated modes and in which the second nucleation event occurs relatively late in the batch are likely to be feedback controllable in an in-batch sense. Control of the second, and subsequent nucleation events, and control of the growth rate are used to produce the desired target through the modulation of the relative number of particles in the two modes and the size of the modes.

Even if these pre-requisites are satisfied, a feedback control action may still not exist because of discontinuities in the process, the strong interaction between PSD and the rate processes and the need to limit the possible negative effect of the control moves on the solids content, again due to the interrelation of these two process variables. Thus, PSD profiles with clearly distinct modes and nucleation events separated by a sufficient time to allow for few PSD measurements, are only likely to be controllable. On the other hand, PSD classes with overlapping modes and produced by processes in which nucleation events follow each other after a short time, with not enough time for PSD measurements in between, are to a major extent feedback uncontrollable.

In all those cases where in-batch feedback control is applicable a model predictive control formulation may be implemented. The implementation of this optimisation-based advanced

control strategy would be highly facilitated by the use of knowledge-based optimisation formulations of the type presented in this thesis. It would reduce the computation requirements and lead to the desired solution through the planned reduction of the search space.

For all those distributions that are not controllable a batch-to-batch feedback control strategy is a necessary and viable alternative. A simple implementation of the batch-to-batch strategy as a combination of dynamic optimisation and model update is possible if a detailed model is used. A batch-to-batch feedback control strategy for the control of PSD in a semi-batch emulsion polymerisation was presented in section 4.3.

6.1.4 Experimental validation of optimal policies

The advantage of using a comprehensive mechanistic model for the process was demonstrated through the ability of the model to reproduce accurately experimental results with only a little tuning of a limited carefully selected number of parameters. This result highlights the importance of a detailed mechanistic model for model update in a feedback control strategy. The validation of more open-loop policies are still needed to confer robustness to the model update strategy and to eventually lead to a globally valid model for the process.

6.2 Future work

In many complex applications, the need for a careful formulation of the optimisation problem is crucial. The use of straightforward optimisation such as gradient-based optimisation algorithms may result less effective and the formulation of an alternative optimisation strategy may help to find pseudo globally optimal solutions for these non-convex problems with multiple optimal solutions. The implementation of a global optimisation strategy (Adjiman et al., 1997) is a valid alternative as well as the formulation of objective functions tailored on the desired characteristics of the solution. An example of the latter scenario is the multi-objective strategy (Immanuel and Doyle III, 2003c) implemented in chapter 3. The knowledge-based formulation proposed in section 4.2.4 is another example of the steering of the solution towards the desired characteristics. These formulations of the optimisation problem can provide a crucial aid to the computation of the feedback control actions by simplifying the feedback

control problem. The use of a global optimisation technique and the subsequent refinement of the solution using a local search method such as a gradient-based technique, as proposed by Immanuel and Doyle III (2002), is also another valid alternative for the solution of these complex non-convex problems.

Tests of the optimisation routines on more complex profiles may fully exploit the abilities of the multi-objective formulation compared to the single-objective scheme, with the simultaneous optimisation of different objective functions that may drive more efficiently the simulated profile towards the required target. The robustness of the open-loop identification of optimal operating conditions may be enhanced using more robust optimisation strategies accounting for potential model uncertainties or through the use of mixed-integer algorithms. When mixed-integer methods are implemented the time intervals in which the batch is discretised, for the computation of the optimal trajectories that lead to the desired target distribution, can be used as decision variables. Different forms of the addition policy may also be used. Mixed-integer routines can also be implemented to account for carryover of particles in real processes, with the integers that may be used to account for the presence or absence of the latex carryover. Different knowledge-based optimisation approaches for the inferential control of end-use properties different from rheology may be also formulated.

When implementing a batch-to-batch feedback control strategy via dynamic optimisation followed by model update, the validity of the updated model/parameters is usually restricted to the vicinity of the current operating conditions. This is because of the lumped nature of the model parameters used for update and the sub-optimality of the strategy implemented, in which only few sensitive parameters are selected and optimised, although these may also not be the erroneous parameters. Instead of lumping the errors into a fixed set of parameters, estimability considerations (see, for example (Asprey and Macchietto, 2000; Kou et al., 2005; Li et al., 2004b,c)) for the identification of the most suitable parameters for model update may be applied. Also an alternative strategy can be used. A second target can be considered and the data from batches obtained during the iteration toward the first target could be used to perform the iterative feedback correction for the second target. This would increase the range of validity of the updated model. The use of the same approach for a range of PSD

may eventually lead to a globally valid model, which use will reduce the overall number of batches necessary for convergence.

Batch-to-batch feedback control was implemented using a surrogate of a real semi-batch emulsion polymerisation process. A true validation of the control strategy should be carried out implementing the optimal trajectories on a real experimental facility. Eventually the number of batch needed for convergence to the optimal final recipe would be larger compared to those needed using a surrogate to the actual process. Still, a larger number of PSD measurements for each batch, and also other data such as latex density measurements, could be combined together and used for model update. This would result in a faster convergence to the optimal recipe.

The careful formulation of the optimisation method should be combined with a state estimation strategy for the computation of the unavailable states and a feedback control scheme to account for parametric and structural uncertainties of the model, and unavoidable disturbances such as measurement noise and experimental uncertainties. Whenever the system is in-batch feedback controllable, a combination of the batch-to-batch and in-batch feedback strategies can be implemented. A carefully designed open-loop strategy for input generation, combined with further studies on the in-batch feedback controllability of the process and a robust state estimation strategy, could be used to build a reliable and efficient advanced control strategy of the type of MPC.

MPC and other advanced control strategies are able to perform on-line parameter identification and update the model while controlling the process, so to have a progressive enhancement of the real system reproduction by the model. Thus, if there is a variation in any of the parameter values, the controller will adjust itself consequently to ensure the correct performance. A crucial aid for MPC can be the knowledge-based formulation of the objective function, which would facilitate the identification of (*sub*-)optimal feedback control actions.

List of Publications and Presentations

Refereed journal publications:

Immanuel, C. D., Wang, Y., Bianco, N., 2008. Feedback controllability assessment and control of particle size distribution in emulsion polymerisation. Chemical Engineering Science 63, 1205-1216.

Refereed conference proceedings:

Bianco, N., Immanuel, C. D., 2006a. Modeling and control considerations for particle populations in particulate processes within a multi-scale framework. In: Gorban, A. N., Kazantzis, N., Kevrekidis, I. G., Öttinger, H. C., Theodoropoulos, C. (Eds), Model Reduction and Coarse-Graining Approaches for Multiscale Phenomena. Springer-Verlag, Berlin, pp. 443-464. Oral presentation, 2005, Leicester, UK.

Bianco, N., Immanuel, C. D., 2006b. Optimal open-loop generation for particle size distribution control in semi-batch emulsion polymerisation. In: Bogle, I. D. L., Žilinskas, J., (Eds), Computer Aided Methods in Optimal Design and Operations. World Scientific, Singapore, pp. 99-108. Oral presentation, Optimal Process Design - International Networking for Young Scientists, 2006, Vilnius, Lithuania.

Conference presentations:

Bianco, N., Immanuel, C. D., 2007. Optimal control of particle size distribution in semi-batch emulsion polymerisation: recipe optimisation and experimental validation. Oral presentation. AIChE Annual Meeting, Salt Lake City, USA.

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