STUDY OF BATCH EMULSION POLYMERIZATION OF PMMA: MODELING AND CONTROL

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(Parul Arora)

ABSTRACT

Emulsion polymerization involves nucleation and growth of particle nuclei, followed by consumption of residual monomer in a heterogeneous reaction system. The propagation reaction of free radicals with monomer molecules takes place primarily in the latex particles and the emulsified monomer droplets only serve as a reservoir to supply the growing particles with monomer. Polymerization in non-uniform latex particles is a potential candidate for offering various application properties. Emulsion polymerization has huge application in industries of textile, paint and pharmaceutical.

Only a small number of industries uses large scale batch reactor for production of polymer. However, from batch emulsion polymerization reactor, we can produce narrower distribution of particles, higher molecular weight and can get higher rate of polymerization as compared to that of semi-batch and continuous reactor.

To study the end-use properties of the polymer we developed models for molecular weight distribution and particle size distribution. The moment equations are utilized to find molecular weight distribution, and average molecular weight. The model for the particle size distribution is taken from literature (Crowley, Meadows et al. 2000). Zero-one model was selected for the study, the particles are assumed to contain either one or zero radical. In such a system, the average number of radicals per particle cannot exceed 0.5. Termination occurs only between an entering radical and a growing radical.

Batch reactor was used for the experiments in the laboratory. The experiments were carried out in a reaction vessel maintained at 70ºC. The reactor contents were agitated using impeller at 750 rpm. The impeller was connected to a variable speed motor, thus allowing changing the speed of the agitator. Vessel contains the thermocouple to monitor the temperature of the reaction mixture with on/off control system. Prior to start the reaction, the reactor was purge with nitrogen gas to dissipate the oxygen, if present. A nitrogen blanket was maintained throughout the reaction. A reliable apparatus Malvern Mastersizer 2000E was used to study particle size

distribution and monomer droplets size. The system operates on scattering pattern of light. Samples are added to the unit and circulated after sonication, distilled water was used as dispersant. Different concentrations of monomer, initiator and surfactant were used in analysis for particle size distribution and molecular weight.

As the polymerization reactors are exothermic and reactor thermal runaways can occur, effective control strategies have to be implemented. Here, we have made an attempt to develop three control systems for batch reactor viz. PID, MPC and NNPC.

A simulink model was developed for batch reactor using PMMA for the study. In this study, two different strategies were used for PID to control the temperature of the reactor. First PID controller used split range and second PID uses heater power as manipulative variable. We, further, pursue with model predictive control and neural network control. The molecular weight and PSD of the polymer are the most important elements to the properties of the product. However it is difficult to measure the molecular weight or PSD in real time. Therefore, the control of the molecular weight and PSD is often carried out by controlling the reaction temperature.

To make the quantitative comparison of the controllers, performance criteria for good control action were applied. These are the integral of time weighted absolute error (ITAE), integral of the square of the error (ISE), the integral of the absolute of the error. This helped in obtaining insights on aspects of simulation. All the criteria were analysed carefully and the model validation was done with experimental data. Nitrogen gas is used during the process, as the viscosity increases probability of entrapment of gas bubbles increases. A model is introduced in this work and simulated using MATLAB.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A_H	Heat transfer area	[m2]
ai	Diameter of bubble	[m]
C(s)	The controller transfer function	-
C_j	Heat capacity of water	[kJ/kg ^{0}K]
C_{polym}	Density of polymer in polymer-monomer Mixture	[kg m^{-3}]
d_0,d_1,d_2	Paremeter in the viscosity correlation	-
Dw	Diffusivity of monomer radicals in water	-
Dw/i $_{1/2}$	Corresponding diffusivity of a radical in water with I monomer reapeating unit	-
e	The control error	-
E	Uncharged monomer radicals	-
f	Factor efficiency of initiator	-
F_{hot} and F_{cold}	Flow rate of the hot and cold streams	[kg/s]
h_c	Enthalpy of liquid cooled	[kJ/kg]
H_s	Enthalpy of incoming hot water	[kJ/kg]
ΔH	Heat of Polymerization	[J/kmol]
I	Initiator	[moles/l]
[IM_i]	ith numer of monomer in growing radical	-
k_d	Decomposition rate constant for initiator	[per min]
k_p	Rate of propagation	[l/mol min]
k_t	Rate of termination	[l/mol min]
M	Monomer	[moles/l]
M_0	Molecular weight of monomer	[g/mol]
n_0(r)	Population containing zero radical	-
n_1^p	Polymer radicals which would not diffuse out from the particles due to large size.	-
n_1^m	Population containing one radical.	-
N_A	Avogadro's Number	[6.0221x 10^{23}]
N_p	Number of polymer particles	-

p_0-p_5	Entrapment function parameters	-
Q	Heat transfer rate	-
R	Initiator Radical	-
$R[\eta, a_i]$	Emperical entrapment function	[Number of bubbles^{-1} –time $^{-1}$]
R_p	Rate of polymerization	[g/l- min]
(s)	The overall process transfer function.	-
T_j	Temperature of cooling water in jacket	[^{0}K]
Tj0	Inlet cooling water temperature	[^{0}K]
u	The controller output	-
$\bar{u}$	Bias value	-
$u_{x,t}$	Dead polymer chains	-
U	Overall heat transfer coefficient	[w/m2-k]
U_j	Internal energy of hot water in jacket	[kJ/kg]
V	Volume of the reaction mixture	[l]
V_j	Jacket volume	[l]
W_{fo}	Initial weight fraction of monomer	[gm/mol]
W_M	Weight of monomer taken	[gm]
W_T	Total weight of reaction mixture	[gm/mol]
y_{sp}	The set-point of the controlled variable	-
y_d	The disturbance signal	-
y	The response signal of the controlled variable	-

Greek Letters

$\delta(r- r_{nuc})$	Nucleation of particle	-
η	Viscosity of polymer solution	[Pa.s]
η_0	Viscosity of solvent	[Pa.s]
ρ	Density	[g/cm^3]
ρ_j	Density of water	[gm/cm^3]
ϵ	Expansion factor of volume	-
$\lambda_{x,t}$	Live polymer chains	

ABBREVIATIONS

PMMA : Polymethyl methacrylate

PSD : Particle size distribution

MWD : Molecular weight distribution

CCD : Co-polymer composition

SLD : Sequence length distribution

LCB : Long chain branching

SCB : Short chain branching

LIST OF PUBLICATION

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- Arora,P., Jain,R., Mathur,K., Sharma,A., Gupta,A.(2010), “ Synthesis of poly (methyl methacrylate) by batch emulsion polymerization”. *African Journal of Pure and Applied Chemistry*. 4(8), p. 151-157.
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Research paper Communicated in International Journal

- Arora, P., Gupta, A.” Model predictive control and PID controller to control molecular weight in batch emulsion polymerization: A comparative study”, *Submitted in Asian Journal of Control*.
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Conferences

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Chapter -1
Introduction

1. INTRODUCTION

1.1 Emulsion Polymerization

Emulsion polymerization could be explained mathematically by using particle number, volume, chain length and number of radicals. Smith and Ewart (1948) were the first who gave the population balance equation, which describes the complete particle balance in the system followed by Katz and his co-workers (Katz et al. 1969) who solves the population balance equation. These population balance equations are used to predict the behaviour of the particle size and their distribution. Immense research has been done on the subject of emulsion polymerization. Emulsion polymerization has immense application in contemporary industries like textile, paint industries used in producing stiffening agents, binders, binders for pigments, bonding agent, synthetic rubbers, adhesives, sealants, trade paints, industrial coatings, printing inks, thermoplastics, toners, immunoassay and drug delivery in pharmaceutical industries.

Emulsion polymerization has a nature gain over others. These are: safe, faster and easy to control because of the colloidal nature and in some cases product can be used without further separation. Additionally, they have less thermal and less physical problems in contrast to other processes like bulk polymerization. Along with physical gain there is a kinetic lead also, that is emulsion polymerization is the only process where relationship between molecular weight and rate of polymerization is not inverse like other processes. Emulsion polymerization facilitates change in molecular weight without altering rate of polymerization by adding chain transfer agents. From literature, it is clear that emulsion polymerization is an important field and it is worthy to pursue further research and development.

Emulsion polymerization brings into play water as a solvent, which enable the process to be very swift, excellent heat transfer and enhances the control of heat of reaction, this aqueous phase bring down the viscosity of the emulsion.

Water based polymerization has vast significance in industry as it endows an environmental friendly process, removes the reaction heat easily during polymerization and enables feasible handling of the final product.

Research in controlled/free radical polymerization has increased significantly during the past two decades. Arora and co-workers synthesised the poly-methyl methacrylate by batch emulsion polymerization and also compared their results with mathematical model solved by computer programming in C. (Arora et al. 2010).

Chern (2006; 2008) reviewed emulsion polymerization mechanisms and kinetics. Polymerization process engrosses the propagation reaction of free radicals with monomer molecules in a hefty number of discrete polymer particles distributed in the continuous aqueous phase. The nucleation and growth of latex particles actually controls the colloidal and physical properties of latex products. Emulsion polymerization involves nucleation and growth of particle nuclei, followed by consumption of residual monomer in a heterogeneous reaction system. This propagation reaction of monomer molecules takes place primarily in the latex particles; emulsified monomer droplets only serve as a reservoir to supply the growing particles with monomer. Polymerization in these non-uniform latex particles enhances various application properties of the product. The interfacial tension between polymer pairs and the particle–water performs an eminent role in the development of particle morphology.

1.1.1 Modelling and Control

Tools and technologies for process modelling of the polymer process extended in excess of past 30 years. A short time ago polymer industries have hurriedly and profitably adopted polymer process modelling technology.

Control means “regulation the operation in such a tactic as to certify a desire outcome.” Online control of emulsion polymerization reactor is vital in order to optimize the productivity (Ramagnoli et al. 2006).

It was found in literature that, emulsion is the only process which gives 100% conversion but practically we must use a control scheme. Extensive literature is present on offline control of emulsion polymerization; during last few years inferential control of emulsion polymerization gained researcher’s curiosity.

In polymerization processes, the end-use properties are currently controlled directly or indirectly by controlling the molecular properties. A fact well accepted is that the behaviour of the majority of the chemical processes is best described by nonlinear models. Despite this reality, linear controllers still dominate in process industries.

For purposes of product quality control, safety, and overall economic operation, it is necessary to monitor polymerization conversion and temperature. Obviously, these goals are difficult to achieve without efficient and reliable on-line measurement techniques.

In last twenty years, very accurate off-line techniques/apparatus for the characterization of polymer quality have been developed. For example, molecular weight distributions (MWD) can be determined by NMR techniques and gel-permeation chromatography (GPC). These are used to calculate the composition distribution of polymers. However, there are relatively few on-line sensors available, especially for emulsion polymerization systems. Currently, most major difficulties in on-line sensor technology arise from the complex nature of these systems, and sensor development requires a multidisciplinary effort.

The most common controllers are the feedback type that receive sensor signals and send a proportional signal to the controlling element which executes the action. This Computer control approaches have been used to control the emulsion polymerisation. These depend on mathematical models of the emulsion polymerisation process. Statistical process control is supplementary frequently used in emulsion polymerisation.

Polymerization processes are decidedly non-linear, therefore use of linear controller for the non-linear model results in inadequate performance. A good number of chemical process systems are non-linear. Some are only slightly non-linear and can be analyzed and controlled effectively with linear techniques; and others are highly non-linear so that some form of non-linear control is desirable. A polymerization reactor is highly non-linear due to the heat of reaction [highly exothermic] and the complex reaction networks.

It is found that (Attarakih 2013) Population Balance Equations are a promising tool for modeling of various important facets of emulsion polymerization, including Particle Size Distribution and molecular weight distribution. Advances in computational power and the development of numerical algorithms, coupled with progress of modeling emulsion stability will make PBEs omnipresent tools for the modeling of Emulsion Polymerization in the near future.

The most significant variables, those which have an effect on end-use properties of the polymer and are necessary to control namely molecular weight, MWD, particle size, conversion, composition, PSD and temperature, are reported in this study.

1.1.2 Evolution of Distributions

Water borne polymerization such as emulsion polymerization is of enormous significance in industry as it is an environmental friendly process. Removal of reaction heat is easy during polymerization and feasible handling. Research in controlled/free radical polymerization has increased significantly during the past decades.

It should be noted that a thermodynamic analysis gives the ultimate particle morphology (when the aging time approaches infinity). Nevertheless, this is generally not the case because other physicochemical parameters and polymerization conditions also come into play in determining the particle morphology (Chern 2008).

Emulsion polymerization is essentially a process in which an aqueous dispersion of a sparingly soluble monomer or a mixture of monomers is converted into a stable dispersion of polymer particles (Friis et al. 1973).

Chern and his co-workers (2000) concluded that the probability of capturing free radicals by micelles decreases with increasing number of micelles per unit of volume of water. Thus higher the concentration of micelles the smaller will be fraction of micelles which can be successfully converted into latex particles. As a matter of fact Chern claims about 85% of latex particles originate from homogeneous nucleation for the polymerization system with surfactant concentration 10 mM. The concentration of latex particles originating from homogeneous nucleation increases with increasing surfactant concentration. This is due to the fact that micelles do not contribute in the formation of latex particles; they only serve as a reservoir to provide the growing latex particles. Waterborne free radicals first polymerize with monomer molecules dissolved in the continuous aqueous phase and then these oligomeric-radicals become hydrophobic in nature.

After propagation, when a desired chain length is achieved by the oligomeric-radical, they become hydrophobic, and start showing a strong tendency nature to enter the monomer-swollen micelles and continue to propagate by reacting with those monomer molecules present in the micelle. As a result, monomer-swollen micelles are successfully transformed into particle nuclei. These embryos continue to grow by acquiring the reactant species from monomer droplets and monomer-swollen micelles. In order to maintain proper colloidal stability of the growing particle nuclei, micelles that do not contribute to particle nucleation dismantle to supply the demand for surfactant. The Smith–Ewart theory formulated that the number of particles nucleated per unit volume of water (Np) is proportional to the surfactant and initiator concentration to the 0.6 and 0.4 powers, respectively (Odian 2004).

The majority of monomer is consumed in this particle growth stage within 60% monomer conversion. The particle growth stage (Interval II) ends when monomer droplets completely disappear in the polymerization system. Smith–Ewart case-2 kinetics has been used to calculate the rate of polymerization.

$$Rp = k_p \ [M]p \ (n\ Np/NA)$$

Where propagation rate constant is k_p, [M]p is the concentration of monomer in the particles, average number of free radicals per particle is denoted by n, and NA the Avogadro number which is a universal constant, Np is the number of polymer particles. .

This kinetic model was developed based on the following assumptions:

(1) Coagulation of particles does not occur and the number of particles per unit volume during the process remains constant. .

(2) Monodispersed particle size distribution.

(3) Neglect Desorption of free radicals from the particles.

(4) Bimolecular termination of the radical inside the particle after the entry of second oligomeric radical from the aqueous phase is instantaneous.

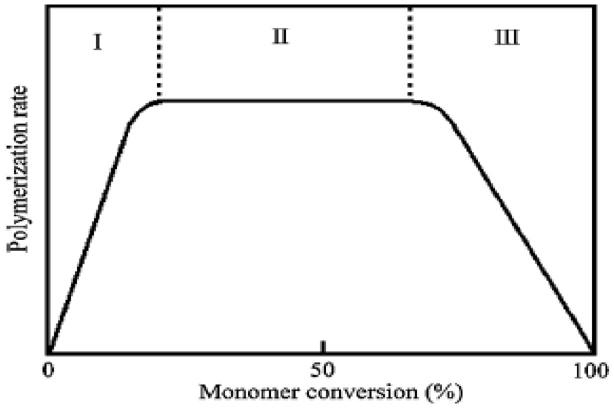


Fig. 1.1: Rate of polymerization as a function of monomer conversion.

The most important parameter that controls the particle nucleation process is the surfactant concentration. The particle nucleation period is relatively short (up to about 10–20% monomer conversion), depends on the initiator concentration controls the particle size and particle size distribution of latex products.

1.2 Molecular weight distribution in Emulsion Polymerization

Available literature(Ando et al. 1996) is evidence that low molecular weight material boosts the ease of polymer processing. Vigorous molecular mass control is therefore a key issue in polymer production. On the whole, literature reported that techniques available were not accurate or robust enough for implementation in the process industry. Further, most control strategies developed have been based either on the simulations study or on extensive experimental effort. To overcome this challenge, various online methods have been developed to estimate relevant process variables.

The mechanical properties of any polymer depend on their chemical structure, molecular weight and its distribution. Increase in chain length increases toughness, creep resistance and melt temperature. Higher molecular weight of polymers increases the tensile strength. When we talk about molecular weight distribution, which can be either a broad or a narrow, which is the calculation of molecular weights of the largest and smallest polymer molecules, but these polymer could have the same average. Broader molecular weight distribution means that there are more molecules with differing molecular weights, where as narrow molecular weight distribution means that there are a higher range of molecules of similar length and weight (Altarawneh 2008).

1.3 Particle size distribution in Emulsion Polymerization

In emulsion polymerization, the polymer particles are in large colloidal size range. Particle size distribution (PSD) is strongly correlated with the end product properties of the emulsion. It influences the rheological properties, adhesion and film-forming properties of the final products: adhesives, coatings, emulsion paints, etc. There is a rich literature on modeling of emulsion polymerization processes, starting with the conventional Smith–Ewart model of the late 1940’s.

Emulsion polymerization can be carried out in batch, semi-batch and continuous reactor. Model identification methodology for batch processes is still an unexplored area and needs to be addressed.

There is a unique relationship between PSD and rheology, narrow distribution favours high value of rheology property; thus a process model and a rheology model will be needed in the identification of the PSD target.

Once the PSD that would lead to the desired rheology is identified, the rheology can be achieved by inferential control towards this target PSD.

In emulsion polymerization final latex properties are largely determined by the particle size distribution (PSD) and particle size; therefore, PSD control is a key process objective. For industrial application, a specified final PSD should achieve by following a specified recipe. Feed-back control of easily measured variables, such as temperature, pressure and conversion ensures that the recipe is consistently implemented, but feedback control of PSD is rarely done. One reason may be, until recently, it was difficult to measure the full distribution on-line. Another reason stems from the distributed nature of polymer and the structure of models describing this system.

1.4 This work : Motivation and Outlines

The motivation for this study is the industrial application of batch emulsion reactor. Only few industries use large scale batch reactor for production of polymer because batch reactor has severe problems in controlling the reaction temperature, since free radical emulsion polymerization is highly exothermic reaction and the heat transfer capacity is very limited due to surface to volume ratio and also lack of steady state condition. But from batch emulsion polymerization reactor we can produce narrower distribution of particle size and can get highest rate of polymerization along with high molecular weight than semi-batch and continuous reactor. Second reason is a plenty of work on control of bulk, solution free radical batch polymerization is available in literature but for batch free radical emulsion polymerization little or no literature is present till now. In this study we have tried to design effective and robust control system for batch emulsion polymerization reactor.

The objectives of this research work are:

- To develop a dynamic model for the reactor, Particle size distribution and Molecular weight distribution.
- To study the synthesis of PMMA with different concentrations of initiator, emulsifier and monomer.
- To study the effect of concentration of monomer, initiator and emulsifier on the particle size distribution and molecular weight.
- To implement the advance control methodology for batch reactor using PID, MPC and NNPC to maintain particle size distribution in narrow range with bimodal distribution so that larger portion of polymer has similar particle size and controls the molecular weight to a specific value.
- Validate the experimental results with simulated results.

The core objective of this study is to control the end use properties (particle size distribution and molecular weight) of the final polymer product. For this, a robust control system is required, because the particle size distribution strongly affects the rheological properties and molecular weight affects the thermal, physical and mechanical properties of the final latex product (Kiparissides 2004). Bimodal particle size distribution allows increasing the solid content with low viscosity as compared to mono-modal distribution, and this is specified end-use properties for Paint and adhesives industries (Arevalillo et al. 2006; Krieger et al. 1959; Luckham et al. 1999; Mooney 1951; Silva et al. 2012; Sudduth 1993). Rheological property value increases with narrow distribution. Narrow distribution of polymer is designed mainly for paint industries, especially for methyl methacrylate and its co-polymers; smaller particles also favour the fast rate of film formation. A latex product with smaller particle size shows better colloidal stability because the colloidal stability of the particle is proportional to the particle size to the third power. Narrow distribution of particle size means that larger portion of the polymer particles are of same or nearly same size, where as broader distribution means large variation in size.

It is a well known fact that rate of polymerization increases with increasing temperature. With increase in temperature after a certain temperature, the size of the particle decreases. This inverse dependence between the particle size and the polymerization temperature is due to the increasing decomposition rate of the initiator with increasing monomer solubility in the aqueous phase, which increase the concentration of growing chains and, thus, reduce the latex size. It is given in literature (Tanrisever et al. 1996) that an opposite effect of the polymerization temperature on the latex size may also be expected in MMA polymerization. Rise in temperature is accompanied by narrower particle size distribution, and polymerization at higher temperature gives relatively narrow molecular weight distributions. Polydispersity index approaches 1.4 with increasing temperature. However, as the temperature decreases, molecular weight distribution of polymers becomes broader.

At high molecular weight [order of 10^5 g/mol], the polymer chains become entangled enough to show actual rubbery behaviour. Tensile strength and elongation of polymer is very good with high molecular weight. Broader particle size distribution would necessarily lead to the formation of polymers having broad molecular weight distribution. Broader PSD gives higher weight average molecular weight of polymer. Hence, we use temperature as controlled variable to control the particle size in narrow distribution and molecular weight at the specific value of 12,000 g/mol of the latex particle.

Mathematical modelling is a powerful tool not only for the development of process understanding, but also for the design strategy of advanced process control. As polymerization reactions are exothermic in nature and reactor thermal runaways can occur, thus, to prevent the system from thermal runaway effective control strategies have to be implemented. Another challenge is that online measurements of end use property for example molecular weights, composition, degree of branching and particle size distribution are not always available; this will make control more complicated and difficult. A control system for a polymerization reactor should be robust to handle unmeasured disturbance which impacts on the process of the polymer. The variability within batch reactor and variability from batch to batch is also a challenge when the control setup is decided. It is required to develop optimum and robust control strategies to control the end use properties in a batch reactor.

Table 1.1: Relation between characteristics and properties of the polymer

Characteristics	**Properties of polymer**
Narrow particle size distribution	High Rheological properties, High solid content, Fast rate of film formation, better colloidal stability and low viscosity.
High molecular weight	Good rubbery behaviour, good elongation, good tensile strength, good mechanical strength.

1.5 Thesis Contribution

- Developed a comprehensive mathematical model accounting for molecular weight and particle size distribution of free radical emulsion polymerization. This model was validated against experimental results and found to be capable of accurately predicting PSD, MWD.

- Investigating the effect of changing concentration of monomer, initiator and surfactant on the polymer key properties.
- The dynamic model is used for model based control structure of batch reactor for PSD and MWD.
- Based on this investigation, the manipulating variables that had a significant effect on the MWD, and PSD were determined and their effects were quantified.
- Applied successfully three different controls (namely PID, MPC, and NNPC) on the batch reactor without steady state condition.
- Able to control the narrow particle size distribution with the help of advance controller.
- Efficently control the molecular weight of the polymer at its specific value by using advance controller.

1.6 Outline of Thesis

This thesis is organized as follows:

Chapter 2 gives the literature review and important characteristics of the process, and gives an overview of some significant contributions in the emulsion polymerization, modeling and control of the batch emulsion polymerization.

Chapter 3 is divided into three sections; in first section we discuss kinetics of batch emulsion polymerization, in second section modeling of molecular weight is discussed and in the last section modeling of particle size distribution is detailed. Bubble entrapment function is introduced new in this chapter.

In chapter 4 experimental and control strategies for both particle size distribution and molecular weight distribution are explained. The encountered difficulties are also discussed in this chapter. After explanation of experimental setup three control strategies are discussed for both the models namely PID, MPC, NNPC. Control strategies, control design along with parameter tuning are detailed later.

All the experimental results are collected in chapter 5, simulation results for particle size distribution in chapter 6 and molecular weight distribution for batch emulsion polymerization and bubble entrapment function are discussed in chapter 7. The PMMA system is used for this study.

Last chapter of this thesis contains the conclusion of the work and gives future directions.

Chapter -2

Literature Review

2. LITERATURE REVIEW

Emulsion polymerization allows the production of polymer particles with special properties, including composition, morphology, molecular weight and particle size; and functional groups can also be incorporated to the polymer particle. Different types of polymer latex have been formulated to provide the desired properties without copolymerisation (Fream et al. 2000; 2000).

In polymerization the rate of polymerisation (*R*p) is inversely proportional to the molecular weight. Large numbers of radicals produce a high polymerisation rate and also result in the formation of low molecular weight polymer. However, in emulsion polymerisation, the rate of polymerisation and the molecular weight can be simultaneously high as a result of compartmentalisation within polymerising particles. These advantages are the most fascinating features of the emulsion polymerization.

Additionally low viscosity of latex allows a high rate of heat transfer during polymerisation (Hangquan et al. 1999).

2.1 Historical Perspective

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating monomer, water and surfactant. The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with surfactants) in a continuous phase of water.

The German chemist Fittig and Paul discovered the polymerization process in 1877 that turns Methyl Methacrylate into poly Methyl Methacrylate. The idea of using an emulsified monomer in an aqueous suspension or emulsion was first conceived by workers at Bayer, before World War I, in an attempt to prepare synthetic rubber. During 1920’s the first emulsion polymerization product was used as a surface-active agent and polymerization initiator. Over the next twenty years after the end of World War II, more efficient methods for the production of many forms of synthetic rubber by emulsion polymerization were developed; some historical events are tabulated in Table 2.1.

Table 2.1: History of emulsion polymerization

Time line	Innovation
1843	First acrylic acid was created.
1865	Methacrylic acid was formulated
1877	Fittig and Paul discovered the polymerization process produced polymethyl methacrylate.
1933	German chemist Otto R"ohm patented the PMMA as brand name PLEXIGLAS(R).
1936	The first commercial production of PMMA, production of safety glass began.
1947	Biocompatibility and inertness of polymethyl methacrylate has been well accepted.
1949	Contact lenses were made from a hard plastic (polymethyl methacrylate)
1952	Oct 28 latex dewatering process is disclosed in US.
1966	Dec 27, emulsion polymerized polydiorganosiloxane and its method of manufacture is introduced
1975	Lehigh's EPI, carried out research into the preparation, properties, characterization and applications of latex polymers
1998	Bone Cement was submitted to the FDA for orthopedic applications made from PMMA
2003	Bovine collagen and microscopic plastic spheres made

To induce emulsion polymerization process water-soluble initiator is usually added. Polymerization is induced by radicals forming in the water phase and diffusing to the emulsion phase, where the polymerization starts.

Batch emulsion polymerization is usually represented through following three intervals as, first proposed by Harkins (1947).

Interval I

At the beginning of the reaction, the system contains monomer droplets suspended in the continuous water phase and stabilized by the surfactant then the initiator is charged to the reactor. However, if enough surfactant has been added above the CMC value, other entity also present in the system called micelles, made up of surfactant molecules which dispose themselves with the hydrophilic part towards the water and the hydrophobic part inside. When a water-soluble initiator is introduced, the radical species formed in the water phase enter preferentially the micelles rather than the monomer droplets. Thus, many of the micelles are converted into polymer particles, and are nourished by the monomer diffusing from the monomer droplets.

After some time the micelles disappear completely, at this point interval I ('nucleation stage') is over; the birth of new polymer particles stops and the polymerization carries on inside a constant number of polymer particles.

Interval II

In the second interval polymerization proceeds with a constant number of polymer particles which are swollen by the monomer diffusing from the droplets through the water phase. As long as the monomer droplets exist, the system is in saturation condition. As the polymerization proceeds, the monomer droplets decrease in size and eventually disappear. At this point interval II is over.

Interval III

This is the final stage. The polymerization ends when the monomer is completely depleted. Finally the latex particle is available for further use.

In emulsion polymerization, the reaction takes place in the polymer particles rather than in the much larger monomer droplets.

All most all chemical process systems are non-linear. Some are only slightly non-linear and so can be analysed and controlled effectively with linear techniques and for others non-linear that some forms of non-linear control may be desirable. A polymerization reactor tends to be non-linear due to the heat of reaction [highly exothermic] and the complex reaction networks control the batch polymerization reactor.

For the purposes of temperature and product quality control, safety, and overall economic operation, it is necessary to monitor polymerization conversion.

Obviously, these goals are difficult, but not impossible to achieve with efficient and reliable on-line measurement techniques. In the last twenty years, very accurate off-line techniques for the characterization of polymer quality have been developed. For example, molecular weight distributions (MWD) can be determined by gel-permeation chromatography (GPC), and NMR techniques are used to calculate the composition distribution of copolymers. However, the development and use of on-line sensors, which are required for any feedback control of polymerization processes, have remained rather static. There are still relatively few on-line sensors available, especially for emulsion polymerization systems, where the presence of more than one phase leads to serious complications. Currently, most major difficulties in on-line sensor technology arise from the complex nature of these chemical systems, and sensor development requires a multidisciplinary effort.

A negative aspect of emulsion polymerization is that surfactant used in emulsion polymerization cause undesirable characteristics in the final product. For instance, they are often difficult to remove from the latex, and if removed, may cause destabilization and enhanced coagulation. Furthermore, films produced by the latex product have poor weather durability and water resistance as the small surfactant molecules have a tendency to migrate with time. Particle size distributions can also be rather broad a result of secondary nucleation in systems containing surfactants. Finally, surfactant released into the environment may have serious consequences for subsequent biological processes(Dobie et al. 2010).

2.2 Modeling and Control

Several sensors have been developed over the years for offline monitoring of process/product attributes (conversion, composition, molecular weight, particle size, etc.) of polymers. Emulsion polymerization is often monitored using gravimetry, Dilatometry and gas chromatography (GC).With gravimetric and GC analyses, handling of samples requires special care.

These techniques are limited in accuracy and in the extent of data obtainable. Online sensors such as densitometers require a sampling device and an auxiliary recirculating loop. These present difficulties such as coagulation of polymer particles within the device and in the circulating loop, sensitivity to polymer viscosity and requirements of extensive in situ calibration. These techniques are often implemented offline, resulting in considerable measurement delay, undesirable for real-time control. Thus, most reported techniques were not accurate or robust enough for implementation in industry. Further, most control strategies developed have been open- loop, based on simulations only or on extensive experimental effort. To overcome the challenges mentioned above, various online methods have been developed to estimate relevant process variables.

Chistofides and Daoutidis (1996) describes first-order hyperbolic partial differential equations (PDEs), for which the input, controlled output and the measured output are distributed in space. A general feedback control methodology was developed employing a combination of theory of PDE’s and concepts from geometric control. Concept of characteristic index was introduced and used for the synthesis of distributed state-feedback laws that guarantee output tracking in the closed-loop system. Analytical algorithms of distributed output-feedback controllers were derived through combination of appropriate state observers with state-feedback controllers. The developed control methodology was implemented on a non-isothermal plug-flow reactor and its performance was evaluated through simulations. A novel model (Kwang S. Lee 1999; Lee et al. 1999) predictive control technique geared specifically toward batch process applications was demonstrated in an experimental batch reactor system for temperature tracking control. The technique, called Batch-MPC (BMPC) is based on a time-varying linear system model representing a nonlinear system along a fixed trajectory and utilizes not only the incoming measurements from the running batch, but also from the past batch histories. In a series of experiments performed on a batch reactor system, the technique was found to give satisfactory performance, by overcoming a large amount of model uncertainty and various process disturbances.

Most research efforts in batch process control have therefore been dedicated to the problem of designing a feedback controller that can compensate for strong effects of nonlinearity. Nonlinear cascade control(Marroquin 1972), successive linearization-based control (Lee et al. 1999) , generic model control and its variants

(Cott B. J. 1989),feedback linearization (Soroush 1992), adaptive MPC (Jarupintusophon 1994) , non linear MPC (Nagy et al. 2003) and adaptive control (Cabassud M. et al. 1989 .),are some of the approaches by which problems have been solved by gain-scheduling the PID control parameters, sometimes with appropriate feed-forward compensations, such as those for the heat of reaction inferred from a calorimetric balance (Juba 1986)(Dimitratos 1994).

On-line sensors for emulsion polymerization are more difficult to develop, due to the thermodynamically unstable nature of the latex particles (Chien 1990). Consequently, most of the control strategies developed in the last two decades have been open-loop, based on mathematical models of the process or on extensive experimental work (Broadhead 1985) ,(Hamielec 1987).

Mutha et al. (1997) presented an experimental evaluation of a non-linear model-based estimator and predictive control strategy on a continuous MMA solution polymerization reactor. The proposed estimator was successfully implemented for both single-rate and multi-rate measurements.

A model-predictive software sensor was developed for on-line estimation of monomer conversion and average molecular weight during bulk polymerization of systems exhibiting a gel effect. The temperature and viscosity of the reaction are the measured secondary variables, which allow the state of the system to be estimated. Manker et.al modified the viscometer assembly to measure the viscosity of the reaction mass during bulk polymerization of methyl methacrylate (MMA) at temperatures higher than those reported in paper (Manker et al. 1999),(Mankar et al. 1998). Further Manker et all have developed a viscometer-reactor assembly The viscosity of the polymerizing mixture has been measured continuously at two different temperatures (isothermal) and initiator concentration. Samples have also been taken out at several different times and analysed for monomer conversion and the weight-average molecular weight. The data taken have been fitted using the Martin equation with KM treated as an empirical parameter this was the first attempt in the open literature to measure the viscosity of a polymerizing mixture during bulk polymerization.

Fevotte et al. merged off-line and on-line measurements, with the on-line measurements being used in the kinetic and process models to estimate the current state of the reaction such as copolymer composition distribution. Techniques used by them are of great potential use in the control of industrial processes, and are merely possible using process computers. (Fevotte et al. 1996).

To control the polymerization reactors every single system should be sorted: those are to be controlled or those which may be manipulated to get controlled and very last disturbances whether measured or unmeasured.

There are fundamentally two levels of control for batch processes. The elevated level control is the control of final product quality at the end of the batch. The subordinate level control is the set-point tracking of certain process variable trajectories. Several approaches to both these control problems have been proposed and applied. The product quality is usually only measured off-line in a quality control lab after completion of the batch nowadays online measurement is expected to control the whole process at craving point.

2.2.1 Control of Particle Size Distribution

Particle size distribution (PSD) in emulsion is also an important factor in determining the end-use properties of the latex product, for example a narrow PSD is required for a glossy finish to latex paints. Smaller particles are generally very stable and have useful process advantages such as faster reaction kinetics and more scalable and reproducible preparations: these have useful optical properties (e. g., lower turbidity), higher viscosity, greater surface area, and easier coalescence to form more uniform or thinner films. These properties may be advantageous in typical applications such as adhesives, dispersants, and coatings.

A key first study on PSD control is the controllability analysis by Semino et.al. (1995), this was followed by several contributions to this field. Initially offline optimization was based on the process model to determine the optimal input profiles that give the desired PSD. Then, these obtained input profiles were applied experimentally by assuming perfect process modelling (Crowley et al. 2000).

The modeling of the particle size distribution is a special case of population balance equation (PBE) modeling which plays a crucial role in control of the PSD (Abad et al. 1994; Coen et al. 1998; Min et al. 1974). Several PBE models for different types of emulsion polymerization processes have been developed during the last two decades (Mallikarjunan et al. 2010; Melis et al. 1998; Paquet et al. 1994; Rawlings et al. 1998; Saldivar et al. 1997; Zeaiter et al. 2002).

A batch to batch control strategy was proposed (Flores-Cerillo et al. 2002) by adding an online correction of the surfactant concentration in the middle of the reaction using a prediction of the PSD obtained by partial least square models. Genetic control algorithm , hybrid model based approach (Doyle et al. 2003) were used to predict the control profile to obtain desired PSD (Immanuel et al. 2002).

Modelling of emulsion polymerization processes leads to complex models describing different physical and chemical phenomena. The population balance is very important to describe particle nucleation, coagulation and growth. According to Immanuel (Immanuel et al. 2003) the pseudo-bulk model has a general form and is available for almost all particle sizes during most of the reaction since it has no assumptions on the number of radicals in the particles. The Zero-One model (Gilbert 1995) is adapted only for systems where the number of radicals per particle can be either zero or one and is applicable at the beginning of most reactions where the gel effect is negligible. It distinguishes: particles that have one radical, particle that has zero radicals and those that have an oligomeric radical. Edouard (2003) have proposed a new representation of Zero-one model called bulk like model. The interest of this model is that it describes the number of particles of a specific size independent of number of radicals they contain.

A comprehensive dynamic model for the simulation of limited particle coagulation in emulsion polymerization has been developed (Mayer et al. 1996). They discussed that there is a reasonable agreement between simulations with the dynamic model and experimental data (e.g., conversion time history, particle number, and particle size distribution). The dynamic model can be a useful tool to predict the occurrence of limited particle coagulation and its influence on the polymerization process. Solution of the model equations with a simple first-order Euler integration method (resulting, among other things, in a discrete particle size distribution) has the advantage that the dynamic model can easily be extended with other chemical or physical processes that may be important in emulsion polymerization (e.g., limited particle coagulation). A soap titration method was also used for determining the average latex particle size (Ali et al. 1987).

Alamir and his co-workers applied an iterative learning control of the PSD by proposing a simplified behavioural model to describe the particle size distribution. Besides the correction of the model and control inputs, online measurements (delayed) of the particle size distribution were used in the feedback control (Alamir et al. 2010).

Sahani et al. (2011) developed a model to stimulate the entrapment and growth of vapour bubble in bulk polymerization system. A empirical function is formulated which used five parameters which captures the phenomena of entrapment of vapour bubble.

Ohmura et al (Ohmura et al. 2012) proposed compartment reactor consisting of well mixing compartments. This reactor has advantage that each compartment of the reactor can keep a different non-equilibrium steady-state with respect to each other. An emulsion polymerization was categorized into four function module and these modules were assigned to different compartment. First two modules Contacting and Activation were assigned, and third module chemical reaction and last compartment with particle growth function module. The reactor used by authors was set vertically, and the lower middle and upper compartment named first, second and third respectively. They found use of turbine impeller in compartment gave higher monomer conversion. They stated that strong agitation enhances the reactivity to obtain higher monomer conversion, further more the compartment reactor successfully produced stable and monodisperse particles.

Recently inferential, and a two step MIMO MPC control strategy was used (Immanuel et al. 2008; Silva et al. 2012) for free surfactant concentration (Santos et al. 2007) trajectories, which was pre-calculated offline by model to get bimodal distribution and also to maximize the concentration monomer in the polymer particle by constraining the set-point to its saturation value, monomer and surfactant flow rates were used as manipulative variable.

Recently, Hosseini et al. ((Hosseini et al. 2012)) showed that the standard PBE models of emulsion polymerizations do not predict the broadening of the PSDs that was observed experimentally for the growth dominated in semi-batch emulsion polymerization. Hosseini then proposed two approaches, which were found to be effective in overcoming the limitations of the basic PBE models of emulsion polymerization to describe experimental results (Alireza Hosseini et al. 2013).

2.2.2 Control of Molecular Weight Distribution

The molecular weight (or molar mass) is one of the most important properties of a polymer. It is directly related to the strength of the polymer particle (De Brouwer et al. 2000).A minimum molecular weight of 10^5 g/mol is recommended for sufficient chain entanglement and the resulting film toughness. Broad molecular weight distributions are required for pressure sensitive adhesive applications.

The molecular weight is not uniform throughout the polymer sample, but a distribution of polymer chain lengths is present (Bonfils et al. 2000). The molecular weight distribution is analysed and expressed in terms of averages: the number-average molecular weight (Mn), the weight average molecular weight (Mw), and the viscosity average molecular weight (Mv).

Molecular weight and molecular weight distribution is one of the important end-use properties of the polymer. Early work in this area was carried out first by Katz et. al.(1969). Resulting in a set of partial differential equations from which the MWD theory could be obtained. After that Lichti et al. (1980) improved the work of Katz and others by generating a set of ordinary differential equations that describe the evolution of the number molecular weight distribution by accounting radical entry and exit from polymer particles, bimolecular termination, and chain transfer, Clay and Gilbert adopted the solution of that differential equations (1995).

Often in practice, a single molecular weight average (e.g., viscosity average molecular weight, weight average molecular weight or number molecular weight) is controlled to yield the target polymer properties such as tensile strength, impact strength, etc. Sometimes it is necessary to control the polymer molecular weight distribution (Bersted et al. 1990). The breadth of polymer MWD is measured by the ratio of weight average molecular weight to number average molecular weight (named as polydispersity index). Polydispersity is a useful and convenient measure of polymer molecular weight distribution. It is feasible that polymers of different chain length distribution can have the same polydispersity index but exhibit different end-use properties (Crowley et al. 1997; Schork et al. 1993; Storti et al. 1992).

Zhang and his co-researchers (Zhang et al. 1998) developed stacked neural network which was a combination of multiple neural networks. The individual neural network was trained using different training data sets from different initial weights. They applied the proposed technique to the free radical solution MMA polymerization reactor and found that this technique can accurately predict trajectories of polymer quality variables even in the presence of impurities. They compared the stacked neural network with single neural network model and concluded that stacked neural network model performs much better than single neural network model.

The mathematical model developed by Sayer et al.(2000) was presented in detail with all parameters required for simulation. The model contains a system of coupled differential equations that describe the time evolution of the concentrations of different chemical species, of the average molecular weights and of the MWD (Sayer et al. 2001).

GMC and IMBC controllers were presented by Epko (2008) to successfully track and control the batch solution polymerization reactor operation. Neural network has proved to be accurate and fast on-line dynamic estimators. Matlab toolbox was used for the study. To evaluate the performance of controller test was conducted which shows that effect of disturbance increases heat of polymerization by 25 %. The performance of GMC-NN was found better than the neural based

IMBC controller. IMBC gave lower performance than GMC-NN in robustness test. The lower performance of the IMBC controller highlights its poor extrapolation capabilities.

In neural network, ideally, a large number of data set covering different operating conditions should be used in neural network training. Thus a batch process model should be a non-linear model. A neural network based batch to batch control strategy was proposed by Zhang (2008). Linearization of a stacked neural network model was used in calculating optimal control profile. This method can effectively overcome the problems of model plant mismatches and unknown disturbance.

Thomson et al. were (2010) the first to present the population balance calculations which encompass the complete molecular weight distribution (MWD) to discuss the implications of both radical and catalytic chain transfer agent (CCTA) compartmentalization in a catalytic chain transfer (CCT) mediated emulsion polymerization system. In 2009 ((Lenzi et al. 2005; Smeets et al.) They have been given the theoretical evidence of multimodal MWDs (Lenzi et al. 2005) experimentally.

Recently Tjiam and Gomes (2011) developed an online estimation and monitoring system for conversion and molecular weight in batch and semi-batch emulsion polymerization, conducted with and without CTA. Calorimetric model was used for determining heat of reaction from the temperature profile measurements in the reactor by using heating/cooling circuit.

Table 2.2: Summary of Control of polymerization process.

Controller used	Manipulative variable	Remarks	Reference
PI and PID	Concentration of Initiator and Chain transfer agent	When dynamics is speedy PI controller is able to control well and when dynamics is slow PID controls better	(Rawlings and Ray 1988)
Neural Network with MPC	Feed flow rate	NARX perceptron was modified for better training	(Su et al. 1993)

Controller used	Manipulative variable	Remarks	Reference
NNPC,MPC,PID	Feed flow rate	NNPC works better	(Mauricio et al. 1993)
PI, PID, NMPC	Feed flow rates	NMPC controlled better	(Ogunnaike 1994)
P, PI, PID	Concentration of Initiator, Surfactant	They bring to close that conversion/initiator control and total particle number/ surfactant control are most easily implementable.	(Semino 1995)
Bootstrap re-sampling	Monomer feed rate	MWD	(Zhang et al. 1998)
Non-linear feedback controller	Population balance equation	Controllers cope effectively with model uncertainty and measurement delays.	(Chiu et al. 1999)
On line control using Non-Linear model based controller	Monomer flow rate, Chain transfer agent	Controller significantly control the variables	(Vicente et al. 2001)
NLMPC	Co-monomer ratio and ratio of the overall unreacted monomer	Control strategy allowed the production of linear co-polymer of any composition and MWD.	(Vicente et al. 2001)
Feed forward neural network	Jacket temperature	Controlled temperature of batch reactor	(Kuroda et al. 2002)
NLMPC	Monomer addition rate, CTA addition rate and coolant flow rate	NLMPC reduces the possibility of failing to meet product specification.	(Valappil 2002)
Model based controller	Concentration of monomer, emulsifier, Initiator	They found nucleation growth and coagulation exhibit reversible characteristics.	(Immanuel and Doyle III 2004)
NMPC	Monomer flow rate	They manipulate the concentration of monomer at the same	(Othmana, Fevotte et al. 2004)

Controller used	Manipulative variable	Remarks	Reference
		time able to maintain the polymer composition at the desire value.	
Hybrid Neural network	Feed flow rate	Control reactor temperature	(Ng et al. 2004)
Hybrid neural network	Jacket temperature	Control reactive impurities and reactor fouling	(Tian et al. 2004)
Hybrid forward neural network	Jacket Temperature	Bulk batch process	(Curteanu et al. 2006)
PI	Monomer feed rate, Jacket Temperature	Controller allows to lessening the process time.	(Othman and Othman 2006)
gPROM and computational fluid dynamics	Population balance equation	Found good performance.	(Elgebrandta, Fletchera et al. 2006)
MPC	Heating and Cooling media	Authors realized good control performance for wide temperature range.	(Noguchi and Kobari 2007)
Hybrid neural network	Jacket Temperature	Simulated batch reactor	(Chang et al. 2007)
Stacked neural network	Jacket Temperature	Number average molecular weight and weight average molecular weight	(Zhang 2008)
P controller	Coolant flow rate	Found significant control on reactor temperature	(Singh, Arora et al. 2010)
Online-control	Concentration of CTA	Results harmonized well with experimental results.	(Altarawneh 2009)
Latent variable MPC	Temperature	Found good off set free performance.	(Golshan, MacGregor et al. 2010)
input/output linearization coupled with proportional controller	Jacket temperature and monomer feed flow rate	MWD	(Sheibat-Othman et al. 2011)

Controller used	Manipulative variable	Remarks	Reference
MPC	Monomer and surfactant feed flow rate	PSD	(Silva et al. 2012)
GMC	Feed flow rate	GMC resulted in marginal improvement	(Rani 2012)
NNPC	Heat Input	Effect of initiator, temperature and monomer	(Hosen et al. 2012)

Emulsion polymerisation is a sensitive process, so care should be taken to ensure that the polymerisation is carried out properly. It is desirable to monitor the emulsion polymerisation process on-line (although in practice, online estimation of end-use properties is difficult) (Vieira et al. 2001). The most critical parameters to be considered are the conversion, free surfactant concentration, particle size and molecular weight.

Effective process control (Vogel et al. 1997) is crucial in keeping the production process running safely.

The simplest controllers are the feedback controllers that receive signals and send a proportional signal to actuators. Computer control approaches have been used to control continuous and semi-batch emulsion polymerisations (Liotta et al. 1998). Table 2.2 summarized some papers on application of controllers on the polymerization system.

2.3 Industrial Application

Polymer products are usually not used in their original form, but can be used after post processing with other components to tailor them to their intended applications. Pigments (Erdem et al. 2000) and thickeners (Lapasin et al. 2001) are added to latexes to modify their optical and rheological properties, respectively. Latex coatings provide chemical resistance to the exposed surfaces of industrial equipment, and latex binders enhance stability to fabrics (Wootton 2001). Total of at least 8 million metric tons of dry latex are produced annually. We use PMMA (acrylic polymer) in this case study, so we emphasis here on the industrial application of acrylic polymer.

2.3.1 Paper Coatings

Polymers produced by emulsion are used in paper industry. Acrylic polymers are commonly used as coatings. They are used for improving the strength (wet strength) of the paper (Keim 2000; Yumin et al. 2001), they are also used as binders and fillers for the pigments, it gives colour and opacity with gloss to the paper. These polymers are also used in fibreboard and cardboard (Alince et al. 2000).

2.3.2 Textile

Co-polymers of acrylic are commonly used in textile industries as binders. Softness and toughness of the fabrics are controllers by these binders (Lorenz et al. 1998; Tullo 1999).

2.3.3 Adhesives

Viscous materials are mostly used as adhesives because of their high molecular weight. Polurethane and polyacrylics are used as adhesives. They are crosslinked to improve the strength (Charmeau et al. 1996).

Few uses of acrylic polymers are mentioned above, beside these, there are many more industrial applicaltions of emulsion polymerization printing inks (De Krom et al. 2001), cosmetics industry (Corp. 1999), toughening agents (Hazor et al. 2000), modifiers (Kim et al. 1998; Liucheng et al. 1996), resins and latex foams.

2.4 Issues in control of distribution

In past, researchers treated these processes as lumped processes because

- Lack of Instrumentation to determine distribution attributes of the process
- Deficient in computation tools to deal with the complexity of models.
- Being short of knowledge of the underlying mechanisms.

According to Ray (1986) one of the greatest difficulties in achieving quality control of the polymer product is that the actual customer specifications may be in terms of non-molecular parameters such as tensile strength, crack resistance, temperature stability etc. The quantitative relationship between these product parameters and reactor operating conditions may be the least understood area of polymerization reaction engineering.

Automation control of polymerization reactor is complicated for the following reasons

- Polymerization process are highly non-linear: The use of linear controller often result in poor performance
- Many polymerization systems are open loop unstable; therefore safety considerations are mandatory.
- Polymerization reactor control systems are multivariable in nature. Process interactions, dead time and constraints complicate the control system design.
- Many of the important variables such as molecular weight, molecular weight distribution and Mooney viscosity can’t be measured directly. They must be inferred from other measurements .Inferential measurements lead to erroneous results and therefore automation of control system that is based on such measurements must be designed to accommodate such errors.

There are multiple steady states in polymerization reactors, and this is known both experimentally and theoretically. As polymerization reactors are exothermic and reactor thermal runaways can occur, effective control strategies have to be implemented.

Another challenge is that online measurements of i.e. polymer molecular weight, composition and degree of branching are not always available. We have to rely on polymer properties from laboratory analysis of reactor samples or from analysis of the final product. The control system for a polymerization reactor should be robust to handle unmeasured disturbances which can impact the operation of the polymer reactor.

Chapter-3
Mathematical Modeling

3. MATHEMATICAL MODELING

Emulsion polymerization is a very complex heterogeneous process which involves transport of monomers, free radicals and other molecules between both aqueous and suspended phases. Emulsion polymerization is known to be the most complicated system, compared to suspension, bulk or precipitation polymerization. Developing a fundamental mathematical model for the polymerization reactor is a very challenging task. Models are valuable as they put forward a powerful tool for process control, optimization, and operator training. Models also give a better understanding of underlying mechanisms in the process. Examples are reaction mechanism, physical transport phenomena (e.g. mass and heat transfer and mixing), reactor type and reactor operating conditions that affect the "polymer quality" of the final product.

Polymerization rate in the organic phase is not only controlled by monomer partitioning, but it is also influenced by particle nucleation and radical absorption and desorption, these factors make the modeling very complicated. Particle stability is affected by ionic strength, surfactant type and amount of surfactant in the dispersion media. Other difficulties in modeling of emulsion polymerization are the solution of these nonlinear ordinary differential equations combined with algebraic equations. Lack of information of certain model parameters makes adjustments towards a real process complex.

In literature several models are present which describe different aspects of emulsion polymerization.

The problem is that most of these models deal with specific aspects in emulsion polymerization and are not general models that can readily be utilized for other process conditions and purpose. The objective is therefore to develop a more general model; this model should be simple and cover both physical and chemical phenomena in emulsion polymerization. Models should consist of a set of differential equations combined with algebraic equations, based on mass, energy and population balances.

Typical Assumptions Utilized in Modeling

Different assumptions are utilized when a dynamic mathematical model is derived for a batch emulsion polymerization reactor. Some assumptions are normal to utilize, and some are required to make the model fit its purpose. These are listed below. Other assumptions will be given when they are utilized in the modeling.

- Model nucleation occurs through only micellar mechanism because of high surfactant concentration. The other type of nucleation, homogeneous nucleation, is considered negligible.
- Monomer droplet diameter as well as those of the growing particles is considered to be mono-disperse.
- Propagation and termination in the aqueous phase are neglected.
- Transfer to polymer chain reaction is not considered much in this work.
- Coagulation between particles is neglected. The extension of coagulation is often not known.
- The mixture in the reactor is assumed to be perfectly mixed.

In latex reactor systems, the level-one balance are strongly coupled with the particle population balances, thereby making level-one models of limited value. In recent years, considerable advances have been made in the modeling of emulsion polymerization reactors. Until 1974 models for these systems did not include the particle nucleation phenomena, nor did they consider population balances to account for the particle size distribution. Now, both homogeneous nucleation, and micellar nucleation mechanisms (collision or diffusion theory) are usually included in the models. Again, two levels of model are used to account for particle size. The "monodisperse approximation model" is based on modeling the development of the number of polymer particles and the total particle volume. Assuming monodisperse particles, the particle size is calculated as proportional to the cube root of the total volume of polymer phase divided by the number of particles.

The surface area of polymer particles (needed to calculate the micelle area) is also obtained as proportional to the two-thirds power of the volume. The second level of emulsion polymerization model employs a population balance approach (or an age distribution analysis) to obtain the full PSD. By treating the moments of these population balance equations to get total or average properties, the set of equations that must be solved is greatly simplified. Since the method of characteristics gives the PSD as a function of (birth/growth) displaced back along the age axis, the moment equations may provide sufficient information to obtain the PSD.

Models for emulsion polymerization vary in their complexity. The first level model involves reactor, material balance and energy balance which are used to predict the temperature, monomer concentration in the reactor and pressure. Second level can not only predict the above parameters but also polymer properties like particle size distribution, molecular weight distribution. In this thesis we worked upon second level.

The model is developed to describe the temperature control in the batch emulsion polymerization and emulsion polymerization of methyl methacrylate. Conservation of energy accounts for the heat generated by the propagation reaction and heat removal through the wall of the reactor and by convective fluid flow. The density of the mixture is a function of the conversion, the amount of solvent introduced in the feed and the temperature.

3.1 Kinetics

The following mechanisms are found in free radical emulsion polymerization for PMMA production.

$$I \xrightarrow{k_d} xR^{\cdot}$$

$$R^{\cdot} + M \xrightarrow{k_1} RM_i{}^{\cdot}$$

$$RM_n^{\cdot} + M \xrightarrow{k_P} RM_{n+1}$$

$$RM_{n+1} \xrightarrow{k_{dP}} RM_n + M$$

$$RM_n^{\cdot} + RM_P^{\cdot} \xrightarrow{k_{tc}} RM_n + RM_p$$

$$RM_n^{\cdot} + TA \xrightarrow{k_{trTA}} RM_n^{\cdot}T + A$$

The reaction kinetic has already been given in the above part, and these reactions have been utilized in the modeling part.

Only the most important reactions were considered to make the model more manageable. If more kinetic is considered several rate constants have to be known, and often no information is available about these. To estimate all parameters that are included in the model, different measured values have to be known and available. As the purpose is to utilize the model for PID, MPC and NMPC the model has to be made simple and therefore the most important kinetics is given.

3.1.1 Mass Balance Equation for Batch Emulsion Polymerization Reaction

A fundamental law state that mass cannot be produced nor destroyed, and mass is therefore conserved. Another fundamental law is ‘conservation of energy’. Energy can change its form, but it cannot be created or destroyed. These laws provide the basis for two tools which are utilized in engineering and science; energy and material balances. Energy and material balances are plays important role, and material balances are fundamental for model development. As the energy cost has increased in the last years, industries have to find methods to reduce energy consumptions in processing. Energy balances are important for this reason, and they are utilized in the various stages of a process, and over the whole processes.

Mathematical modelling of emulsion polymerization is crucial in gaining a fundamental understanding; it is also a valuable tool for product development, reactor design. Important assumptions should include

1. Nucleation and coagulation of particle do not occur and the number of particle per unit volume of water remains constant during polymerization.
2. Desorption of free radicals out of the particle does not take place.
3. Bimolecular termination of the polymeric radical inside the particle upon the entry of an oligomeric radical from the aqueous phase is instantaneous.
4. Micelle nucleation and the rate of polymerization is a function of monomer conversion.

3.1.2 Mass Balance for Initiator I

Initiator is consumed through decomposition in the aqueous phase, and the corresponding reaction rate is given in Equation 3.1. Moles of every species have decided fate.

$$\frac{d[I]}{dt} = -k_d I \tag{3.1}$$

$$I = I_0 \exp(-k_d t) \tag{3.2}$$

$$R_i = f\,\frac{dRi}{dt} = 2\,fk_d[I] \tag{3.3}$$

Here f is the factor efficiency of the initiator.

A free radical initiator should be relatively stable at room temperature, but in polymer processing the initiator decomposition can occur either by thermal or by redox reaction. The decomposition rate (k_d) of the initiator will also depend on the solvent/monomer system. The effect of solvent molecules causes secondary wastage reactions including recombination of radicals to regenerate the initiator (known as cage effect). As viscosity in the solution increases, this cage effect becomes more significant. The activity of an initiator can be defined as its half-life, $t_{1/2}$, and if it is known for more than two temperature conditions, then one can calculate the factor efficiency and activation energy of the initiator.

The homolytic decomposition of initiator molecules can be represented schematically as given in reaction above. Homolytic decomposition of covalent bonds occurs after absorption of energy, which may be in form of heat, light or high energy radiation, depending on the type of initiator used.

3.1.3 Mass Balance for Monomer M

Monomer conversion is given by

$$R_P = -\frac{d[M]}{dt} = k_1[R^\cdot][M] + k_P[M^\cdot][M] \tag{3.4}$$

$$[M^\cdot] = \sum_{i=1}^{\infty}[M_i] \tag{3.5}$$

$$\frac{d[M^\cdot]}{dt} = R_i - 2k_{tc}[M^\cdot][M^\cdot] - 2k_{td}[M^\cdot][M^\cdot] \tag{3.6}$$

$$\frac{d[M]}{dt} = R_i - 2k_t[M^\cdot]^2 \tag{3.7}$$

$$k_t = k_{tc} + k_{td} \tag{3.8}$$

$$[M^{\cdot}] = \left(\frac{R_i}{2k_t} \right)^{1/2} \tag{3.9}$$

$$R_P = \frac{d[M]}{dt} = k_P \left(\frac{R_i}{2k_t} \right)^{1/2} [M] \tag{3.10}$$

$$R_P = \frac{d[M]}{dt} = k_P \left(\frac{fk_d}{k_t} \right)^{1/2} [M][I]^{1/2} \tag{3.11}$$

Rate of propagation is proportional to the monomer concentration in the particle. It is assumed that if there is no more than one radical per polymer particle present the termination occurs spontaneously, and is very rapid compared to radical entry.

3.1.4 Mass Balance for Polymer P

$$\frac{d[P]}{dt} = k_{tc}[M^{\cdot}]^2 + 2k_{td}[M^{\cdot}]^2 + k_{trM}[M^{\cdot}][M] + k_{trI}[M^{\cdot}][I] \tag{3.12}$$

$$\frac{d[P]}{dt} = \left(\frac{fk_d}{k_t} \right) k_{tc}[I] + 2\left(\frac{fk_d}{k_t} \right) k_{td}[I] + \left(\frac{fk_d}{k_t} \right)^{1/2} k_{trM}[M][I]^{1/2} + \left(\frac{fk_d}{k_t} \right) k_{trI}[I]^{3/2} \tag{3.13}$$

3.2 Energy Balance for Batch Emulsion Polymerization

Energy balance is an accounting of

- Rate of heat flow into the reactor with reactants.
- Rate of heat flow out of the reactor with products.
- Rate of heat generated / absorbed by reaction.
- Rate of heat added/removed from reactor.
- Work done by stirrers and friction.

3.2.1. General Energy Equations

Rate of energy accumulation = (Rate of energy entering system by inflow) – (Rate of energy leaving system by out flow) + (Rate of heat added to system) + (Rate of work done on system)

$$\frac{dE}{dt} = m_0 \hat{E}_0 - m_1 \hat{E}_1 + Q^{\bullet} + W^{\bullet} \tag{3.14}$$

Reactor energy equation

$$\frac{d\left(U+K+\phi\right)}{dt}=m_0\left(\hat{H}+\hat{K}+\hat{\phi}\right)_0-m_1\left(\hat{H}+\hat{K}+\hat{\phi}\right)_1+Q^{\bullet}+W_s^{\bullet}+W_b^{\bullet} \tag{3.15}$$

For batch reactor flow stream will be zero

$$\frac{d\left(U+K+\phi\right)}{dt}=m_0\cancel{\left(\hat{H}+\hat{K}+\hat{\phi}\right)}_0-m_1\cancel{\left(\hat{H}+\hat{K}+\hat{\phi}\right)}_1+Q^{\bullet}+W_s^{\bullet}+W_b^{\bullet} \tag{3.16}$$

We find

$$\frac{d\left(U+K+\phi\right)}{dt}=Q^{\bullet}+W_s^{\bullet}+W_b^{\bullet} \tag{3.17}$$

3.2.2 Energy Equation, Process

$$\rho VC_P\frac{dT}{dt}=\Delta HR_P-h_iA_i\left(T-T_M\right) \tag{3.18}$$

$$\frac{dT}{dt}=\frac{\Delta HR_P}{\rho C_PV_R}-\frac{h_iA_i\left(T-T_M\right)}{V_R\rho C_P} \tag{3.19}$$

$$\frac{dT_{R_I}}{dt}=\frac{-\Delta Hfk_d[I]}{\rho C_PV_R}-\frac{UA(T_{R_i}-T_j)}{V_R\rho C_P} \tag{3.20}$$

$$\frac{dT_{R_M}}{dt}=\frac{-\Delta Hk_P\left(fk_d/k_t\right)^{1/2}[M][I]^{1/2}}{\rho C_PV_R}-\frac{UA(T_{R_M}-T_j)}{V_R\rho C_P} \tag{3.21}$$

$$\frac{dT_{R_P}}{dt}=\frac{-\Delta H[\left(fk_d/k_t\right)k_{tc}[I]+2\left(fk_d/k_t\right)k_{td}[I]+\left(fk_d/k_t\right)^{1/2}k_{trM}[M][I]^{1/2}+\left(fk_d/k_t\right)k_{trI}[I]^{3/2}]}{\rho C_PV_R}-\frac{UA(T_{R_P}-T_j)}{V_R\rho C_P} \tag{3.22}$$

Energy having different forms, i.e. heat, kinetic energy, chemical energy and potential energy. Because of inter-conversion it is not always readily to isolate constituents of energy balances, but under some circumstances certain aspects predominate.

3.2.3 Energy Equation, Metal Wall

$$\rho_M C_{PM} V_M \frac{dT_M}{dt} = h_i A_i \left(T - T_M\right) - h_{os} A_o (T_M - T_J) \tag{3.23}$$

3.2.4 Energy Equation, Hot Water

$$V_J \frac{d\left(U_J \rho_J\right)}{dt} = F_S \rho_S H_S - h_o A_o \left(T_J - T_M\right) - W_C h_C \tag{3.24}$$

Where U_j = internal energy of hot water in jacket, Btu/lbm
H_s =enthalpy of incoming hot water, Btu/lbm
h_c = enthalpy of liquid cooled, Btu/lbm

The internal energy changes usually neglected if compared with the latent heat effects, thus a simple algebraic steady-state energy equation can be used

$$W_C = -\frac{h_o A_{os}\left(T_M - T_J\right)}{H_S - h_C} \tag{3.25}$$

The equation of state for hot water can be used to calculate temperature T_j and pressure P_j from density $\rho_{j,}$ the perfect-gas law and a simple vapour-pressure relation can be used for the calculation

$$\rho_J = \frac{M}{RT_J} e^{A_{VP}/T_j + B_{VP}} \tag{3.26}$$

Where M = molecular weight of hot water =18 lbm/mole.

A_{vp} and B_{vp} are vapour pressure constant for water.

3.2.5 Energy Equation, Cold Water

During the period when cooling water is running in the jacket, only an energy equation for the jacket is required, we assume the water is incompressible and water in the jacket is perfectly mixed. We assume that the temperature is uniform in the jacket and that is T_j. The heat transfer rate of the process (as temperature T and the cooling water at temperature T_j) is described by an overall heat transfer coefficient (Singh. 2010).

$$Q = UA_H \left(T - T_J\right) \tag{3.27}$$

Where Q = heat transfer rate

U = overall heat transfer coefficient

A_H = heat transfer area

Jacket energy equation:

$$C_J \rho_J V_J \frac{dT_J}{dt} = F_W C_J \rho_J \left(T_{J0} - T_J\right) - h_o A_o \left(T_M - T_J\right) \tag{3.28}$$

Where T_j=temperature of cooling water in jacket, ^{0}K

ρ_j =density of water, lbm/ft3

C_j =heat capacity of water, Btu/lbm ^{0}K

Tj0 =inlet cooling water temperature, ^{0}K

3.2.6 Overall Energy Equation, Reactor Jacket

$$\frac{d\left(C_J \rho_J V_J T_J\right)}{dt} = F_s C_J \rho_J V_J T_{hot} + F_w C_J \rho_J T_{cold} - \left(F_s + F_w\right) C_J \rho_J T_J + UA_J (T_{R_I} - T_J) \tag{3.29}$$

Where F_{hot} and F_{cold} are the flow rate of the hot and cold streams fed to the circulating water system going through the jacket or the external heat exchanger with volume V_j

$$\frac{dT_J}{dt} = \frac{F_{hot} T_{hot} + F_{cold} T_{cold}}{V_J} - \frac{\left(F_{hot} + F_{cold}\right) T_J}{V_J} + \frac{UA_J (T_M - T_J)}{V_J \rho_J C_J} \tag{3.30}$$

The second energy balance can be utilized to calculate outlet temperature of the cooling jacket. The cooling jacket could have been modelled as multiple sections, but instead only inlet and outlet temperature are considered. An average temperature is utilized, as control of the reactor temperature becomes simpler to perform. The energy balance for the cooling jacket is given in Equation 3.30. The first term is rate of energy added and removed to the system by the water mass flow in the jacket. The second term is heat loss to the environment and the last term is for the heat transfer from the jacket to the reactor. As no energy balance for the temperature of the reactor metal is utilized, a term in the denominator is included as the steel of the reactor has to be cooled or heated.

We can use another set of reactor and jacket energy balance equation with out using flow rate of hot water

$$VC_p\rho\frac{dT_r}{dt} = Q + (-\Delta H)R_pV - UA(T - T_j) \tag{3.31}$$

$$V_cC_{pc}\rho_c\frac{dT_j}{dt} = M_cC_{pc}(T_{ji} - T_{j0}) + UA(T - T_j) \tag{3.32}$$

Where Q is heater power, U overall heat transfer coefficient.

3.2.7 Estimation of Kinetic Chain Length

The kinetic chain length “v” of a radical chain polymerization is defined as the average number of monomer molecules consumed per radical, which initiates the polymer chain.

The value of the kinetic chain length is given by the following formula:

$$v = \frac{k_p[M]}{(2fk_dk_t)^{1/2}[I]^{1/2}} \tag{3.33}$$

Assuming that mode of termination is disproportionate the kinetic chain length is equal to the number avg. degree of polymerization.

$$X_n' = v \tag{3.34}$$

The number average molecular weight of a polymer is given by the

$$M_n = M_w * X_n' \tag{3.35}$$

Where: M_w= molecular weight of monomer

3.2.8 Estimation of Kinetics Coefficient

The kinetics coefficient k_P, k_d, k_{trM} follows the Arrhenius’s law

$$k_P = k_{P0}e^{\left(-\frac{E_P}{RT}\right)} \tag{3.36}$$

$$k_d = k_{d0}e^{\left(-\frac{E_d}{RT}\right)} \tag{3.37}$$

$$k_{trM} = k_{trM0}e^{\left(-\frac{E_{trM}}{RT}\right)} \tag{3.38}$$

Rate constants can be measured experimentally, but for us it is not possible to resolve the quantities to estimate the individual rate coefficients. Both efficiency (f) and the rate constant (k_I) should be known before, and a common assumption usually made is that radicals are not being consumed or trapped by impurities in the system. These constants are reported in the literature (Adebekun et al. 1989; Chen et al. 2009; Curteanu et al. 1998; Silva-Beard et al. 1999). The values of the rate constants are varying with temperature .We have taken the value of rate constants from the literature.

3.3 Molecular Weight Distribution

The energy and mass balance equation of a single element is already discussed earlier. Assumptions must be taken in the model is concerning the initiation step. Thermal initiation with three monomer molecule has a small probability of taking place. Volume contraction during polymerization is also considered as well as gel and glass effect.

The monomer conversion and volume contraction is defined as

$X= (M_oV_o-MV)/M_oV_o$ (3.39)

$V= V_o (1+\epsilon X)$ (3.40)

$M_{o,}V_o$ are the monomer concentration and volume at zero conversion. Є is the expansion factor of the volume, which depends upon monomer and polymer densities dm and dp respectively.

Є= (dm-dp)/dp (3.41)

From the equations above

$$M = M_o \frac{1-X}{1+\varepsilon X} \tag{3.42}$$

The final structure of the moments is given later, Long chain hypothesis (LCH) and quasi -steady state approximation (QSSA) are applied to the model to simplify the equations. LCH implies that the monomer is consumed in the propagation phase only; its consumption in the initiation reaction is being neglected.

QSSA assumes that the effective rate of the increasing radical chain formation is close to zero.

$$\frac{1}{V}\frac{d(VR*)}{dt} = 0 \tag{3.43}$$

$$k_i R * M = 2fk_d I \tag{3.44}$$

Using these assumptions we get the final model

Moment balances for dead and live polymers were derived, even though they are available in different literature. Often the moment balances are given in literature(Curteanu et al. 1998; Shahrokhi et al. 2002), but the derivation of these balances are not given. The derivation of some of these equations is therefore given below. To find the weight average molecular weight, six new states are introduced into the model. The moment equations are utilized to find molecular weight distribution and molecular weight.

The kinetic consider in derivation was initiation, propagation, termination, and chain transfer to monomer and chain transfer agent. The first step is to find balances for live radicals and dead chains of length n, accounting for all the consumption and generation terms from the kinetic mechanisms listed above.

Based on the above kinetics, we can derive the following population balance equations for the live $\lambda_{x,t}$ and dead $u_{x,t}$ polymer chains of length x. Assuming that the degree of polymerization, x, can only take discrete values (x:1:2:3).

Live Polymer Chain

$$\frac{d\lambda_0}{dt} = 2fk_d I - k_t\lambda_0^2 - \lambda_0 \epsilon \left(\frac{1-x}{1+\varepsilon x}\right)[k_p\lambda_0 + k_{tm}\lambda_0] \tag{3.45}$$

$$\frac{d\lambda_1}{dt} = 2fk_d I - k_p M_0 \frac{(1-x)}{(1+\epsilon x)}\lambda_0 - k_t\lambda_0\lambda_1 - \lambda_1\varepsilon\left(\frac{1-x}{1+\epsilon x}\right)[k_p\lambda_0 + k_{tm}\lambda_0] - k_{tm}M_0\left(\frac{1-x}{1+\varepsilon x}\right)(\lambda_1 - \lambda_0) \tag{3.46}$$

$$\frac{d\lambda_2}{dt} = 2fk_d I - k_p M_0 (\frac{1-x}{1+\in x})(2\lambda_1 + \lambda_2) - \mathrm{k}_t \lambda_0\lambda_2 - \lambda_2 \in (\frac{1-x}{1+\in x})[k_p\lambda_0 + k_{tm}\lambda_0] - k_{tm}M_0(\frac{1-x}{1+\in x})(\lambda_2 - \lambda_0) \tag{3.47}$$

Dead polymer chain

$$\frac{du_0}{dt} = k_t\lambda_0^2 - u_0 \epsilon\left(\frac{1-x}{1+\epsilon x}\right)[k_p\lambda_0 - k_{tm}\lambda_0] + k_{tm}M_0\left(\frac{1-x}{1+\epsilon x}\right)\lambda_0 \tag{3.48}$$

$$\frac{du_1}{dt} = k_t\lambda_0\lambda_1 - u_1\,\epsilon\left(\frac{1-x}{1+\epsilon x}\right)[k_p\lambda_0 - k_{tm}\lambda_0] + k_{tm}M_0\left(\frac{1-x}{1+\varepsilon x}\right)\lambda_1 \qquad (3.49)$$

$$\frac{du_2}{dt} = k_t\lambda_0\lambda_1 - k_t\lambda_1^2 - u_2\epsilon\left(\frac{1-x}{1+\epsilon x}\right)[k_p\lambda_0 - k_{tm}\lambda_0]k_{tm}M_0 \qquad (3.50)$$

The right hand side term in equations above represents the net production of Live and Dead polymer chains. The method of moments is based on the statistocal representation of the average molecular properties of the polymer (number average, weight average molecular weight) in terms of leading moment of the number chain length distribution (NCLDs) of Live and Dead polymer chains.

This model can be used for higher temperature range, for below 100^{o}C only chemical decomposition of initiation was considered, so k_{iterm} =0, but beyond this temperature both thermal and chemical decomposition are considered. During the polymerization, the k_{tc}, k_p, k_{tm} constants decreases because of diffusion constraints like gel effect and glass effect.

3.4 Particle Size Distribution

Polymer particles in emulsion polymerization system are generally having a distribution of sizes. This distribution is due to two factors: Particles nucleated at the same time will have a statistically distribution of periods of radical residence and growth and secondly particles nucleated over a long period of time will have different sizes because of there different duration of growth.

Gibbs free energy is directly proportional to the Hamakar constants. Hamakar constant can be calculated by relation

$$A_{H,\,eff} = A_{H,\,11} + A_{H,\,22} + A_{H,\,12} \qquad (3.51)$$

Where $A_{H,\,11}$ and $A_{H,\,22}$ represents the Hamakar constant of component 1 and component 2 respectively in vacuum. $A_{H,\,12}$ is assumed to be geometric average of component 1 and 2.Particles are normally assumed spherical in shape so that surface area and particle diameter are easily calculated from particle volume. Hamakar Constant for PMMA is 6 X $10^{-20.}$ This constant uses only Vander wall attraction, larger the value of Hamakar constant, stronger will be the tendency for the pair of colloidal particles to coagulate with each other (Ali et al. 1986; Zollars et al. 1985). The value of Hamakar is very small hence we avoid coagulation in the model (Zollars et al. 1987).At high concentration of surfactant, particle size distribution shows self preserving nature which causes decrease in crate of coagulation of particles (Ali et al. 1988).

Some assumptions are made

1. Particle contains either zero or one radical.
2. Instantaneous bimolecular radical termination occurs.
3. Neglect glass transition.
4. Assumed lower radical entry rates and higher radical exit and termination rate.

Theses assumption favours instantaneous bimolecular terminationThe particles are assumed to contain either one or zero radical; this system is called zero one model. Population balance equation for particle size distribution is given by equation (Crowley et al. 2000; Sood.A 2008).

$$\frac{\partial n_o}{\partial t} = \rho(r)[\mathrm{n}_1^p(\mathrm{r}) + \mathrm{n}_1^m(\mathrm{r}) - \mathrm{n}_o(\mathrm{r})] + \mathrm{k}_{o(r)} \times n_1^m(r) \tag{3.52}$$

$$\frac{\partial n_1^p(r)}{\partial t} = k_p \times n_1^p\,(r) + \rho_{ini}\,(r) \times n_0\,(r) - \rho(r) \times n_1^p\,(r) - k_{tr}\,[M]_0\, n_1^p\,(r) + \sum_{j=z}^{jcri} k_{em,i}\,[micelles][p_i^{\bullet}]\,\delta(r - r_{nuc}) \tag{3.53}$$

$n_0(r)$ is the population containing zero radicals and $n_1(r)$ is the population containing one radical , polymer radical $n_1^p(r)$ which would not readily diffuse out of the particle due to its size. Monomer radicals formed from chain transfer reaction is $n_1^m(r)$, which presumable can readily exit particle. j_{crit} is the chain length which becomes insoluble in water and participates in a new particle.

Particle growth rate is given by

$$G(r) = \frac{k_p[M]w_m}{4\,\pi r^2 \rho_p N_A} \tag{3.54}$$

Here k_p is propagation rate, w_m molecular weight of monomer, density of polymer represent by ρ_p.

Quasi –steady state assumption is applied and we get

$$n_1^m = \frac{k_{e,t}\,(r)[E]\,n_0\,(r) + k_{tr}\,[M]_p\,n_1^p}{\rho_r + k_{p,e}\,[M]_p + k_0\,(r)} \tag{3.55}$$

$n(r) = n_0(r) + n_1^p(r) + n_1^m(r)$ (3.56)

$n_1(r) = n_1^p(r) + n_1^m(r)$ (3.57)

Zero –one system is where entry of a radical into a particle which already contains a growing radical causes termination at a rate much faster than overall polymerization. In such a system the average number of radicals per particle cannot exceed 0.5, termination occurs only between an entering radical and a radical which has been growing at the same time.

$$\rho(r) = \rho_{ini}(r) + \rho_{re-entry}(r) \tag{3.58}$$

$$\rho(ini) = \sum_{i=Z}^{jcrit-1} \square\, k_{e,i}(r)[IM\,i] \tag{3.59}$$

$$\rho_{re-entry} = k_{e,E}(r)[E] \tag{3.60}$$

$$k_{e,i} = \frac{4\Pi r_s N_A D_w}{i^{\frac{1}{2}}} \tag{3.61}$$

$$k_{em,i} = \frac{4\Pi r_{micelle} N_A D_w}{i^{\frac{1}{2}}} \tag{3.62}$$

$$k_{e,E} = 4\Pi r_s N_A D_w \tag{3.63}$$

$$r_s = \left[\frac{\rho_m}{\rho_m - [[M]_p]w_m}\right]^{\frac{1}{3}} r$$

The mathematical dynamic model is actually a set of algebraic and differential equations (DAE). The algebraic equations (AE) in the model are possible to order so that they can be solved as intermediate calculations instead of solving a DAE equation set. A solver in MATLAB was utilized, ODE15s, as this solver is a variable-order solver for stiff systems.

3.5 Bubble Entrapment

In highly viscous system like bulk polymerization, the process is associated with a rapid increase in viscosity of the reaction mass; this increase in viscosity makes the reaction diffusion control. Recently Sahani et al (2011) carried out bulk polymerization of MMA in 1 L fully instrumented stainless steel batch reactor. They observed that small vapour bubbles get entrapped in reaction mass and because of high viscosity those bubbles are enable to escape. They start growing with the process. In our present study we introduce equations for batch emulsion polymerization which only focus on entrapment of gas bubbles as the viscosity of reaction mass increases. Inert gas nitrogen is used to suppress the vaporization of MMA and prevent degradation of the polymer. In industrial practice similar problem of entrapment arises, usually a devolatilization step is carried out to avoid this phenomenon. In fact industrial polymerization is carried out in two steps. Firstly pre-polymerization is carried out in batch reactor until bubble entrapment starts. Then the reaction mass is transferred to a tubular reactor to further complete the process.

Few assumptions are taken for the theoretical treatment of the model , which makes model more simplified.

- Batch reactor is assumed to well stir.
- There is no nucleation of bubble.
- Instantaneous breakage of bubble into smaller size bubbles is taking place.
- No coalescence of bubbles.
- Mass transfer from liquid to the vapour is controlled by liquid mass transfer coefficient.

Kinetic equations are same as discusses above used in this model and the molecular weight distribution model used is again the same model given in equation numbers 3.39- 3.50.

Bubble entrapment is given by equation

$$R[\eta, \mathrm{a}_i] = 60(1+\frac{p_1\exp(-\eta)}{\exp(A^{p2})})(1+[(\frac{2.3\eta}{\eta_f})(\frac{a_i}{p_3})^{\frac{p3}{a_i}}]^4\frac{p_4}{A^3})(\exp[-(\ln\mathrm{a}_i - p_5)^2]) \qquad (3.64)$$

For $0 \le t \le t_1$

Moment equations should be

$$\lambda_0 = \lambda_1 = \lambda_2 = u_0 = u_1 = u_2 = 0$$

Growth rate

$$\frac{da_i}{dt} = G(a_i) = 2k_i(\frac{RT}{P_T})([\mathrm{M}]-[\mathrm{M}]_0); i = 1, 2... \tag{3.65}$$

Population balance

$$\frac{dN_i}{dt} = R[\eta(t), a_i(t)](a_{i+1} - a_i); \mathrm{i} = 1, 2... \tag{3.66}$$

Viscosity of the liquid reaction mass

$$\phi_m = ([\mathrm{M}](\mathrm{MW}_m)/\rho_m)/(\frac{[M](\mathrm{MW}_m)}{\rho_m} + \frac{([M]_0 - \xi_m - [M])(\mathrm{MW}_m))}{\rho_p}) \tag{3.67}$$

$$\phi_p = 1 - \phi_M \tag{3.68}$$

$$\eta = \eta_{sol}[1 + \eta_{\mathrm{int}} C_{polym} \exp\{d_0 + d_1(\eta_{\mathrm{int}} C_{polym}) + d_2(\eta_{\mathrm{int}} C_{polym})^2\}] \tag{3.69}$$

$$\mathrm{C}_{polym} = (1 - \phi_m)\rho_m \tag{3.70}$$

Where a_i is bubble diameter, Ni is total number of bubbles in the ith range at time t, C_{polym} is density of polymer in monomer-polymer mixture.

There is no concentration gradient for the polymer to diffuse into the bubble. The polymer is assumed not to diffuse out in the liquid phase.ODE15s is used in MATLAB to solve the set of model equations, it select the optimum stepsize.

3.6 Discussion: Modeling

In this work we model: modeling of monomer distribution and radical of the polymer particles, molecular weight and particle size distributions; other possible cooling solution like split range was also considered during control of the reactor. When modeling of emulsion polymerization started, decisions about how advanced the model should have to be made in the start. The more advanced the model gets, including different aspects in the process, several more parameters have to be estimated and introduced in the model. To estimate all these parameters a broad collection of measured process data has to be available. These measurements are costly to perform, and some variables are actually impossible to get information about. This makes it difficult to implement complex models with several parameters in a control system. It was therefore decided to develop models that are as simple as possible, but still get satisfying predictions.

There were two energy balances, one for outlet cooling temperature and the other for reactor temperature in the model. To utilize the energy balance for the reactor temperature and achieve correct temperature a controller had to be implemented in the model. This controller should control the cooling water flow rate or the temperature of the inlet cooling water, as this was tested in the model. We found after implementation of PID controller that is very difficult to proceed with it further because of the drawback of ‘dead zone’ and occurrences of oscillation somewhere in the control process. We concluded other control systems can probably also be utilized, but independent of control configuration implemented in a plant, the controller had to be tuned.

The problem in implementation of a simple PID controller was the time delay, and this would cause a problem in the simulation of the model. By performing model reduction and simplifications, a less complex model can be obtained.

Simple models that do not require a heavy computational load but capture the entire essential process features are readily agreeable to the reactor optimization and control studies. Some aspects were therefore modelled in different ways, to make the model simpler and to reduce stiffness.

As ODE15s was utilized, stiff models were not a problem and calculation time for simulating the model over a long time interval was short. A batch on 7-8 hours was simulated and this took about 1 hour to calculate in MATLAB.

As the model was both complex and stiff in some cases, i.e. extremely fast dynamic for some states, the step size had to be quite small (about 0.0001) and this gave a calculation time around 1000 seconds. In this case h was kept constant through the whole batch simulation.

In particle size distribution moles of radicals in the polymer particles or the average number of radicals per particle was also an important value that influences the polymerization rate. The calculated moles of radicals in the polymer particles, and this method should predict correct values for Np. It was therefore not necessary to have moles of particles with zero, one, two etc. as states, and more ODEs has to be solved.

The zero-one system could also be a reasonable method to utilize when modeling an emulsion polymerization process, but this solution only count for processes with a low $n < 0.5$ average number of radicals per polymer particle according to Smith-Ewart theory.

Different grades can be made by using another recipe or concentration of initiator, monomer and surfactant in different ways into the reactor. In the mole balances of monomer, surfactant and initiator it was possible to change dose but small changes had to be done in the mole balances and the programming files for the initiator and monomer. The recipe given is readily to make change in, as change in recipe only change amount of chemicals and temperature utilized.

Different grades can be produced if different factors in the reactor are changed, and some are listed below.

- Chain transfer agent (CTA) can be utilized to change molecular weight (MW).
- Large increase in MW can be done by decreasing the polymerization rate, by decreasing the initiator concentration or by lowering reaction temperature. Temperature profile can be readily changed by changing the flow of cooling water.
- The number of polymer particles (Np) is the prime determinant of the rate and degree of polymerization. This depends on surfactant.

Moles of particles also depend on rate of radical’s generation. High particle numbers are associated with small particle size and low particle numbers with large particle size. Number of particles can be increased by increasing surfactant concentration in the reactor recipe.

Predictions about PSD could be utilized to determine when the batch should end. The partial differential equations of particle size distribution are converted into ordinary differential equations by finite collocation method which is out of the scope of this thesis.

3.7 Challenges in Polymerization Reactor Modeling

Product quality in polymerization system is very complex issue than other chemical system. Polymer quality includes all the polymer molecular properties [eg. MWD, copolymer composition distribution (CCD), sequence length distribution (SLD), Long chain and short chain branching (LCB, SCB), PSD etc]. One of the most difficult issues in polymer reactor optimization and control is to determine the relation between the product's physical, mechanical, chemical, thermal, rheological and morphological polymer properties. Table -3.1 summarizes some quality control measures.

The analysis of polymerization process is rather complex problem due to the highly coupled kinetics, heat and mass transfer, thermodynamics in the emulsion polymerization being a heterogeneous process.

Table3.1: Some measures of polymer quality

Morphological properties	End use properties
• Average molecular weight And Molecular weight distribution (MWD)	Physical and thermal properties (e.g. Density, Temperature, melting point).
• Particle Size Distribution(PSD)	Rheological (e.g. Viscosity, Melt Index, flow properties).
• Sequence length Distribution (SLD)	Chemical
• Copolymer composition Distribution (CCD)	Chemical
• Particle Porosity and surface area	Rheological properties
• Long chain Branching Distribution (LCBD)	Mechanical properties (e.g. Strength, resistance, shear Viscosity).

Chapter-4

Control and Experimental Methodology

4. Control and experimental Methodology

PMMA batch emulsion polymerization was run using various concentrations of surfactant, initiator and monomer. The following sections give a detailed description of the materials, experimental techniques, apparatus and analytical procedures that were employed to carry out the experiments and analysis of sample.

4.1 Materials

Table 4.1: The material used during the course of project

Elements	Name	Specification
Monomer	Methyl-methacrylate	Analytical Reagent Central Drug House (P) LTD, New Delhi
Surfactant	Sodium oleate	Analytical Reagent Central Drug House (P) LTD, New Delhi
Initiator	Potassium persulfate	Analytical Reagent Central Drug House (P) LTD, New Delhi
Gas	Nitrogen	Grade – Instrumental Gas

4.1.1 Monomers

Typical monomers are those that undergo radical polymerization, are liquid or some gaseous at reactor condition, may be soluble or poorly soluble in water. Some monomers are in solid state, which are hardly diffuse in water. If the solubility of the monomer is too high, as a result particle formation may disappear from the system and the system is transformed into solution polymerization.

Methyl Methacrylate monomer is used as a main ingredient, which was purchased from Central Drug House (P) LTD, New Delhi, batch No-05114and product No-029234.

Structures

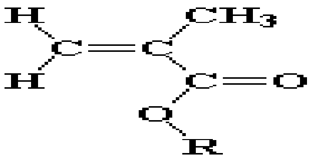


Fig. 4.1: Structure of MMA

Properties

Table 4.2: Properties of methyl methacrylate monomer

Molecular formula	$C_5H_8O_2$
Molar mass	100.12 g/mol
Appearance	colourless liquid
Density	0.94 g/cm³
Melting point	-48 °C (225 K)
Boiling point	101 °C (374 K)
Solubility in water	Soluble in methyl ketone
Viscosity	0.6 cP at 20 °C
Minimum assay	99.5%
Refractive Index	1.414-1.415
Maximum Impurity , free acid & water	1ml N% &0.1%

Application

- Consuming approximately 80% of the MMA for the manufacturing of acrylic plastics (PMMA).
- It is used for the production of the co-polymer methyl Methacrylate-butadiene-styrene (MBS), used as a modifier for PVC.

4.1.2 Initiators

Thermal and redox generation of free radicals have been used in emulsion polymerization. Persulfate ions are commonly used in initiation process. The persulfate ion readily break off into sulphate radical ions above about 50°C, providing a thermal source of initiation.

Potassium persulfate are used as initiator in PMMA synthesis, which was purchased from Central Drug House (P) LTD, New Delhi, batch No-01036 and product No-029861.

Structure

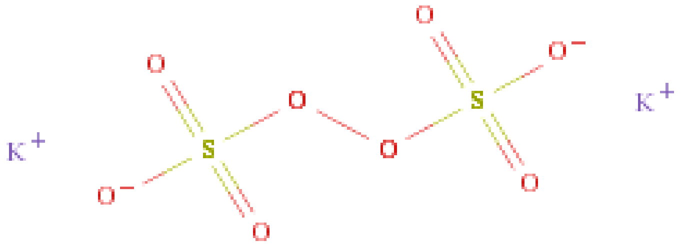


Fig. 4.2: Structure of potassium persulfate

Properties

Table 4.3: Properties of potassium persulfate initiators

Molecular formula	$K_2S_2O_8$
Molecular Weight	270.322 g/mol
Appearance	white crystal powder (solid)
Density	2.477 g/cm^3
Melting point	100 °C
Solubility in water	1.75 g/100 mL (0 °C), 5.29 g/100 ml (20 ºC)
Minimum assay	98.0%
Chloride	Not more than 0.04%

Applications

- Potassium Persulphate is used for textile designing, bleaching as an oxidizing agent and antiseptic, for manufacture of soap and pharmaceuticals.
- It is a food additive, and in hair dye substances as whitening agent with hydrogen peroxide.
- It plays an important role as initiator in polymerization reaction.

4.1.3 Surfactants

The surfactant must enhance rate of polymerization, minimize coagulation or fouling in the reactor and other process equipment, prevent from high viscosity during polymerization (which leads to poor heat transfer), and improve end-use properties of the final product such as rheological, tensile strength, gloss, and water absorption and other properties. Anionic, non-ionic, and cationic surfactants have been used; by far anionic surfactants are used widely surfactant. Normally surfactants having low critical micelle concentration (CMC) are favoured; the polymerization rate shows an increasing trend when the surfactant level is higher then the CMC, where as minimization of the surfactant concentration is chosen for economic reasons and also avoided for the adverse effect of surfactant on the physical properties of the polymer. Mixtures of surfactants are often used, including mixtures of anionic with non-ionic surfactants. Mixtures of cationic and anionic surfactants form insoluble salts and are not useful.

Sodium oleate ($C_{18}H_33NaO_2$): It is used as surfactants in the PMMA synthesis, which was purchased from Loba chemie Pvt. Ltd., Mumbai, Batch No-G110406.

Sodium oleate occurs as a white powder, or as light yellow coarse powder. Since it is a fatty acid, sodium oleate is not generally found free in nature, rather found in the form of complex lipid.

Structure

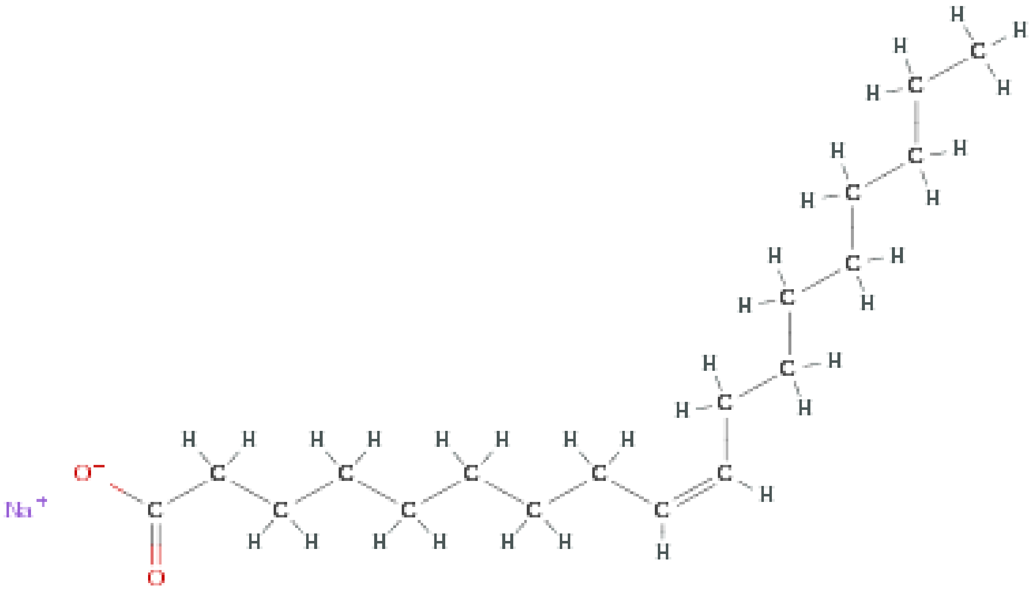


Fig. 4.3: Structure of sodium oleate

Properties

Table 4.4: Properties of sodium oleate emulsifier

Molecular formula	$C_{18}H_{33}NaO_2$
Phase	Solid (at STP)
Appearance	White to slightly yellow powder
Melting point	233.5 ° C.
Density	1.1 g/cm^3
Minimum assay	99.0%
Maximum limit of Impurities	
Assay of fatty acid	>82%
Free alkali (as NaOH)	<0.5%
Heavy metal (as Pb)	<0.005%
Chloride	<0.2%

Applications

- Used in saponification.
- For the production of metallic stearates.
- For the production of industrial lubricants various oil-based cosmetics

4.2 Experimental Apparatus

The experiments were carried out in 2.4 litre reaction vessel maintained at 70 ^oC. The reactor contents were agitated using impeller at 750 RPM. The impeller was connected to a variable speed motor, thus allowing changing the speed of the agitator.

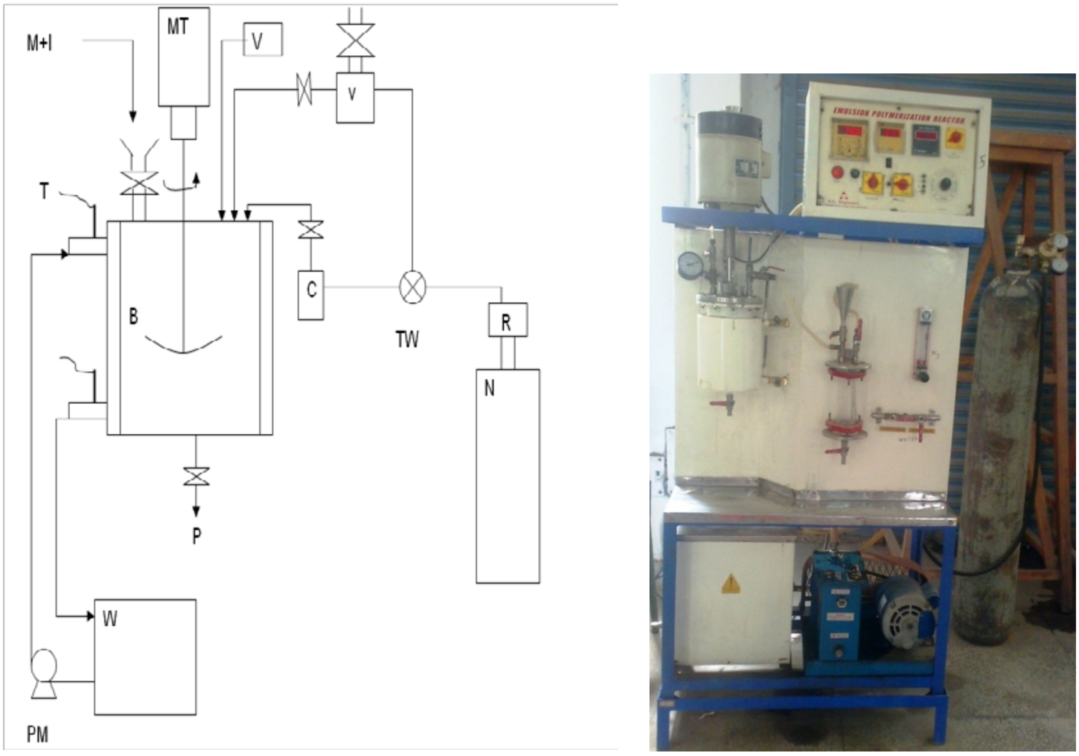


Fig. 4.4: A schematic and physical representation of batch emulsion polymerization process.

(B = batch reactor; N = N_2 gas cylinder; R = gas regulator; C = gas supply controller; TW = three way valve; v = initiator vessel; V= vacuum pump; MT = motor; T = thermometer; PM = pump; W = water tank; M = monomer; I = Initiator, P = Polymer)

Fig. 4.5: Parameters calculation in Batch reactor

Fig. 4.6: Close view of the reactor

Vessel contains the thermocouple with on-off controller to monitor the temperature of the reaction mixture. Sampling point is given at the bottom of the reactor. This on-off controller system is basic control system, if the temperature of the reactor is higher than set-point the heater is turned off and if the temperature is lower that set-point then the heater is turned on to reached the desired temperature. Notice that an on–off controller is based on the error between the set-point and measured output. Prior to the start of the reaction the reactor was purge with nitrogen gas to dissipate the oxygen if present. A nitrogen blanket was maintained throughout the reaction. Figure 5 illustrates the apparatus that was used, close view is given in figure 6 and 7.

4.3 Experimental Procedure

System with various amounts of initiator, surfactant were use .Table 5 summarize the various formulation that were investigated. These parameters were varied to create a wide range of conditions over which to access the reliability of the technique. Varying these parameters will ultimately affect the rate of polymerization.

Table 4.5: Summary of the formulations that were investigated.

Experiments	Monomer (ml)	Water (ml)	Initiator (gm)	Surfactant (gm)
1st Recipe	200	300	2	2
2nd Recipe	160	640	1.5	1.5
3rd (Flory) Recipe	160	640	1	2

The steps used in batch reactor for synthesis of polymer

1. Fill the hot water tank up to 2/3 depth, select the reaction temperature 70 °C and set it on the TIC (Temperature indicator controller) fixed at the front panel. Start the heater and wait until desired temperature is reached.
2. Inhibitor is removed by heating methyl Methacrylate at a temperature of 60°C.
3. Prepare the aqueous solution of emulsifier by thoroughly mixing with water.
4. Charge the aqueous solution of emulsifier and monomer into the reactor (total volume = 500ml) through the feed inlet fixed at the top head of the reactor.
5. Prepare the initiator solution in about 20 ml of water and store it in the vessel provided at the top rear of set-up under an atmosphere of N_2.
6. Evacuate the reactor up to 50 mm Hg with the help of vacuum pump provided at the base of setup then stop the vacuum pump and flash point with pure N_2 for some time.
7. Start the agitation at the rate of 700 to 750 rpm and simultaneously bubble the N_2 (@ 3 LPM into the reaction mixture. (Please ensure the absence of O_2 in the reactor).
8. Raise the temperature of reaction mixture to a constant reaction temperature by circulating hot water through the jacket of the reactor. Wait until the desired reaction temperature is reached and remains constant.
9. During the reaction, the stirring rate is to be maintained constant and N_2 supply has to be maintained all through.

10. After exactly one hour's mixing, add initiator to initiate the reaction from initiator vessel under N_2 pressure. Close the initiator feed valve after its delivery and also close the N_2 supply to the initiator storage vessel.
11. After the reaction is initiated, collect 20 ml of reaction mixture at regular intervals of time. Weigh the sample accurately, and add 50 ml of methanol containing small amount of hydroquinone as a terminator. The polymer formed will precipitate in each sample.
12. Dry the polymer in oven at 70 to 80 ^oC.
13. Repeat the procedure for different concentrations.

Experimental Calculations

Initial weight fraction of (MMA) monomer in the mixture

W_{f0} = (weight of monomer taken)/Total weight of mixture

$$W_{f0} = \frac{W_M}{W_T}$$

Average density of the feed mixture=total weight of mixture taken (gm)/total volume taken (ml)

$$\rho_{avg} = \frac{W_T}{V_T}$$

Weight of polymer = weight of sample before drying–weight of sample after drying

$$W_P = W_{samp1} - W_{samp2}$$

At a particular time "t" degree of conversion X

X=weight of dry polymer in the sample/ (weight of sample*weight monomer fraction)

$$X = \frac{W_P}{\left(W_{samp} * W_{f0}\right)}$$

For each time, "t", degree of conversion is calculated and data is fitted to a 4th degree polynomial passing through origin (0, 0)

$$X = a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$$

$$\frac{dX}{dt} = a_1 + 2a_2t + 3a_3t^2 + 4a_4t^3$$

4.4. Analytical Procedure

Several analytical techniques were employed. The following sections describe the various equipment and techniques, as well the procedures that were used.

Viscosity

The viscosity of polymer solution is basically a resistance force tending to cause the fluid to flow. The solution viscosity is empirically related to molecular weight for linear polymers. Therefore viscosity measurements constitute an extremely valuable tool for the molecular weight characterization of polymers.

Measurements of solution viscosity (η) are usually are made by comparing the efflux time t required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time t_0 for the solvent (of viscosity η_0)

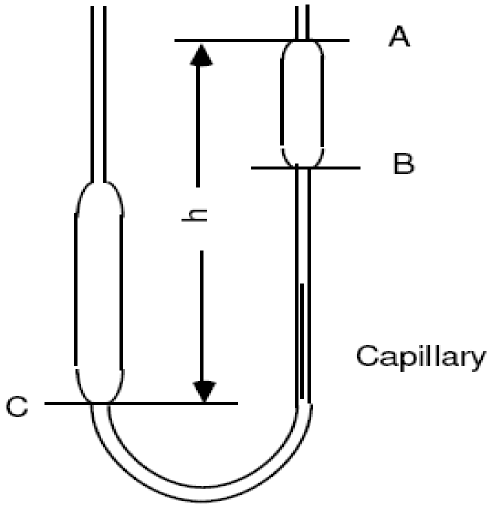


Fig. 4.7: Ostwald viscomter

Ostwald viscometer

Relative viscosity

$\eta_{rel} = \eta / \eta_0 = t / t_0$

Where η = viscosity of polymer solution

η_0 = viscosity of solvent

t = efflux time required for polymer solution

t_0= efflux time for solvent

pH

A pH meter is used to measure the pH of a sample. A typical pH meter containing a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the reading taken by pH meter. The probe measures pH as the activity of hydrogen ions surrounding a thin-walled glass bulb at its tip. The probe produces a small voltage (about 0.06 volt per pH unit) that is measured and displayed as pH units by the meter.

Calibration with at least two, but preferably three different buffer solution standards is usually performed every time a pH meter is used. One of the buffers has a pH of 7.01 and the second solution is selected having pH range near the pH of the sample to be measured usually pH 10.01 for basic solutions and pH 4.01 for acidic solutions at 25°C.

Electrical Conductivity

Electrical conductivity or specific conductance is a measure of a material's ability to conduct an electric current. When ever the difference in electrical potential occurs across the conductor, movable charges flow and an electric current is generated. The conductivity σ is defined as the ratio of the current density J to the electric field strength E: $J = \sigma E$

Conductivity is the reciprocal of electrical resistivity (ρ), and has the SI unit is $S \cdot m^{-1}$ and CGS units of inverse second (s^{-1}): $\sigma = 1/\rho$

An electrical conductivity meter (EC meter) measures the electrical conductivity of a solution.

The electrodes of the conductivity meter are usually made of platinum. An alternating current is passes through the outer pair of the electrodes and measured the potential between the inner pair of electrodes.

Mastersizer

A reliable apparatus Malvern Mastersizer 2000E was used for the study of particle size distribution and monomer droplets size. The system operates on scattering pattern of light. Samples are added to the unit and circulated after sonication distilled water used as dispersant. Drawback of the apparatus is that it is not able to detect the polymer particles in the presence of monomer droplets until approximately about 30% conversion has been reached. The reason behind may be that unit passes laser light through an optical unit and based on the way the light is scattered can deduct the size of the polymer particles that are present.

As the sample removed from the reactor for particle size measurement and immediately transfer to the Malvern mastersizer. In order avoid coagulation it is important to add sample as soon as it is removed from reactor. The agitation speed was set at 2000rpm, measurement time would be 12 seconds and that 12000 snaps would be taken on that time. At each sampling point a small amount of latex was taken out from the reactor for particle size measurement and transferred to a glass and without delay added to the Malvern.

It is imperative to add the sample as smoothly and quickly as possible. In order to lessen the coagulation of the particles it was also significant that the sample was added to mastersizer immediately after removal from the reactor to avoid the coagulation.

Fig. 4.8: Mastersizer 2000 E

End Group Analysis

Molecular characterization of polymers, particularly linear polymers, by end group count assumes importance, particularly for low polymers, and the relevant analytical data may be used for the determination of polymer molecular weight. Chemical methods as tools of molecular weight determination are only selectively applicable in systems where end groups are easily characterizable chemically. Counterfeit sources of end groups admitted into the system inadvertently and not taken into account in the assumed reaction mechanism become more and more consequential as the molecular weight increases.

Procedure

1. Weight accurate 5 gm of potassium hydrogen thylate/hydrochloric acid or KOH.
2. Dry for three hours.
3. Freshly boil water and cool. Mix with water [75 ml of water].
4. Take 0.1 N of KOH [10 ml].
5. Mix 10ml of sample in acetone.
6. When the colour start changing add phenophthaline.
7. Note down the reading.

4.5 Control Methodology

The word control implies “A device or mechanism used to regulate or guide the operation of a machine, apparatus or system. Prior to the 1940s, most chemical processing plants operated manually, with increasing labour and cost in the 1940s and 1950s it become uneconomical and near to impossible to operate plants without controllers. At that stage feedback controllers were introduced to the plant with little real consideration of, or appreciation for the underlying process dynamics. By the year of 1960s, chemical engineers were experimenting with the new developments in dynamic analysis and control theory.

A batch reactor starts from some initial conditions and proceed to change dynamically with time over some batch time. The batch reactor is usually small but their surface-to-volume area is very large so heat transfer is extreme good. In early seventeenth or eighteenth centuries most commercial reactors were batch (Richards and Congalidis 2006). In twentieth century, continuos reactors were developed for many reactions because they proved to be more economical in some systems. However, batch reactors have very important kinetic advantages for some systems, so they still widely used, even when production rates are high. Two important classical examples are polymerization and fermentation. Batch polymerization reactors allow the production of polymer with a narrower molecular weight distribution.

The polymer industry experienced very fast growth over the last five decades. The heart of the polymerization process is its reactor. The design and control of batch reactors are more difficult than CSTR's because of there time-varying nature. Defining of optimum variables or operating condition is quiet complex. Control of these systems are important because final product properties such as viscosity, molecular weight distribution, particle size distribution and composition depends upon temperature and few of these properties can be measured online.

Suffice it to say that the control of such complex systems like polymerization reactors is most challenging and difficult job.

Control Issues

- **Tuning**

Tuning of the controller is one of the major issues with batch reactor. Physically Steady –state condition cannot be achieved in the batch reactor hence tunning of the controller can be done with the help of trial and error method.

- **Time Constant**

In a batch reactor the reaction proceed in such a way that any disturbance in the initial or the intermediate condition would definitely affect the operation. Once the disturbance introduce in the process, it is often difficult to take remedial action.

- **Time Specific Control Action**

In batch process, the ability to influence the reaction decreases with time. It is generally required to take control action at very specific time instants. For example in control of PSD in emulsion polymerization the control actions need to apply at the time either the nucleation take place or before the nucleation is over.

- **Quality Related Measurement**

Process variables can be measured easily in most reactor system but in batch reactor usually long time-delay is often expected in analysing sample.

- **Trajectory Independent**

A batch process is considered satisfactory if the end-use properties are achieved. No matter what has been runway followed by the process trajectory.

- **Highly Non-Linear Nature**

Polymerization system is highly non-linear so that control system must capable of handling the non-linearity of the system.

4.5.1 Proportional-Integral-Derivative (PID)

4.5.1.1 Background

The PID controller was first arrived in the market in 1939 and has remained the most widely used controller in process control till present. A research has been performed in 1989 in Japan indicated that more than 90% of the controllers used in process industries are PID controllers and advanced PID controller. PI controllers are quite common, while derivative action is very susceptible to measurement noise.
“PID control” is the method of feedback control that uses the PID controller as the main tool. The fundamental structure of feedback control systems is shown in Figure 4.5.1 below, using a block diagram representation. The rationale of control is to make the process variable y follow the set-point value r. To accomplish this idea, the manipulated variable u is changed at the command of the controller.

Explanation of question how actual a controller works is the controllers first compares a measured value from a process with a reference set-point value. The difference known as error is then used to calculate a new value for manipulable input to the process that keeps the process measured value back to its desired set-point.

Control Law

The control signal c (t) is calculated from the value of error e(t) through a pre defined function

$c(t) = C[e(t)]$ (4.1)

The function C constitutes the control law

Proportional

To handle the present, the error is multiplied by a constant P (for "proportional"), and added to (subtracting error from) the controlled quantity. P is only valid when a controller's output is proportional to the error of the system. Whenever the error is zero, a proportional controller's output is zero.

This mode produces a control signal that is proportional to the error (Ramagnoli and Palazoglu 2006)

$c(t) = K_c\, e(t) + c_b$ (4.2)

K_c represents the proportional gain and defines how sensitive the controller is to error present in the system

Integral

To learn from the past, the error is integrated over a period of time, and then multiplied by a constant I, and added to the controlled quantity. Integral averages the measured error to find the process output's average error from the set point. A simple proportional system either oscillates, moving back and forth around the set point because there's nothing to remove the error when it overshoots, or oscillates or stabilizes at a too low or too high value.

The controller signal for this mode is produced by the integral action.

$c(t) = kc / \tau_I \quad de(t)/dt + c_b$ (4.3)

The new parameter τ_I represents the integral time constant or the reset time. With this mode the controller responds effectively to the error that builds up over time.

Derivative

To handle the future, the first derivative over time is calculated, and the multiplied with constant D. The response towards change in the system is controller by the derivative term. Larger the value of derivative term, the more speedily the controller responds to the changes in the process's output.

In this mode, the controller signal responds to the rate of the change of error signal,

$$c(t) = kc\ \tau_D\ de(t)/dt + c_b \quad (4.4)$$

The new parameter τ_D is introduced as the derivative time constant. The role of this mode is to judge the change in the error.

This is helpful in order to analyze whether it will actually reach a stable value or not. If the values are incorrect, the controlled process input can oscillate, and the process output may never keep on the set point.

4.5.1.2 Control Strategy

Simulations of the various processes were conducted in MATLAB using single-loop feedback controller. A common feedback loop is shown in Figure 4.9 below where

C(s) = the controller transfer function
G(s) = the overall process transfer function.
e = the control error
u = the controller output
y_{sp} = the set-point of the controlled variable
y_d = the disturbance signal
y = the response of the controlled variable

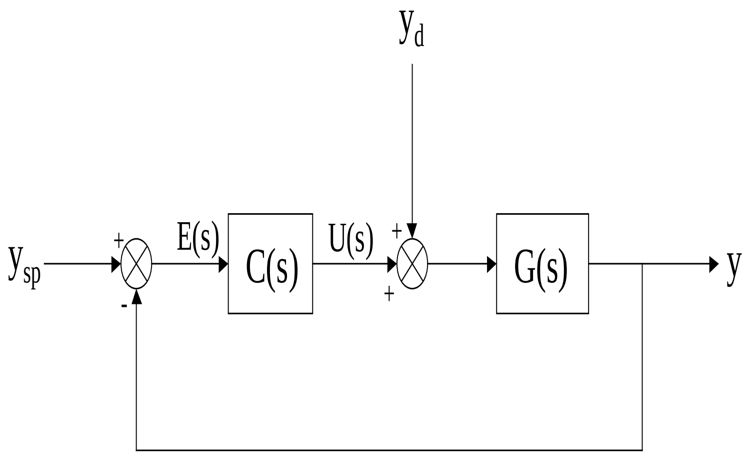


Fig. 4.9: General feedback controller setup.

The equation describing a PID controller is the sum of all three equations explained above for proportional, Integral and derivative action.

$$u(t) = \bar{u} + K_c e(t) + \frac{K_c}{\tau_I}\int e(t)dt + K_c \tau_D \frac{de(t)}{dt} \tag{4.5}$$

Where

$\bar{u}$ = bias value

e = error

K_c = controller gain

τ_I = integral (or reset) time

τ_D = derivative (or rate) time

The controller gain, K_c, determines how much the output from the controller changes for a given change in error. Thus K_c establishes the sensitivity of the controller to an error, that is, how much the controller output changes per unit error. The larger the value of K_c, the more the controller output changes for a given error, the response becomes fast. On the other hand, for most control processes there is a maximum value of K_c, beyond which the process becomes unstable. The controller in Eq. (4.5) is a PID controller. Its main negative aspect is its lack of ability to eliminate the steady-state errors that occur after a set-point change or a sustained load disturbance.

The third term in Eq. (1) is the integral or reset control term, which integrates the error, and is answerable for eliminating the steady-state error offset. The value of the integral time, τ_I, tells how much weight is given to the integral action. When the value is lower, the weight given to this term should be more. The drawback of using τ_I is that it tends to show oscillatory overshoot response in the controlled process and thus cut down the system stability. The controller shown with the first three terms in Eq. (1) is PI controller.

The last term in Eq. (1) is the derivative or rate control term. The function of derivative term is to predict the behavior of the error signal. By providing this predicted control action, the derivative mode used to stabilize the controlled process, and is often used to neutralize the destabilizing tendency of the integral mode. The main drawback of a PID controller is that a sudden change in the set-point will cause the derivative term to become very unstable and thus endow with a large derivative "kick" to the control element.

4.5.1.3 Control Design

By taking Laplace transforms, Equation (1) becomes the transfer function:

$$C(s) = K_c\left(1 + \frac{1}{\tau_I s} + \tau_D s\right) \tag{4.6}$$

This describes an ideal PID controller

The polymerization kinetic model explained above was simulated in matlab. The PID controller was first used in 1939 and is the most widely used controller in the market till today. PID controller is a feedback controller as shown in figure 4.10 below, using a block diagram representation. As shown in the figure, the process is the objective to be controlled.

In our study two different strategies is used for PID to control the temperature of the reactor. First controller strategy used is PID controller using split range and second is PID controller using heater power as manipulative variable. Split range is a controller configuration where a single PID controller outputs to two control valve. In our case PID output signal controls the hot-water and cold water steam as per required. The range of signal is constrained between 0-1.Flow rates are used as manipulative variable and reactor temperature is used as control variable (Luyben 2007). The logic of PID controller is given in figure 4.10 below where proportional, integral and derivative function is clearly defined.

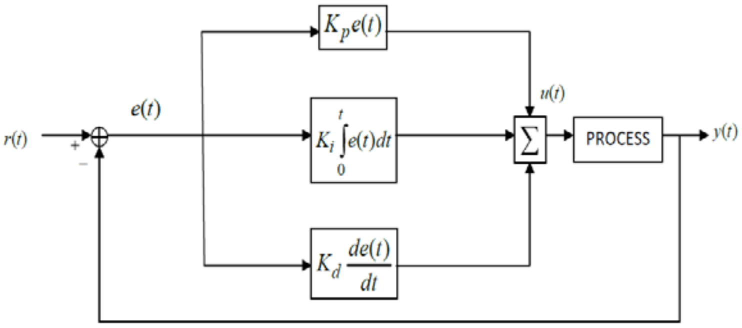


Fig. 4.10: PID control Logic

In second strategy heater power is used as manipulative variable, which may vary from 40-140 W in our case optimum value is 90W. Heater power value is highly correlated with flow rate of stream. The generated results were first compared with experimental data and then further proceeds towards comparison of strategy. Before implementing the controller tunning parameters should be optimised first to achieve the good performance of the controller.

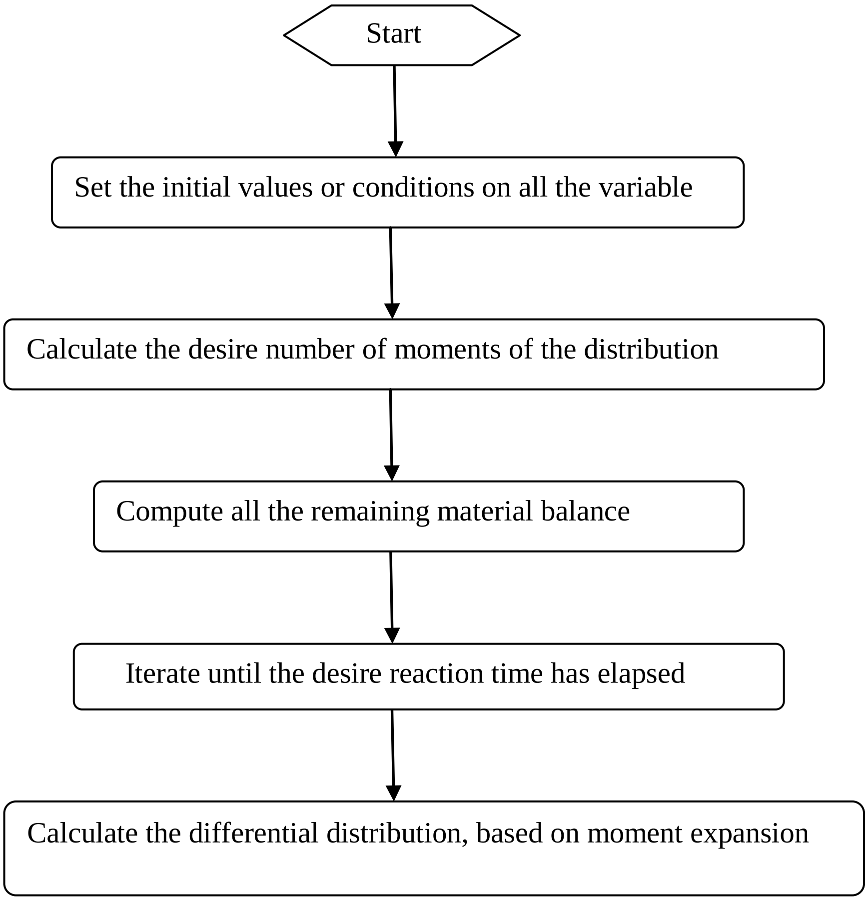


Fig. 4.11: Alogorithm of dynamic simulation

4.5.1.4 Tuning of PID

PID tunning can be done by using Ziegler and Nichols (Z-N) and Cohen and Coon (C-C). In a batch reactor since steady-state can not be achieved hence tunning of the controller become problematic. Trial and error method was used in our case for tunning of PID. Everyone faced with the task of adjusting or optimization of the control parameters to obtain desire behaviour with the control system. There are many ways to do this but the simpler way or may be the only way to optimize the parameter where steady-state cannot be achieved. Increase the gain until the system starts to oscillate, and then lessen the gain by using an appropriate factor.

I. Effect of controller Gain: Increase in value of controller gain over its optimum value oscillation increases, below that again found oscillations. Notice that increasing the controller gain reduces the offset and speeds up the response. In practice , there are time delays or other model uncertainties and that may cause closed loop to be unstable with high K_c value(Bequette 2003).

II. Effect of τ_I: Change in value cause the overshoot and required more time to settle down to its set-point value. Too small value can cause the system to be unstable

4.5.2 Model Predictive Control (MPC)

4.5.2.1 Background

The performance of the Model Predictive control in batch reactor is investigated in this study. MPC is the family of controller in which there is a direct use of explicit model. MPC is a user friendly and applicable technique for different needs, where the objective function and optimization are flexible (Nagy and Braatz 2003).

The advantages of MPC over other control system are as follow:

1. It can handle input or output constraints directly.
2. It can use step and impulse response data.
3. It gives satisfactory performance with the time delays and also with high non-linearity of the system like polymerization system.
4. It is robust in most cases.

5. It is simple to implement.
6. It can optimize over a trajectory.
7. It controls either simple or complex processes.

We aimed to investigate MPC performance for batch emulsion polymerization reactor. A SISO (single- input single- output) MPC is used for the control of temperature of the reactor. In the simulation study MATLAB is used. The performance of the designed controller is checked for set-point trajectory and disturbance rejection for the system.

The mathematical model utilized is important when MPC is implemented, as MPC requires models with satisfying prediction quality.

Various criteria should be fulfill before implementing MPC

- The model should be an ODE system.
- Stiff system should be avoided, or stiffness reduction should be performed.
- The calculation time should be as rapid as possible, so time-consuming calculations should be avoided if possible.
- The parameters in the model have to be possible to estimate. Estimated parameters will capture mistakes in the model.

At present MPC is the most widely used control algorithm in the chemical industries.

4.5.2.2. Control Strategy

The strategy of the MPC is given in fig 14. At the present time n, the future outputs (y (n + k) for k= 1……P) of the system over a prediction horizon (P), are predicted at each instant by using the model, knowing value upto n (past inputs and outputs) and future inputs (u(n), u(n+1)……u(n+C)) where c is the control horizon. In the figure 4.12 the past inputs are shown by solid line and future inputs are shown by dashed lines. The set of future inputs which minimize the objective function are applied to the system. Figure shows the basic structure of MPC. A model is used in the order to predict the future outputs and inputs of the system. A comparison made between the predicted output of the plant and the reference trajectory of it and the future error of the plant are calculated at each step.

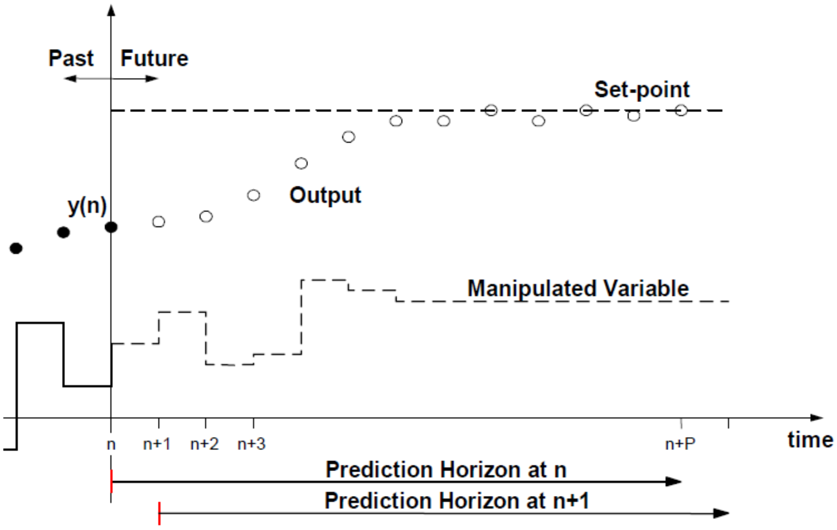


Fig. 4.12: MPC strategy

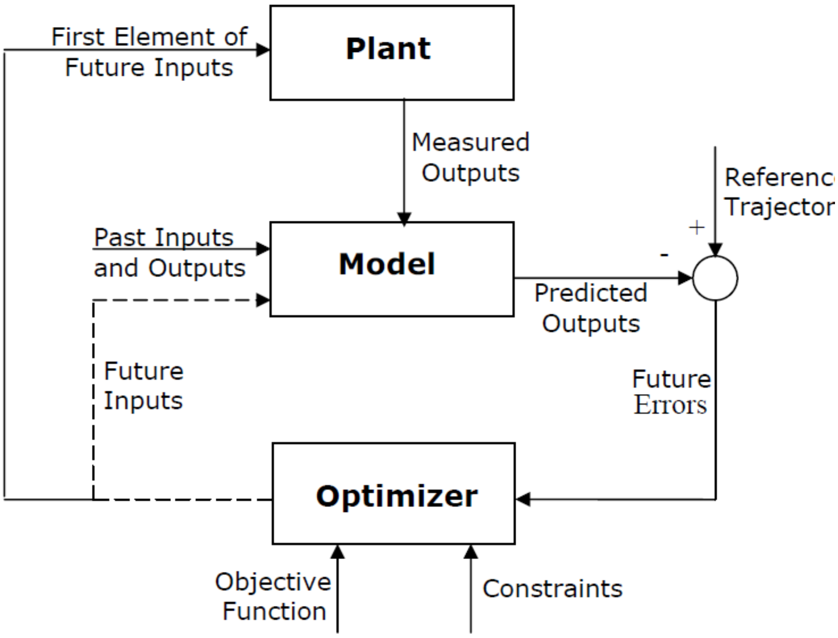


Fig. 4.13: Basic structure of MPC

Model predictive control (MPC) possesses many attributes which makes it successful approach and they are:

1. The basic idea of MPC does not require complex mathematics.

2. All of the basic MPC components can be tailored to the details of the problem in hand.
3. It is often the resolution of problem s such as satisfying control or output constraints.

4.5.2.3 Controller Design

Temperature control of a batch reactor depends mainly on heating and cooling system of the reactor either by flow rates of cooling water or by heater power. In this study we use heater power as manipulative variable. The model developed and solved for simulation by Runge-Kutta integration method. Model predictive control is a generic term for a widely used class of controllers(Cueli and Bordons 2008; Harnischmacher and Marquardt 2007).

Model predictive control is one of the most widely used advance control method. MPC presented a set of future manipulated variable moves is calculated to minimize the objective function over a prediction horizon based on the sum of squares of the differences between model predictive output and desire output(Nagy and Braatz 2003).

The Tool used in MATLAB to compute the manipulated variable moves subject to constraints is cmpc, which solve optimization problem by using QP. The function requires model used for estimation the plant and model which state the controller in step format, limits of both input and output variable and weights of output and manipulated variables.

$$[y_p, u] = cmpc(plant, model, ywt, uwt, M, P, tend, r, ulim, ylim) \tag{4.7}$$

There is some assumptions taken for MPC

1. The output sequence y(k) for ylim is also observed
2. The input u(k) is a continuing driving function of the process
3. The noise is a random sequence with zero mean and is uncorrelated with u(k).

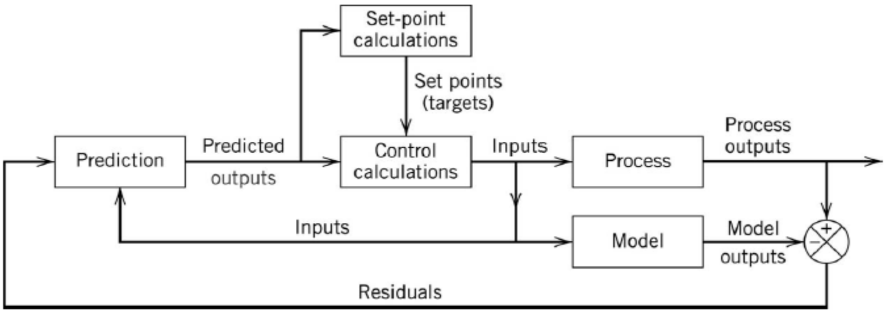


Fig. 4.14: MPC Block Diagram

The structure of MPC is shown in Figure 4.14 The difference between the predicted and actual output variables serve as a feedback signal to the prediction block and are utilized in two types of control calculations that are performed at each sampling instant. These are set point and control calculations.

In MPC future value of output variable is predicted using a dynamic model of the process and current measurements. The control calculations are based on both future predictions and current measurements. Usually MPC used when PID is unable to control the system or when there are some constraints or limitations on process variable and manipulative variable. In this study we compare the performance of PID and MPC for controlling molecular weight of a batch emulsion polymerization.

The flow chart of MPC used in matlab programming if shown in Fig 4.15

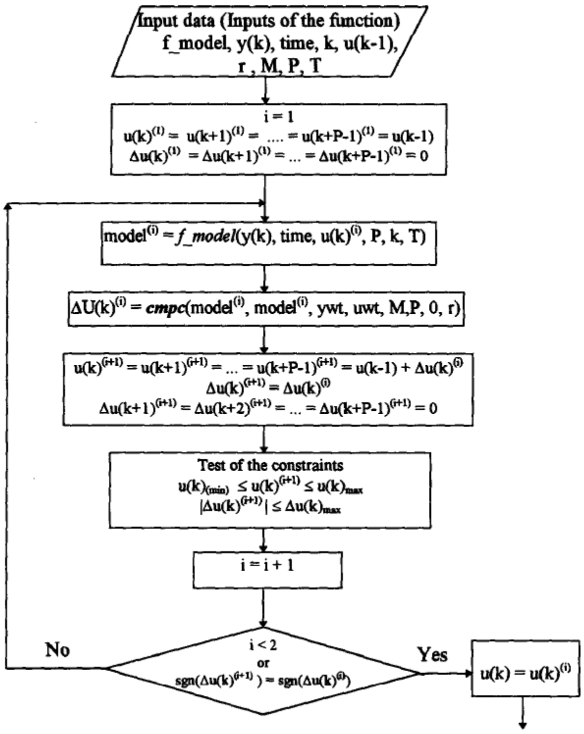


Fig. 4.15: Flowchart for MPC

An advantage of MPC is that inequality constraints can be incorporated in both the set-point and control calculations. These constraints are a result of physical limitations on plant equipment, and set-points for control calculations are often calculated from an economic optimization of the process based on a steady state process. Objective of the control calculations in the control block is to determine a sequence of control moves, so predicted response moves to the set-point in an optimal manner. The quality of MPC dependents on an accurate process model that has to be available and this model have to capture interactions between input, output and disturbance variables.

4.5.2.4 Parameters Tuning

The main tuning parameters for MPC are the control horizon (C), weight tunning (w) and prediction horizon (P).

The model horizon M should be selected to be equal of 99 % of the settling time used. The control horizon C, is used in the optimization calculation in order to reduce the predicted errors. It can be used as 60% of the open loop settling time. Large value of control horizon leads to a robust controller which is insensitive to model errors. Another tunning parameter is prediction horizon P is also used in optimization calculation. Increasing P results in conventional control action but also increases the computational effort. Usually P is chosen as 85 % of model horizon. The weight tunning factor for predicted error is usually selected in terms of identity matrix I.

Predictive Horizon (P)

The prediction horizon specifies the number of future plant outputs to be calculated using the model, the past control actions and the computed future control action. Increasing the prediction horizon results in more conservative control action that has a stabilizing effect, but it increases the computational effort. Large value of prediction horizon would be recommended for only very good model and having limited feedback.

Control Horizon (C)

The control horizon specifies the number of future control actions to be calculated, in order to minimize the objective function, and used in the optimization step to minimize the prediction error. A large value of control horizon (C) than prediction horizon tends to excessive control actions and smaller value leads to robust control. Computational effort is also reduced by decreasing the value of control horizon.

Weight Tuning

Weight tuning is mainly used for move suppression to prevent oscillations behaviour. Increasing weight will prevent oscillations but large value tends to slow down the response time.

In all three cases a lot trial and error tuning had to be performed to get the required optimum value.

4.5.3 Neural Network Predictive Control (NNPC)

4.5.3.1 Background

Neural networks have been able to approximate any continuous non-linear functions and have been applied to non-linear process modeling. The most commonly used is feed forward neural network (Hossen, Hussain et al. 2011; Kuroda and Kim 2002; Ng and Hussain 2004; Su and McAvory 1993). The layer of neural network is consists of neurons which are connected to the neurons of same layer or the adjacent layer. Inputs to an input layer propagated through the interconnection of the input neurons to the neurons of adjacent layer which is known as hidden layer.

Neural network is hidden layer structures which essentially define the mechanism of a feed forward network. Each interconnection has associated with a scalar weight which acts to modify the strength of the signal passing through it.

The neurons associated with hidden layer performs two task

1. They sum the weighted inputs to the neurons.

2. And then pass the resulting summation through a non-linear activation function.

Neural network model is divided into two sets: training data set and testing data set. During network training the network error on the testing data is monitored continuously. Validation is the last step of the training of the neural network which itself minimize the error and check the performance of the network with regression analysis.

4.5.3.2 Control strategy

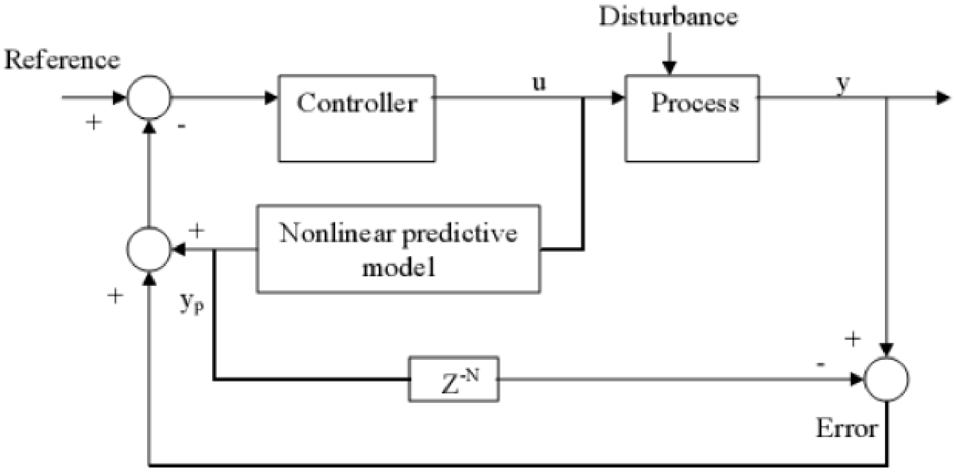


Fig. 4.16: Block diagram of NNPC

In neural network the multilayer feed forward NN architecture is used to model underlying plant. It has hidden layer with sigmoid activation functions. The neural network weights are initialized with small numbers. The inputs of the neural network are the control signals and the past of the plant outputs. Training is used for the neural network with the help of this NN predicts the output of the plant through the prediction horizon.

Neural networks have been applied very successfully in the identification and control of dynamic systems. The use of a neural network for process modelling is shown in Figure 4.17. The unknown function may correspond to a controlled system, and the neural network is the recognized plant model. This neural network is thus two-layer networks, with sigmoid transfer functions in the hidden layer and linear transfer functions in the output layer.

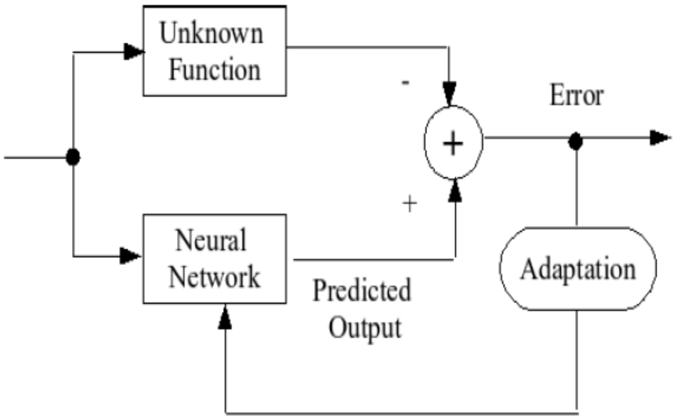


Fig. 4.17: Neural Network as function approximators.

The prediction error between the plant output and the neural network output is used as the neural network training signal. The NN plant model uses previous inputs and previous plant outputs to predict future values of the plant output. The structure of the neural network plant model is given in the Figure 4.18, where *u(t)* is the system input, *yp(t)* is the plant output, *ym(t)* is the neural network model plant output, the blocks labelled TDL are tapped delay lines that store previous values of the input signal, ***IW*** *i,j* is the weight matrix from the input *j* to the layer *i*. ***LW*** *i,j* is the weight matrix from the layer 1 to the layer 2 and here b is value of biases.

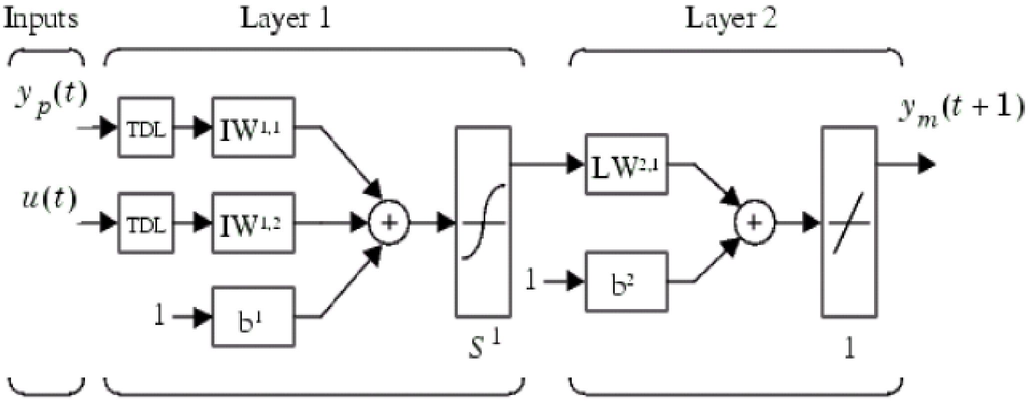


Fig. 4.18: Structure of the neural network plant model
(Vasickaninova and Bakosova 2009)

4.5.3.3 Control Design

The neural network predictive controller as illustrated in Fig. 4.19 implements neural network to predict future plant performance.

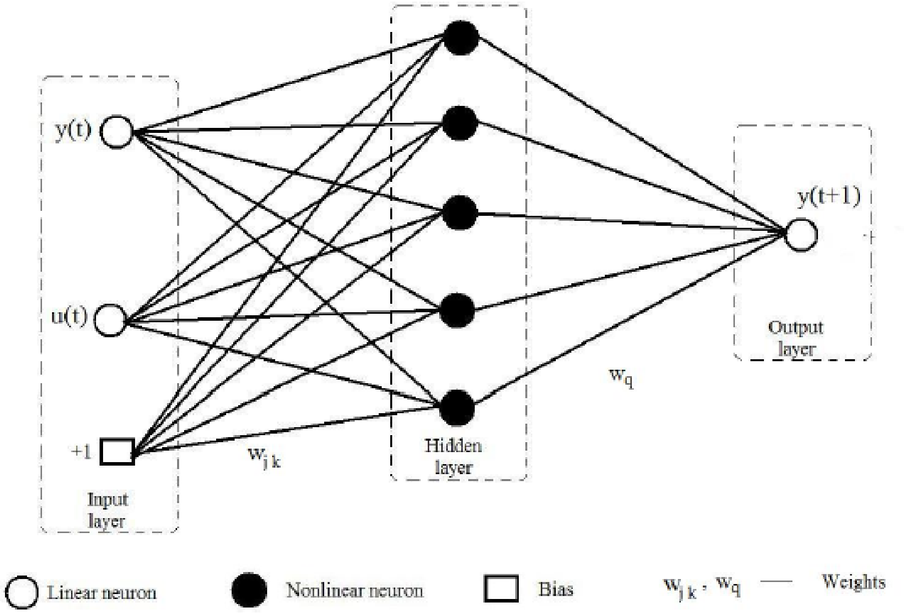


Fig. 4.19: Neural Network structure

For linear systems, the choice of control horizon is normally decided by the time to achieve a steady state. For nonlinear systems, there is no definite selection criteria provided. Hence, the simulation results (trial and error method) are normally used for the determination of the prediction horizon. In a batch system steady state condition can be never achieved hence it is easy to tune the network through trial and error method. With the simultaneous solution and optimization approach, the increase in size of the Cost horizon increases the size of constrained nonlinear optimization problem. The performance of the controlled variable i.e. reactor temperature was observed to determine the best value for the prediction horizon. It was observed that small values for the prediction horizon show oscillatory or unstable responses(Hossen, Hussain et al. 2011).

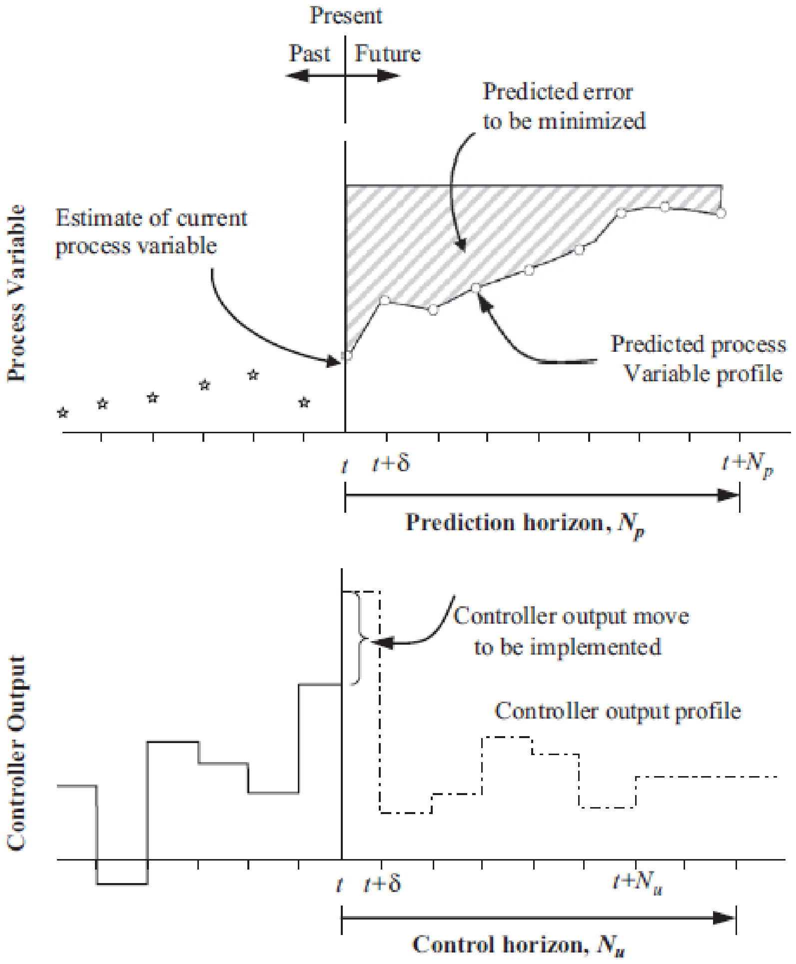


Fig. 4.20: Basic strategy of Neural Network control.

(Hossen, Hussain et al. 2011)

4.5.3.4 Neural Network Training

In the process of NN training, the error, which is the difference between the desired response and the actual response, was calculated. The error was then propagated backward through the network. The error was used to adjust the weights and threshold values of the neuron. This was done to ensure that in the next round, the error would be reduced for the same inputs. Fig.4.21 illustrates the basic concept of neuron weight adjustment.

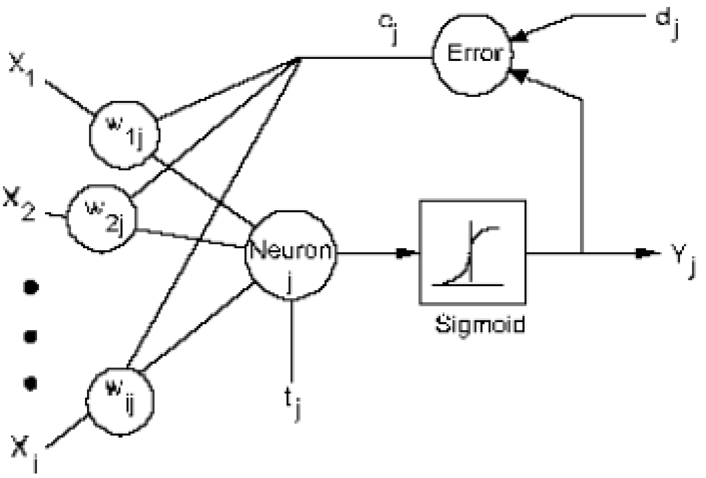
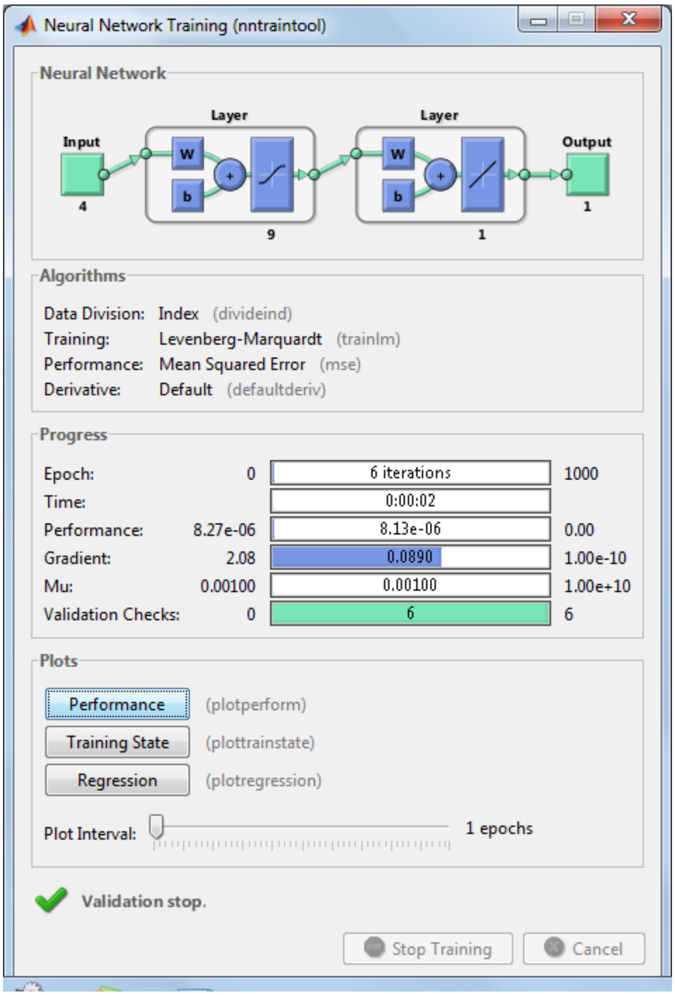


Fig. 4.21: Neuron Weight Adjustment

We train the neural network using back propagation as discussed above in Section. We are using the Levenberg Marquardt algorithm for weight updating in our model, and this algorithm is implemented in the Matlab. While training the neural network using an error function on the training data set, we investigate the performance of the network on the validation data set. Poor generalisation will show as an increasing error function on the validation data set.

This network first trained using data collected from the open loop using same model. The procedure for selecting the network parameters is called training the network. The Levenberg-Marquardt (LM) algorithm is very efficient for training. The Levenberg Marquardt algorithm is an iterative technique that locates the minimum of a function that is expressed as the sum of squares of nonlinear functions.

LM algorithm is used to solve non-linear square problems. It uses iterative improvement to parameters value in order to reduce the sum of square of the error. It is a combination of two improvement methods; one is guass- newton method and second is gradient descent method.



Data Division: Index (divideind)
Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Derivative: Default (defaultderiv)

Epoch:	0	6 iterations	1000
Time:		0:00:02	
Performance:	8.27e-06	8.13e-06	0.00
Gradient:	2.08	0.0890	1.00e-10
Mu:	0.00100	0.00100	1.00e+10
Validation Checks:	0	6	6

✓ Validation stop.

Fig. 4.22: Training of Neural Network

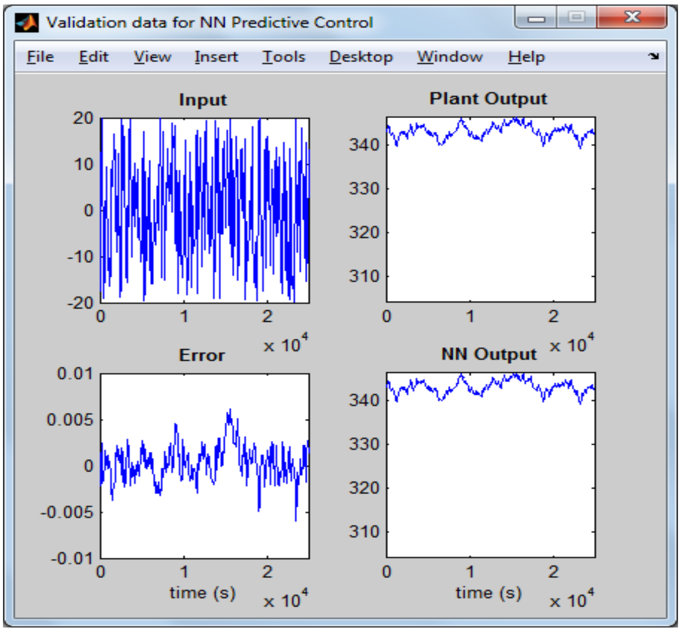


Fig. 4.23: Training Analysis

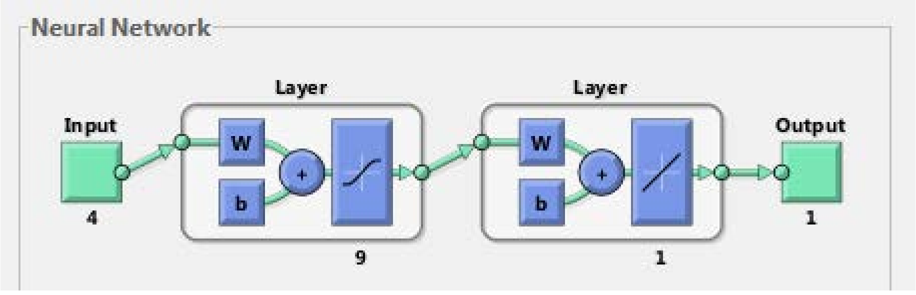


Fig. 4.24: Structure of neural network.

4.5.3.5 Tuning

There are a number of parameters that we have to tune: the control horizon Nu, the costing horizon N2 and the control weight and hidden layer. The accumulation of errors in the prediction of future plant outputs limits the horizon N2. It is not possible to increase N2 beyond a certain limit, where the accumulated error starts to have impact. The costing horizon has to be large enough to extend over the dynamics of the plant. The costing horizon has to be large enough to allow the algorithm to see the outcome of the predicted controls.

At the same time, an increased N2 increases the computation time. The choice of control horizon Nu has nothing serious impact on the computational results.

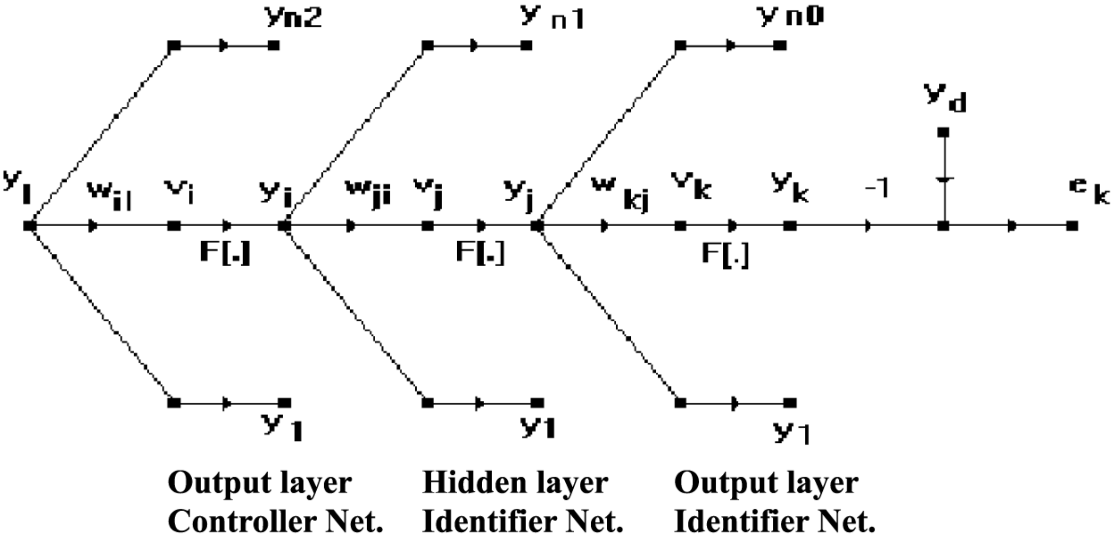


Fig. 4.25: Flow diagram of neurons signals

Control Horizon (Nu)

The quality of any controller can be improved by optimizing there parameters. The effect of parameters on the control quality of the controller are analysed here. The control parameters which have been optimized in this study are Control weight, Control Horizon (Nu) and neurons of hidden layer in the neural network.

Control Weight

Increase in control weight causes the oscillatory behaviour in the control variable. The Nu does not affect the quality of NNPC strongly but during performance analysis. At the same time, an increased Nu increases the computation time. The choice of control horizon Nu has serious impact on the computational results

Hidden Layer and number of Neurons

A single Hidden layer was used in the neural network, the number of neurons highly affect the control ability of the controller. The optimum value of neurons was found using trial and error method. Increase in the number of neurons cause controller sluggish in nature.

This neural network method, however, has two drawbacks. First, the neural network training process must be repeated when the desired output response has been changed. This restricts the practicality of the control method. Second, due to the existence of constraints, the control law may not be a continuous or continuously differentiable function of $\boldsymbol{x}(k)$. As a result, accurate neural network training may be difficult.

In this section, neural network methodology for modeling the PMMA batch reactor process has been introduced to overcome various modeling difficulties. This methodology includes the following steps:

i. Used the same model involving temperature varying kinetic parameters.

ii. Generate reactor temperature profiles by conducting several reaction runs using predefined operating conditions.

iii. Use the generated temperature profiles and the mechanistic model to estimate the kinetic parameters.

iv. Use NN modeling methodology to model the estimated kinetic parameters under the reactor operating conditions.

4.6 New Issues on Optimization and Control

There are limited industrial applications on the dynamic optimization and control of polymerization processes. There are some reasons for lack in quality control application for polymerization processes and they are as follows (Kiparissides 2004):

[1]. Polymerization processes are highly non-linear, containing large number of time varying kinetics and transport parameters.

[2]. Modeling of polymerization system leads to non-linear integro - differential equations. This nature does not allow their direct use for the design of non-linear controller that can be easily implemented in real-time.

[3]. On-line measurement of MWD, CCD, LCB, PSD, etc is very difficult and the available secondary measurements are often insufficient.

[4]. Formulation of distributed molecular properties is not easy especially when the end-use properties of the product need to be controlled.

Chapter-5
Experimental Results and Discussion

5. Experimental Result and Discussion

Experiments have been done in our laboratory in batch for Methyl-Methacrylate system. Few results are tabulated in Tables 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6. This is well documented system for which most of the kinetic and physical parameters are available in the literature.

PMMA can be produced using a variety of polymerization mechanisms. The most common technique is the free radical polymerization of MMA. This unique polymerization process that is heterogeneous in nature exhibits very different reaction mechanisms and kinetics compared to bulk or solution free radical polymerization. Surfactant is generally required to stabilize the colloidal system; otherwise, latex particles nucleated during the early stage of polymerization may experience significant coagulation in order to reduce the interfacial free energy. This feature may also come into play in determining the number of reaction loci (i.e., polymer particles) available for the consumption of monomer.

The free radical polymerization of acrylates and methacrylates is a chain polymerization across the double bond of the monomer. The free radical polymerization of methyl methacrylate can be performed homogeneously, by bulk or solution polymerization and heterogeneously using suspension or emulsion polymerization. It is relatively easy to perform free radical polymerizations.

In order for polymerization to proceed successfully, it is mandatory to remove all oxygen from the polymerization. Oxygen if present acts as a radical scavenger and it is able to terminate free radical polymerizations. Radicals can be generated with radiation, chemical agents or heat.

Emulsion polymerization involves the propagation reaction of free radicals with monomer within the monomer–swollen polymer particle dispersed in the aqueous phase. These discrete hydrophobic particles are stabilized by surfactant sodium Oleate in our case. Micelles are formed when the level of surfactant is greater than its critical micelles concentration (cmc).

Particle nucleation is generated via the capture of radicals by micelles. Water born polymerization such as emulsion polymerization are of great importance in industry application as they provide environmental friendly process, removal of heat of the reaction is quite manageable during polymerization and assume the viable handling of the final latex product having a low viscosity. Research in free radical/controlled polymerization has been increased appreciably during the past two decades.

The most striking feature of emulsion polymerization is the segregation of free radicals among the discrete monomer-swollen polymer particles. This will greatly reduce the probability of bimolecular termination of free radicals and, thereby, result in a faster polymerization rate and polymer with a higher molecular weight. This advantageous characteristic of emulsion polymerization cannot be achieved simultaneously in bulk or solution polymerization. Transport of monomer, free radicals and surfactant to the growing particles and partition of these reagents among the continuous aqueous phase, emulsified monomer droplets (monomer reservoir), monomer swollen polymer particles (primary reaction loci) and oil–water interface are the key factors that govern the particle growth stage.

The colloidal properties of latex products are of great importance from both academic and industrial points of view. Some representative properties include the particle size and particle size distribution, particle surface charge density (or zeta potential), particle surface area covered by one stabilizer molecule, conformation of the hydrophilic polymer physically adsorbed or chemically coupled onto the particle surface, type and concentration of functional groups on the particle surface, particle morphology, optical and rheological properties and colloidal stability. Batch emulsion polymerization is commonly used in the laboratory to study reaction mechanisms, develop new latex products and obtain kinetic data for process development and reactor scale-up. Most of the commercial latex products are manufactured by semi-batch or continuous reaction systems due to the very exothermic nature of free radical polymerization and rather limited heat transfer capacity in large-scale reactors.(Chern 2006)

Emulsion polymerization had a physical gain over the other and is safe, faster and easy to control for the reason of its colloidal system and in some cases product can be used without further separations. Additional physical advantages are less thermal and less other physical problem in contrast to other processes like bulk polymerization. In spite of physical gain there is kinetic lead also, that is emulsion polymerization is the merely process where relationship between molecular weight and rate of polymerization is not inverse similar to other processes. Emulsion polymerization facilitates the change in molecular weight without altering rate of polymerization just by adding chain transfer agents. Up to date leaning clearly point out that emulsion polymerization is an important field and be worthy of further research and development.

Track down from literature the monomer conversion is shown below in Fig.5.1 the rate of consumption of monomer is relatively long-drawn-out, but the molecular weight of polymer builds up hurriedly because of chain addition reaction. The conversion first increases and then gradually levels off with the progress of polymerization. After a certain conversion, the termination rate constant (k_t) becomes chain length dependent due to the influence of diffusion of free radicals on the bimolecular termination reaction. Under these circumstances, k_t decreases significantly with increasing conversion, thereby leading to the severely retarded bimolecular termination reaction and then auto-acceleration of the polymerization rate. This is termed the gel effect or Trommsdorff effect.

The polymerization rate either is constant or increases slightly with time during interval II (explained in chapter 2). The latter behaviour, which may begin immediately or after a constant rate period, is an outcome of the Trommsdorff effect (or gel effect). The polymer particles increase in size as the monomer droplets decrease.

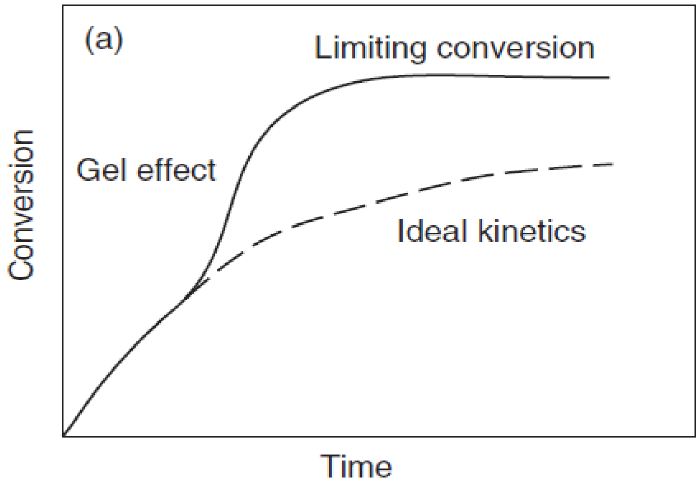


Fig. 5.1: Relationship of conversion with time found in literature.

The experiments were done in our laboratory with three different recipes and results pictured in form of graphs although a vast research has been done from last two decades on this simple study but still we give brief description of the process. Started with rate of polymerization and conversion of monomer as the reaction proceeds with time we have taken number of runs in which few are given which shows the reproducibility of the results. Different runs have been taken at different time and plotted in Fig 5.2, 5.3, 5.4 and tabulated in table no 5.1, 5.2 and 5.3 for rate of polymerization for recipe 1, 2 and 3 respectively..

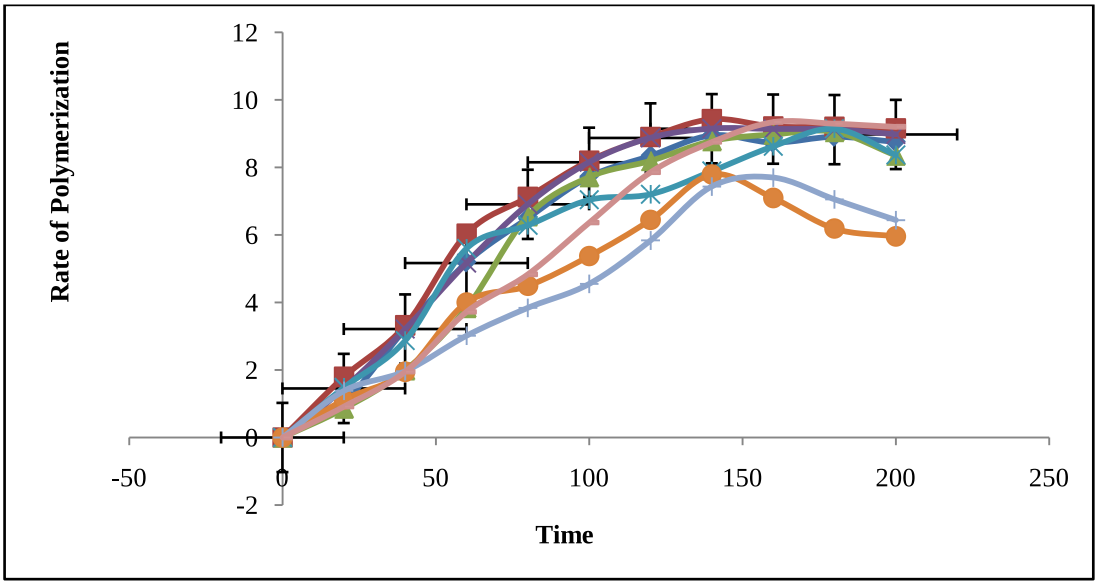


Fig 5.2: Comparison of runs taken at different time for rate of polymerization (using 1st recipe).

Table 5.1: Rate of Polymerization using 1st recipe.

Time	Run 1	Run 2	Run 3	Run 4	Run 5
0	0	0	0	0	0
20	1.0519	1.7955	0.8571	1.4532	1.4809
40	3.2147	3.3199	1.992	3.2145	2.8717
60	5.1849	6.0336	3.8398	5.1693	5.6013
80	6.5008	7.1213	6.5592	6.9091	6.2859
100	7.7239	8.1982	7.71843	8.1558	7.03984
120	8.3444	8.9007	8.199	8.8766	7.20553
140	8.9506	9.4285	8.7864	9.1504	7.8911
160	8.7367	9.2145	8.9798	9.1381	8.6264
180	8.9078	9.2002	9.0576	9.1233	9.1443
200	8.7543	9.1542	8.356	8.9798	8.3676

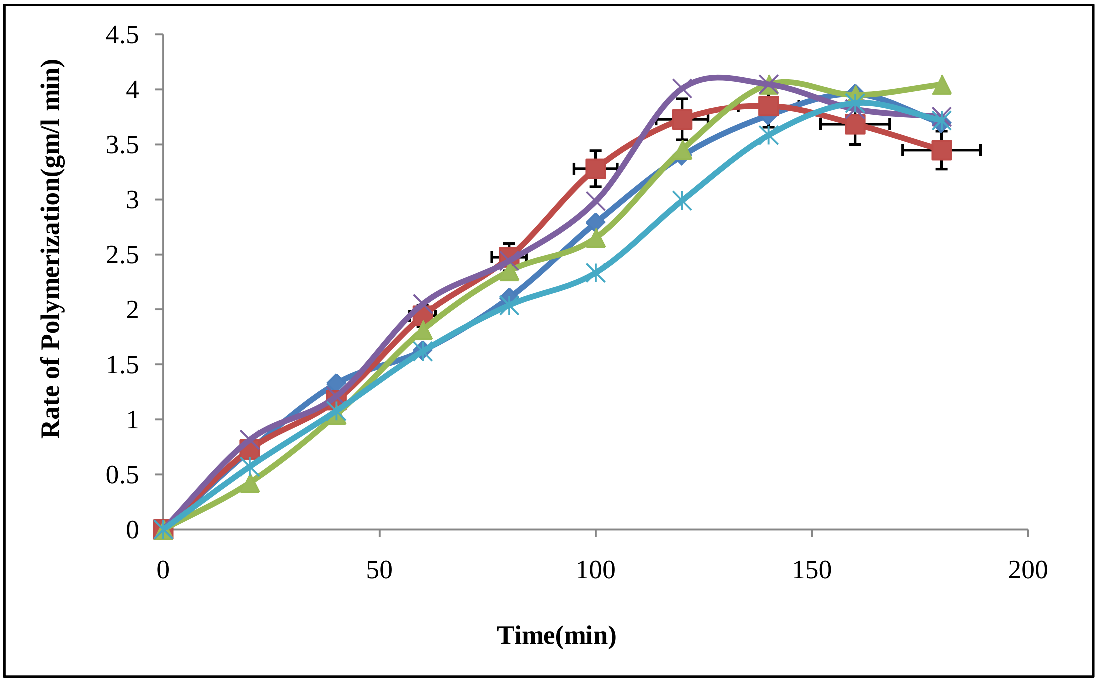


Fig. 5.3: Comparison of runs taken at different time for rate of polymerization (using 2nd recipe).

Table 5.2: Rate of Polymerization using 2nd recipe

Time	Run 1	Run 2	Run 3	Run 4	Run 5
0	0	0	0	0	0
20	0.21725	1.00674	0.42504	0.81486	0.57133
40	1.226143	1.17395	1.0429	1.40944	0.7744
60	2.262525	1.74128	1.81214	2.93484	0.916183
80	2.60056	2.4737	2.34791	3.44405	1.803756
100	2.88799	2.7779	2.6494	4.118402	2.332704
120	3.69731	3.42713	3.45202	4.30661	2.988522
140	3.76449	3.84799	4.043295	4.04329	3.58265
160	3.95852	3.58265	3.9476	3.61823	3.27366
180	3.691704	3.34718	4.34288	3.14833	3.11685

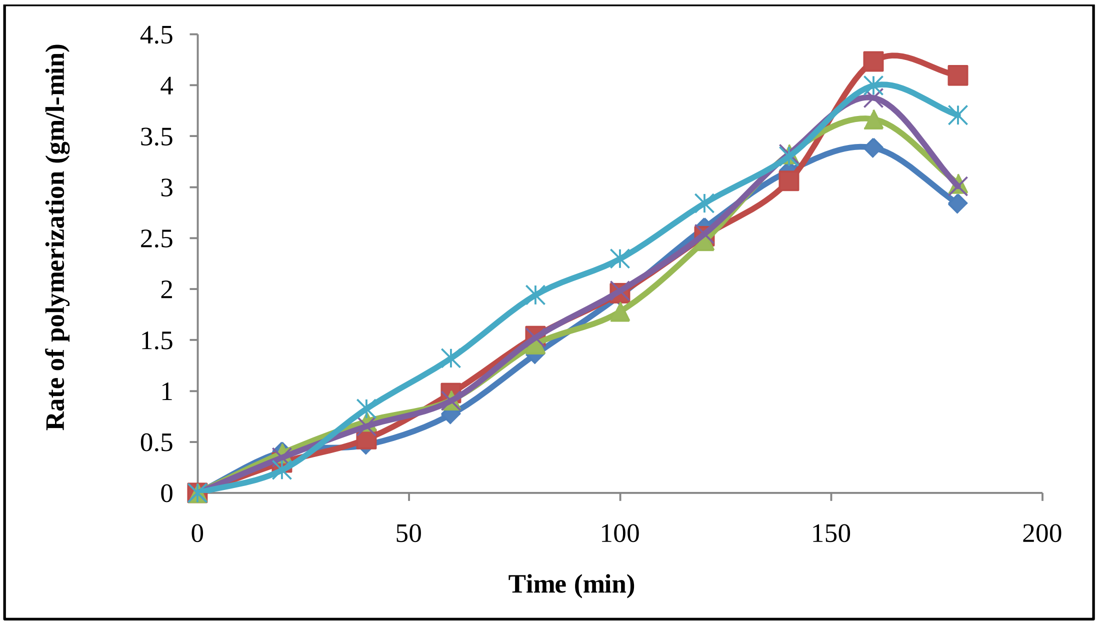


Fig. 5.4: comparison of runs taken at different time for rate of polymerization (using 3rd recipe).

Table 5.3: Rate of Polymerization using 3rd recipe

Time	Run 1	Run 2	Run 3	Run 4	Run 5
0	0	0	0	0	0
20	0.4032	0.29864	0.39047	0.34738	0.42156
40	0.47181	0.32928	0.401766	0.8544	0.54351
60	0.77103	0.47896	0.609918	1.50529	1.0214
80	1.36125	1.538112	0.95989	2.0243	1.852
100	1.93847	1.96125	1.7809	2.5836	2.3836
120	2.60385	2.52033	2.4748	3.05427	3.0122
140	3.1611	3.06368	3.32714	3.3275	3.2351
160	3.38689	4.2353	3.6693	3.8769	3.6998
180	2.83849	4.0991	3.03688	3.00981	3.1567

The fate of most common latex products is the coagulation of polymer particles in our case we use methanol for coagulation in order to minimize the particle – water interfacial area. Moreover, the monomer - swollen particles may even lose their colloidal stability and flocculate with one another in the course of emulsion polymerization.

We bring into play three different recipes and found increase in monomer with initiator and emulsifier concentration intensifies the rate of polymerization. Amusingly originate that the stage of constant rate of polymerization conquer at the same time (150 min.). The increase in concentration of initiator and emulsifier facilitate the rate of polymerization hastily as found in 1st recipe.

The rate of an emulsion polymerization depends upon four major variables: the propagation rate coefficient, the monomer concentration in the latex particles, the total particle concentration, and the radical concentration within the particles.

If most of the monomer in an emulsion polymerization is contained within the latex particles, then this will reduce the rate of polymerization exponentially, this effect cannot be altered in a batch emulsion polymerization process until the monomer partitioning between the latex particle and aqueous phase has been changed.

The monomer partitioning can be easily calculated and its effect on the rate of polymerization deduced. The partitioning of monomer may be altered to favour the latex particle phase by altering the conditions of the reaction (e. g. the temperature), hence enhancing the rate of polymerization.

The final variable that affects the rate of polymerization is the free-radical concentration in the latex particles. It is well known that there are three kinetic events that may alter the concentration of radicals within latex particles: entry, exit and bimolecular termination. Both free-radical exit and termination are free-radical loss mechanisms, and have been shown to be diffusion-controlled. As the weight fraction of polymer in latex particles increases at high conversions, all models predict that the rate of free-radical loss via the mechanisms of exit and termination should be decreased, hence the rate of polymerization increased.

5.1 Conversion

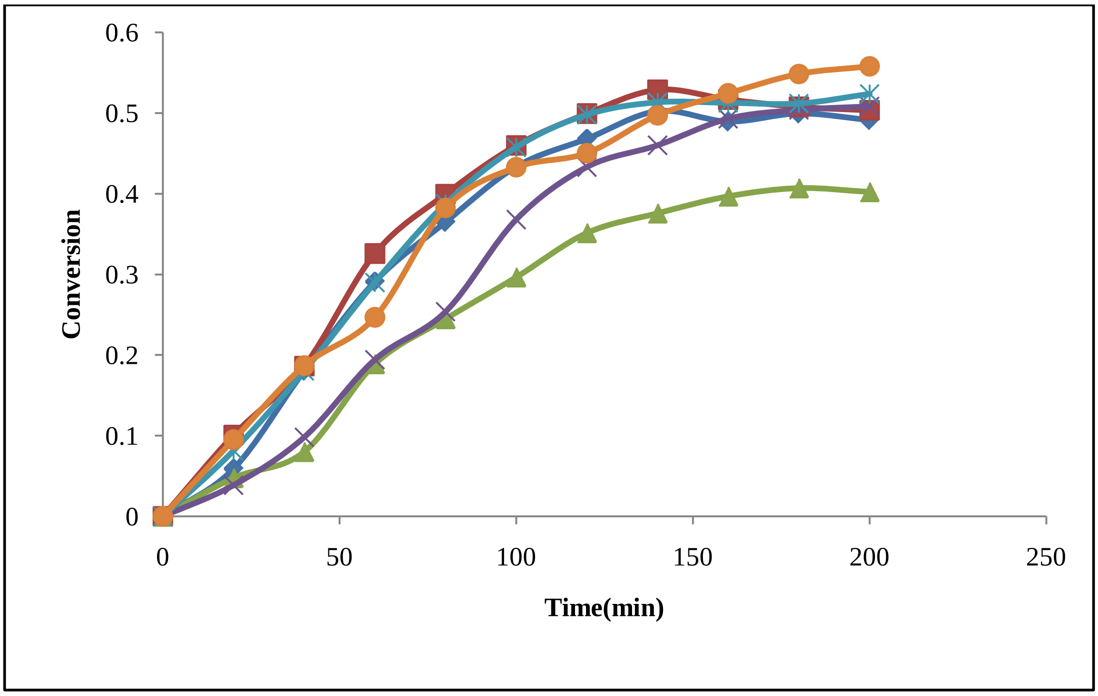


Fig. 5.5: comparison of runs taken at different time for conversion (using 1st recipe).

Table 5.4: Conversion using 1st recipe.

Time	x1	x2	x3	x4	x5
0	0	0	0	0	0
20	0.059	0.1007	0.0776	0.03857	0.08153
40	0.1803	0.1862	0.07499	0.04807	0.18028
60	0.2909	0.3258	0.1888	0.11172	0.289925
80	0.3647	0.3995	0.23465	0.21536	0.38749
100	0.4333	0.4598	0.2664	0.3678	0.45742
120	0.4679	0.4993	0.371229	0.43289	0.49784
140	0.5021	0.5288	0.36563	0.45984	0.5132
160	0.4892	0.5168	0.35665	0.49278	0.51251
180	0.4992	0.5076	0.3768	0.503638	0.51168
200	0.4911	0.5034	0.4021	0.508004	0.52363

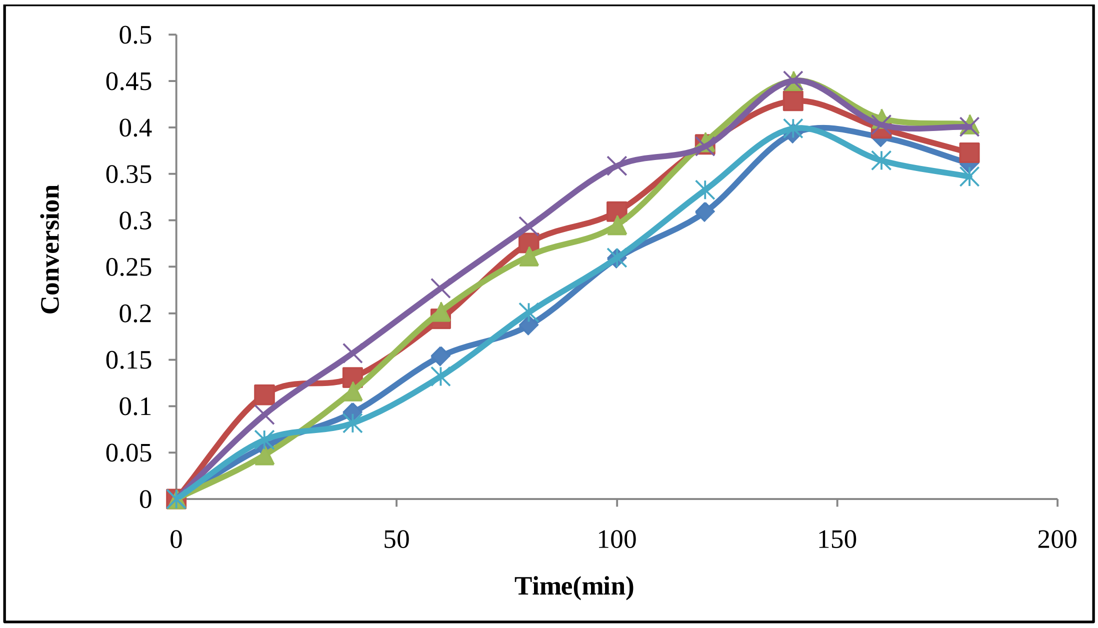


Fig. 5.6: comparison of runs taken at different time for conversion (using 2nd recipe).

Table 5.5: Conversion using 2nd recipe.

Time	x1	x2	x3	x4	x5
0	0	0	0	0	0
20	0.02646	0.1121	0.047323	0.09074	0.06362
40	0.02295	0.13073	0.11613	0.15695	0.04169
60	0.02355	0.1939	0.201798	0.32682	0.10202
80	0.06678	0.27547	0.26146	0.39352	0.20086
100	0.09888	0.30934	0.29504	0.45861	0.25976
120	0.18901	0.38164	0.38441	0.47957	0.332797
140	0.241	0.4285	0.45025	0.450255	0.39895
160	0.32945	0.39895	0.439613	0.40291	0.36455
180	0.4111	0.37273	0.48361	0.45059	0.347088

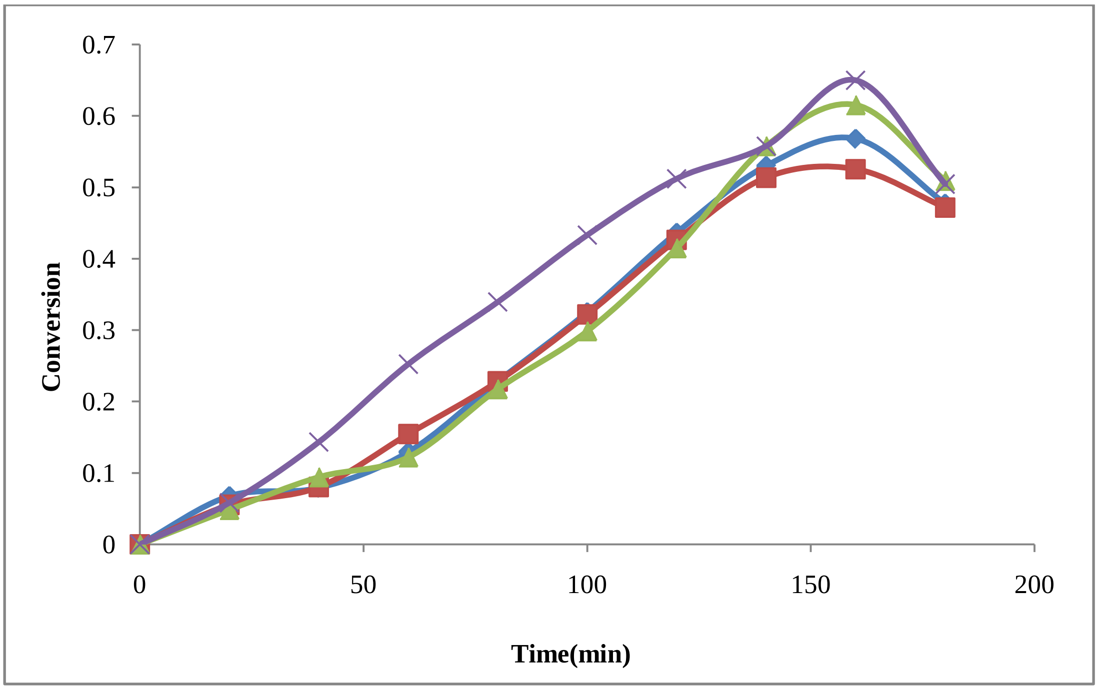


Fig. 5.7: comparison of runs taken at different time for conversion (using 3rd recipe).

Table 5.6: Conversion using 3rd recipe.

Time	x1	x2	x3	x4	x5
0	0	0	0	0	0
20	0.0675	0.0552	0.02834	0.05823	0.05662
40	0.07909	0.08029	0.08412	0.14325	0.07129
60	0.12925	0.15435	0.10196	0.25235	0.1435
80	0.2282	0.2282	0.14739	0.3394	0.2582
100	0.324975	0.32193	0.29855	0.43313	0.2993
120	0.43625	0.4264	0.4148	0.51203	0.4216
140	0.52994	0.51361	0.5577	0.55783	0.5536
160	0.56779	0.52538	0.61514	0.64993	0.5381
180	0.477032	0.47156	0.50918	0.50458	0.4826

The conversion first increases and then gradually levels off with the progress of polymerization. After a certain conversion, the termination rate constant (kt) becomes chain length dependent due to the influence of diffusion of free radicals on the bimolecular termination reaction. Gel effect causes low conversion. In fact when the monomer conversion reaches 0.03 mol/l-sec, the termination reaction becomes diffusion control i.e. miscibility problems occurs so that large free-radical chain terminates hardly and propagation accelerates. Results are tabulated in Tables 5.4, 5.5 and 5.6 for conversion using recipe 1st, 2nd and 3rd respectively

Fascinatingly overall conversion rate drops as the rate of polymerization turn out to be faster. The reason behind this is the polymer particles get saturated with monomer. In the midst of more monomer to convert, the particle stay saturated with monomer for a longer time, the gel effect is delayed and conversion rate is slower then excepted.

We found that increase in concentration of initiator and monomer makes increases in conversion as well which is provided evidence in Fig 5.7. The conversion first increases and then gradually levels off with the progress of polymerization the reason behind is the localized increase in viscosity of the polymerizing system which caused the motion of the radical hindered to approach each other for the termination, hence it decrease the termination rate.

At high conversions the monomer concentration in both the latex particle and aqueous phase decreases, so causing other variables such as the diffusion coefficient of monomer in the latex particles to decrease

Effect of Monomer concentration on rate of polymerization

Polymerization proceeds in the polymer particles as the monomer concentration in the particles is maintained at the equilibrium (saturation) level by diffusion of monomer from solution, which in turn is maintained at the saturation level by dissolution of monomer.

Interval II ends when the monomer droplets disappears completely. The changeover from interval II to interval III occurs at lower conversions as the water solubility of the monomer increases and the extent of swelling of the polymer particles by monomer increases.

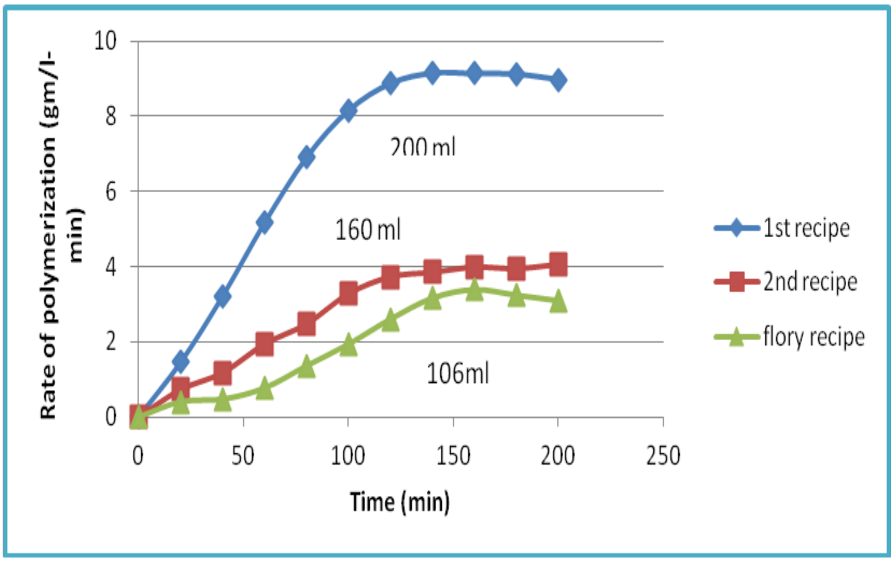


Fig. 5.8: Effect of monomer concentration on rate of polymerization.

The rate of polymerization depends on concentration of monomer as shown in figure 5.8 above. When concentration of monomer used is 106 ml in Flory recipe, the maximum rate obtained is 3.5 gm/l-min whereas rate get hold of maximum value of 9 gm/l-min when 200ml of MMA was used.

The percentage of conversion depends on concentration of monomer, initiator and emulsifier as the concentration increases, conversion also increases.

Flory recipe used gives lesser conversion while modified recipe with higher concentration of monomer and initiator bestow high conversion.

Viscosity

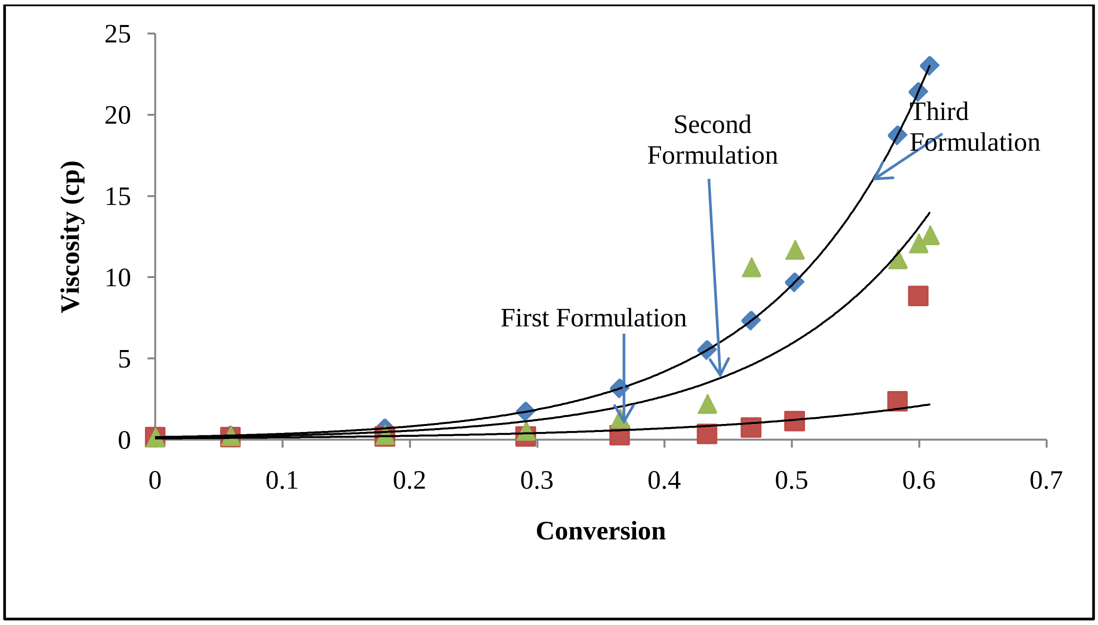


Fig. 5.9: Comparison of viscosity of all three formulations (First= 1gm of surfactant conc.,second =1.5,third =2gm)

In polymer processes, the viscosity increases with conversion and this makes perfect mixing impossible. Viscosity has a significant effect on the heat transfer characteristics as well. Non-ideal mixing conditions in stirred tank reactors are often suspected to be the cause of unexpected broad chain length distribution in free radical chain polymerization. For detail profile of viscosity effective agitation is required.

The emulsion polymerization is characterized by the formation of the polymer in the form of latex. The particle size distribution (PSD) of the latex and the molecular weight distribution (MWD) of the polymer are two important measurable parameters. Not only do they influence the end-use behaviour of the product, but they also replicate the growth history of the emulsion polymerization process.

pH and Conductivity

Conductivity of PMMA solutions varies from 0.0270 to 0.02702. pH of PMMA solutions varies from 5.51 to 5.97. This analysis is done to validate the characteristics of PMMA. The value found in literature is 5.85 pH and the value of conductivity is 0.02.

5.2 Particle Size Distribution

The observable properties of an emulsion polymerization, such as the PSD and MWD, are governed by a set of rate coefficients for the various microscopic processes occurring therein. Although the two distribution functions are interconnected, to discuss separately the mathematical modeling required to compute these two observables (see chapter 3). It must be recognized, however, that the various rate coefficients that can be determined are themselves commonly a function of the PSD and, less commonly, of the MWD.

It is open to criticism in that the results may be ambiguous: the same agreement between theory and experiment could often have been reached with a different set of parameters and/or other equally plausible theoretical premises. Literature values for many rate coefficients for polymerization processes display considerable variation

Interval II of an emulsion polymerization is characterized by polymerization in a constant number of latex particles in the presence of monomer droplets (i.e. nucleation is absent). This situation usually exists in an *ab-initio* polymerization immediately on completion of Interval I; however, for a seeded system, it may exist from the commencement of polymerization.

In the presence of monomer droplets, the concentration of monomer at each polymerizing site in the particles is approximately constant.

As polymerization proceeds, more particles enter the growing state. After some time, the total number of latex particles in each state is equal although the population is marginally further advanced in the size than the non growing population .The overall PSD moves along the size axis and broadens with increasing time. The rate of broadening is greatest when the polydispersity is least.

Two mechanisms for particle nucleation (i.e., formation of polymer particles) have been reported in literature. One is micellar particle nucleation, occurs when radicals from the aqueous phase enter the micelles. (The term heterogeneous particle nucleation has been proposed as an alternative to the term micellar particle nucleation.) The radicals may be primary radicals or, oligomeric radicals formed by solution polymerization. Second homogeneous particle nucleation involves solution-polymerized oligomeric radicals becoming insoluble and precipitating in the same (or onto dead oligomer in solution). The precipitated species become stabilized by absorbing surfactant (from solution, monomer droplets, and micelles) and on subsequent absorption of monomer is the equivalent of polymer particles formed by micellar nucleation. The relative scope of micellar and homogeneous nucleation are expected to vary with the surfactant concentration and its CMC value along with the solubility of monomer in water. Micellar nucleation is the predominant nucleation process when the surfactant concentration is well above CMC. For methyl methacrylate, more than 99% of particle nucleation occurs by micellar nucleation.

Around CMC, micellar nucleation is still the predominant mode of nucleation, but homogeneous nucleation is present—more for vinyl acetate and methyl methacrylate and less for styrene. The circumstances are much different for all monomers when the surfactant concentration is well below CMC. Micelles are absent below CMC and only homogeneous nucleation occurs. In fact, the occurrence of emulsion polymerization in the absence of micelles is evidence for the homogeneous nucleation mechanism. In our experiments we assumed that only micellar nucleation is taking place in the reaction medium

As the sample removed from the reactor for particle size measurement and immediately transfer to the Malvern Mastersizer. In order to avoid coagulation it is important to add sample as soon as it is removed from reactor. The agitation speed was set at 2000rpm, measurement time would be 12 seconds and that 12000 snaps would be taken on that time. At each sampling point a small amount of latex was taken out from the reactor for particle size measurement and transferred to a glass and without delay added to the Malvern.

It is imperative to add the sample as smoothly and quickly as possible. In order to lessen the coagulation of the particles it was also significant that the sample was added to Mastersizer immediately after removal from the reactor to avoid the coagulation.

The result shows materialization of bimodal distribution, having comparable number of particles on both models. We reproduce the results and concluded that most of the distributions results superimposed on each other and indicating good reproducibility.

Bimodality of distribution is instigated by coagulation. Malvern Mastersizer 2000 E is used for particle size distribution and water is being used as dispersant.

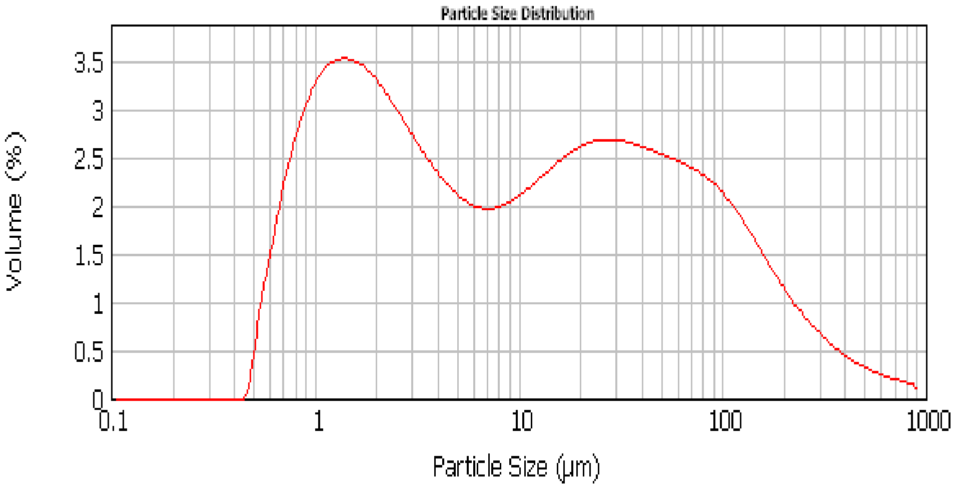


Fig. 5.10: particle size distribution of PMMA latex at 200 min using first recipe.

The graph shows possible coagulation which caused bimodal distribution. Particle nucleation occurs by micellar mechanism and compartmentalization caused bimodal distribution in the latex particles. 90 % particles produced are of 119.852 µm. The emergence of a bimodal after some time is due to the depletion of monomer droplets and the associated release of the surfactant accumulated within back in the aqueous phase, causing a crossing of CMC barrier and coagulation. Bimodal particle size distribution has a great advantage and that property basically used in paint industry, that is bimodal distribution allows increasing the solid content with low viscosity.

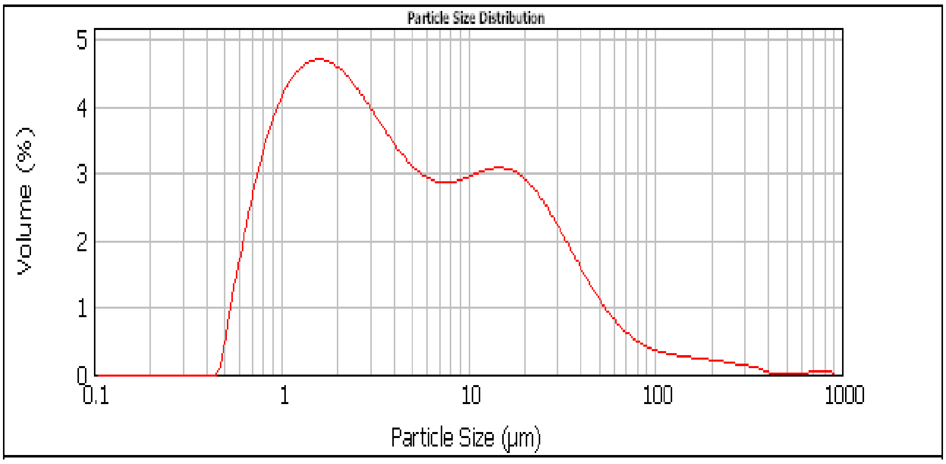


Fig. 5.11: Particle size distribution of PMMA latex at time 120 min using first recipe.

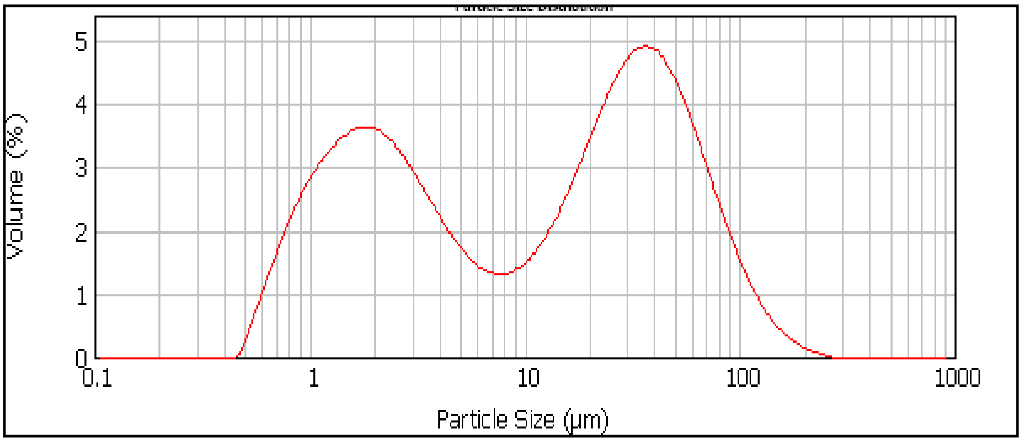


Fig. 5.12: Particle size distribution of PMMA latex at time 200 min using second recipe.

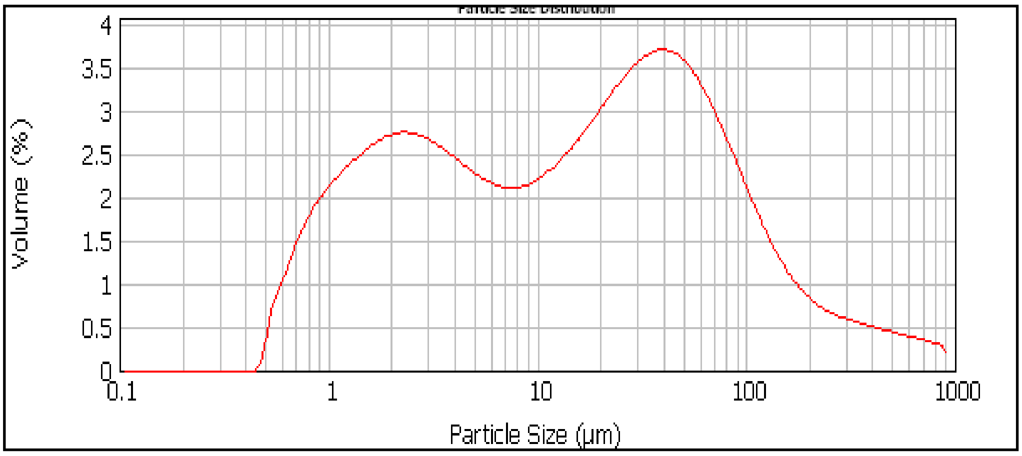


Fig. 5.13: Particle size distribution of PMMA latex at time 120 min using second recipe.

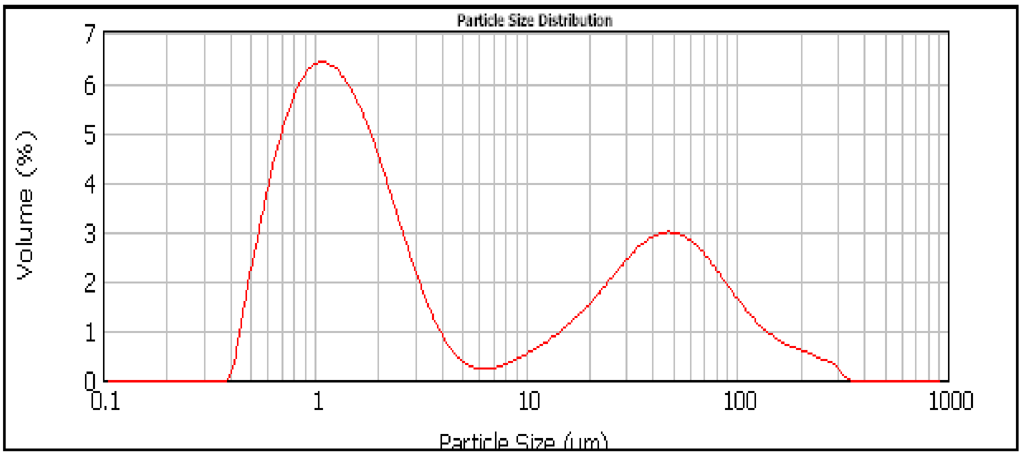


Fig. 5.14: Particle size distribution of PMMA latex at time 200 min using third recipe.

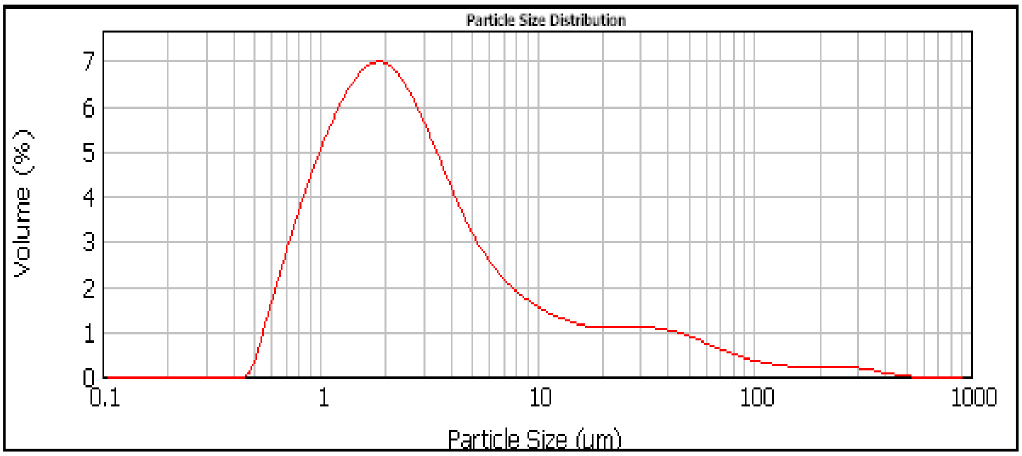


Fig. 5.15: Particle size distribution of PMMA latex at time 120 min using Third recipe.

The final PSD was always considerably narrower than that of initial PSD. At 10 % conversion, the particles are fairly small with essentially 0 or 1 radical per particle. As the conversion reaches at 40 % the distribution has moved to larger particle size. Here 10 % of the volume distribution is of size 0.94µm and 90 % of volume distribution is of size 31.378 µm as given in table also.

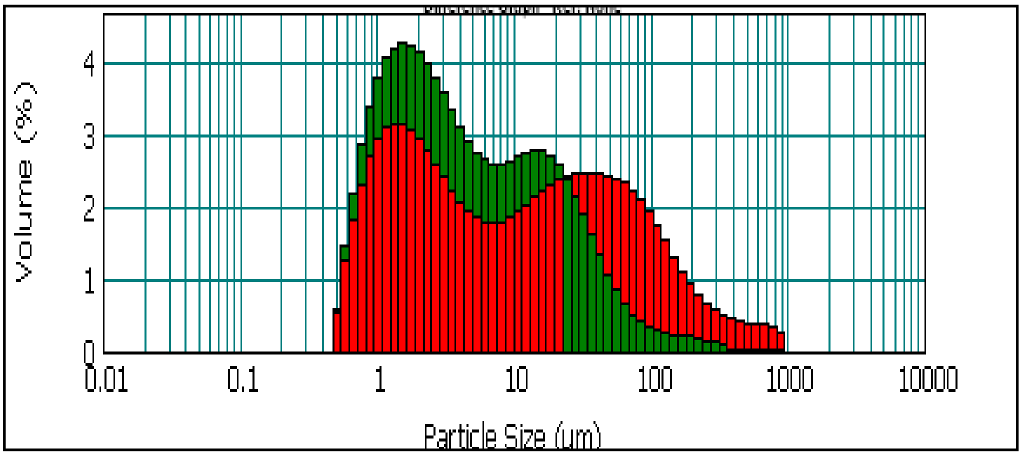


Fig 5.16: Comparison of PSD @120 min and 200 min.
(Green-120min, Red-200 min).

The result shows that final PSD is slightly narrower that the PSD at 120 min. Red color shows the Final PSD of the polymer particles and green shows the PSD at time 120 min. In final PSD at the end the lager particles appeared due to the coagulation. The particles less than 100µm are polymer particle and above that may be monomer droplets or the larger particles because of coagulation.

The ratio of water and monomer mixture is also very important. Owing to the small particle size, the system become very thick if the water/monomer ratio is very low. The particle size decreases gradually as the water content increases

Reproducibility

It is always important to confirm that the results produced by the equipment are reproducible or not. Repeated results proves that the distribution closely comparable with each other, which shows very good reproducibility. Since little disagreement is may be because of coagulation event in the sample. All the results for reproducibility are collected in appendix 1.

Monomer Droplets

Sodium oleate was used as the surfactant during the polymerization. Runs were carried out using three different concentrations i.e. 1 gm, 1.5gm, 2 gm.

The most important parameter which affects the stability of an emulsion is the droplet size and the droplet size distribution which is inclined by emulsification process, type and amount of emulsifier. Much work has been carried out in determining droplet size but very little experimental work has been reported in the area of characterization of monomer emulsion in terms of droplet size distribution and stability. Droplet size distribution of methyl methacrylate emulsion has also been presented in this thesis by utilizing light scattering method of Mastersizer.

In principle, a balance between the rate of droplet breakage and coalescence determine the size of the droplet consequently droplet size is a strong function of numerous parameters like density, viscosity interfacial tension, type and concentration of emulsifier stirring speed and also kinetics of polymerization.

Malvern mastersizer is used for study of monomer droplet size. The results of each run are displayed in a graphical format as a distribution.

The sample analysed was taken before addition of initiator in the reactor. Through in the early stages of polymerization the monomer droplets are appreciably lager than the polymer particle consequently distribution obtain was broader as compared to polymer particle distribution as shown in Fig 5.17a, 5.17b and 5.17c as compared to their respective particle size distribution (Table 5.7).

The large particle (100 µm to 1000µm) at high concentration of emulsifier (2 gm) is the result of coagulation it is well known that emulsion droplet is unstable as the time passes droplet size changes the reason behind is coagulation or coalescence or sometimes break up. Droplets formed spectacularly increases the surface area available for mass transfer and as a result they have reflective impact on rate of polymerization and the final properties of the latex. Increase in emulsifier concentration in the main tends to speed up the emulsifier adsorption which decreases the interfacial tension and droplet breaking which ultimately endorse the formation of smaller droplets (avoiding the large particle which is the result of coagulation). As shown in fig 8 there is not appreciably changes in the width of the distribution. It is observed that the amplitude of the distribution is narrow for high concentration of emulsifier.

As the rate of polymerization increases viscosity of the droplets increases, the rise in viscosity escort towards increase in droplet coalescence rate and decrease of droplet breakage, resulting in a larger particle size

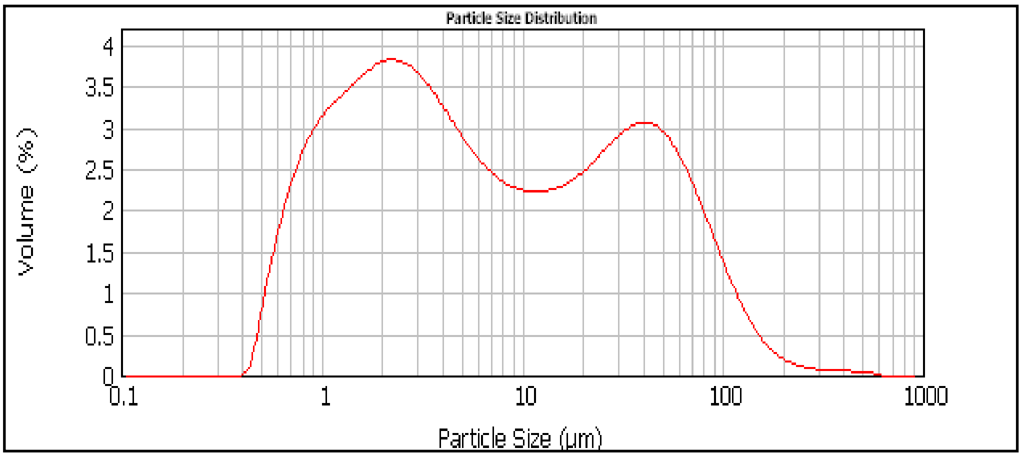


Fig. 5.17 a): Size of monomer droplets (surfactant conc-1 gm).

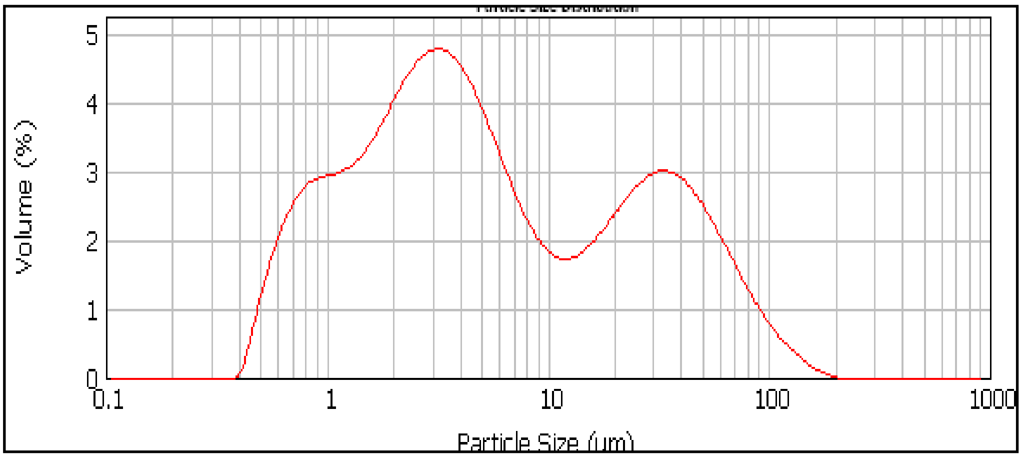


Fig. 5.17 b): Size of monomer droplets (surfactant conc-1.5 gm).

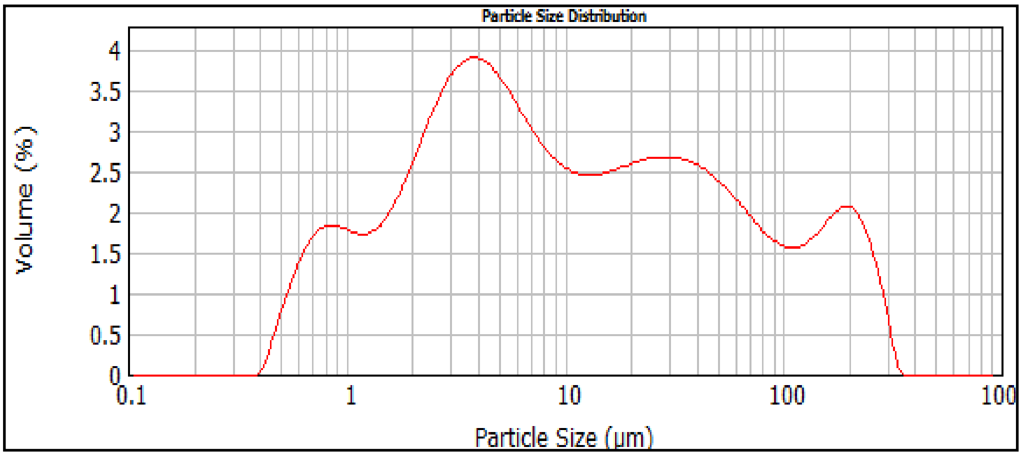


Fig. 5.17 c): Size of monomer droplets (surfactant conc-2 gm).

Increase in the concentration of Surfactant causes multimodal distribution of monomer droplets. Higher the concentration of emulsifier, greater is the number of particles that can be initiated. As the number of particles increases the number of reaction sites also increases, thus faster the rate and lower the reaction time which results in broader particle size distribution. Multimodal distribution is also resulting by considerably coagulation event; increase in the concentration of emulsifier increases the possibility of coagulation. Detailed results are given in the table above.

Table 5.7: Comparison of results of different concentration of surfactant.

Surfactant conc.	**Bimodal distribution**	**90% of volume containing particles of size (μm)**
1gm	Yes	61.849
1.5gm	Yes	41.341
2gm	Yes	128.77

Usually, particle formation by initiation in the monomer droplets is not considered important. This is because of the low absorption rate of radicals into the droplets in emulsion polymerization, relative to the other particle formation rates. Only in cases where the monomer droplets are made very small may they be an important source for particle formation. In literature we found a strong case for droplet nucleation in systems with especially effective preparation and stabilization methods for making and keeping the monomer in a very fine-dispersion. In some cases the particles become larger because some emulsifier is adsorbed on the monomer droplets, leaving less emulsifier in the aqueous phase and thereby leading to the formation of a smaller number of particles.

There are two factors that influence the particle formation conditions: the adsorption of emulsifier on the droplets, which leaves less emulsifier in the aqueous phase to facilitate particle formation there, and the rate of radical absorption in monomer droplets.

Comparison of Size of Monomer Droplets

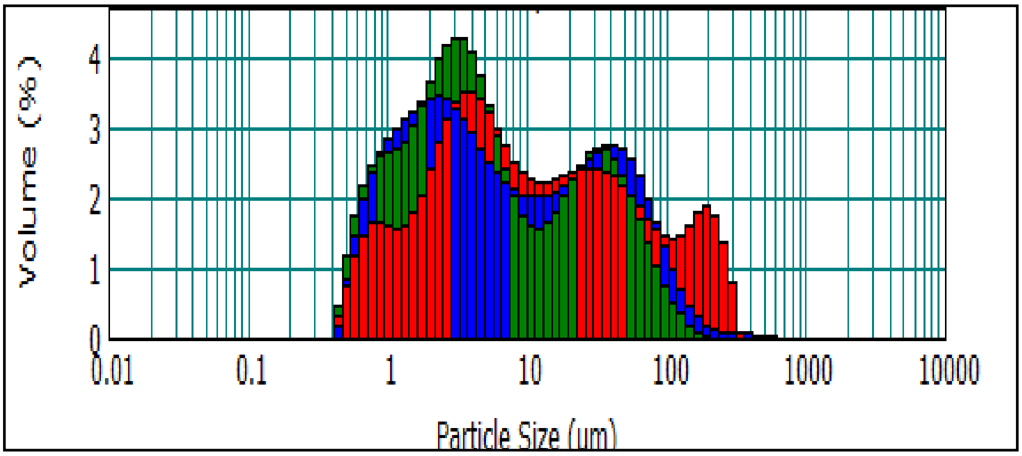


Fig. 5.18: Comparison of monomer droplets @ 1, 1.5 and 2 gm surfactant (Blue – 1gm,Green-1.5 gm, Red-2gm).

Emulsifier is the most important parameter which controls the particle size and particle size distribution of latex product. Latex product with a large particle size can be produced by using relatively low concentration of emulsifier and narrower particle size will be achieved. Higher the concentration of emulsifier, greater is the number of particles that can be initiated. As the number of particles increases the number of reaction sites also increases, thus faster the rate and lower the reaction time which results in broader particle size distribution. Fig 5.18 gives the comparison between particle size distributions using three different concentration of emulsifier.

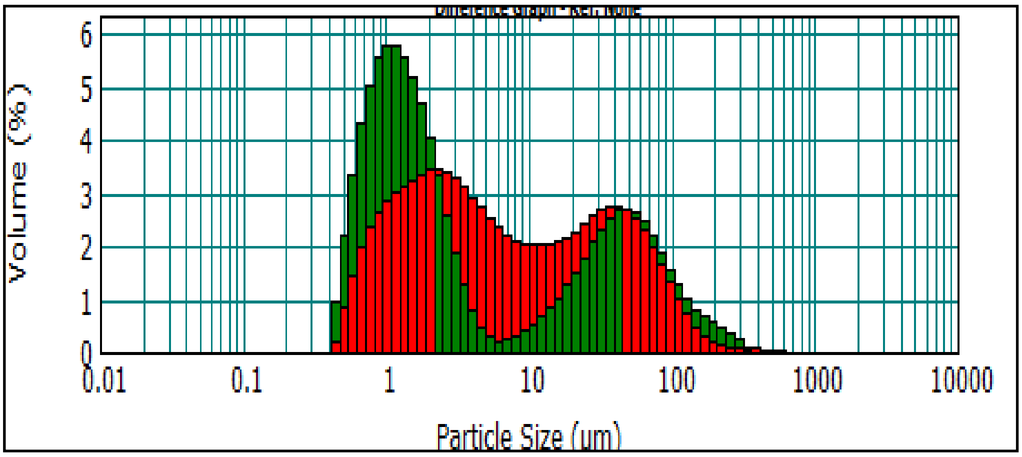


Fig. 5.19: comparison of PSD and monomer droplets for 1 gm concentration of emulsifier (green-polymer particles, red-monomer droplets).

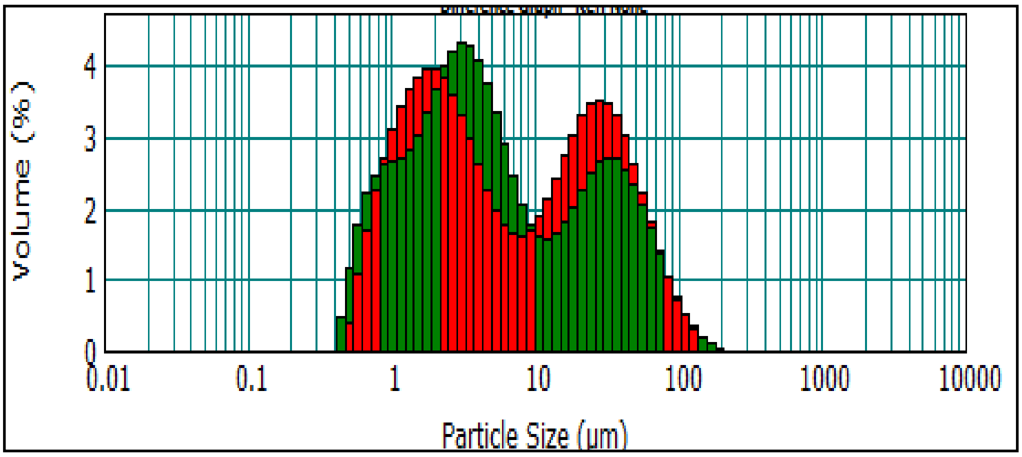


Fig. 5.20: Comparison of PSD and monomer droplets for concentration 1.5 gm (red- polymer particle, green- monomer droplets).

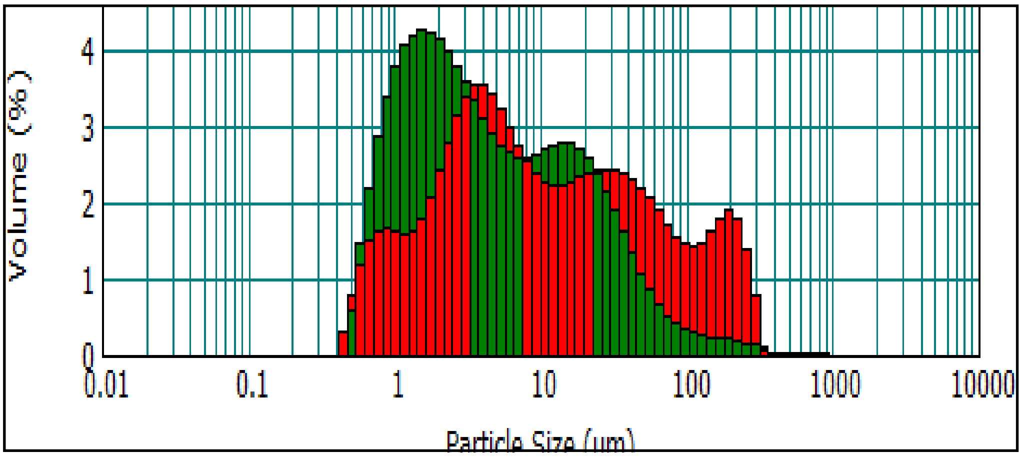


Fig. 5.21: comparison of PSD and monomer droplets for concentration of 2 gm (Green- polymer particle, Red– monomer droplets).

Table 5.8: Results of three formulations.

	Formulation 1	**Formulation 2**	**Formulation 3**
RPM of Malvern Mastersizer	2000	2000	2000
Bimodal distribution	Yes	Yes	Yes
Size of particles in 90% volume distribution.(µm)	170.852	69.094	68.697
Specific surface area(m^2/g)	1.83	1.94	3.38
Surface weighted mean.(µm)	3.282	3.0914	1.775
Volume weighted mean.(µm)	73.517	25.220	23.265

Emulsifier is the most important parameter which controls the particle size and particle size distribution of latex product. Latex product with a large particle size can be produced by using relatively low concentration of emulsifier and narrower particle size will be achieved. Higher the concentration of emulsifier, greater is the number of particles that can be initiated and distribution will be broader. A brief summary is given in table 5.8.

A major drawback of the Mastersizer is that it is not able to detect the polymer particles in the presence of monomer droplets until approximately about 30% conversion has been reached. The reason behind may be that unit passes laser light through an optical unit and based upon the way the light is scattered can deduct the size of the polymer particles that are present.

Sensitivity Analysis

a) Particle size distribution as a function of *surfactant*

The result shows materialization of bimodal distribution, having comparable number of particles on both models. Higher the concentration of emulsifier, greater is the number of particles that can be initiated (Fig 5.22, 5.23). As the number of particles increases the number of reaction sites also increases, thus faster the rate and lower the reaction time which results in broader particle size distribution. Multimodal distribution is also resulting by considerably coagulation event; increase in the concentration of emulsifier increases the possibility of coagulation. At 200 min as shown in Fig 5.23, this exhibits bimodal nature which is due to secondary distribution.

Surfactant plays a crucial role in the micellar nucleation phenomena by forming micelles which serve as precursor.

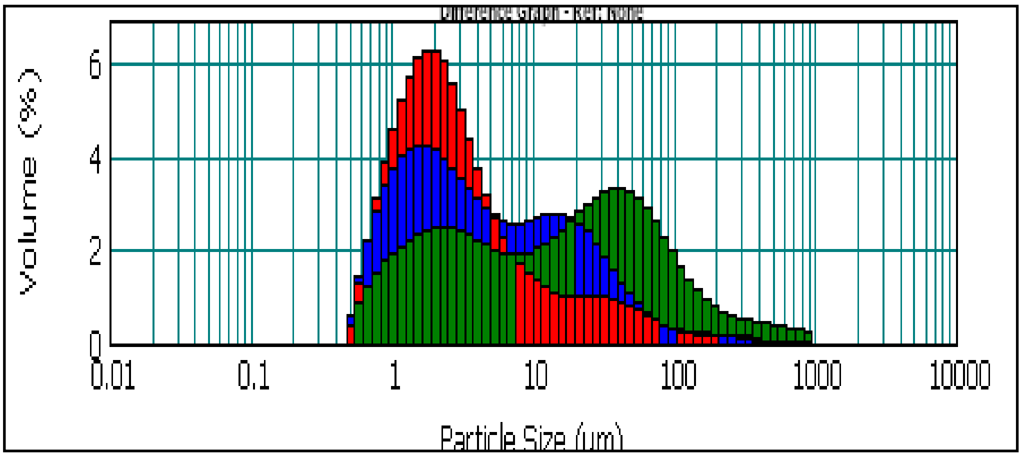


Fig. 5.22: Comparison of Particle Size Distribution using three different concentration of emulsifier at time 120 min (Blue–2gm, green -1.5 gm , Red -1 gm).

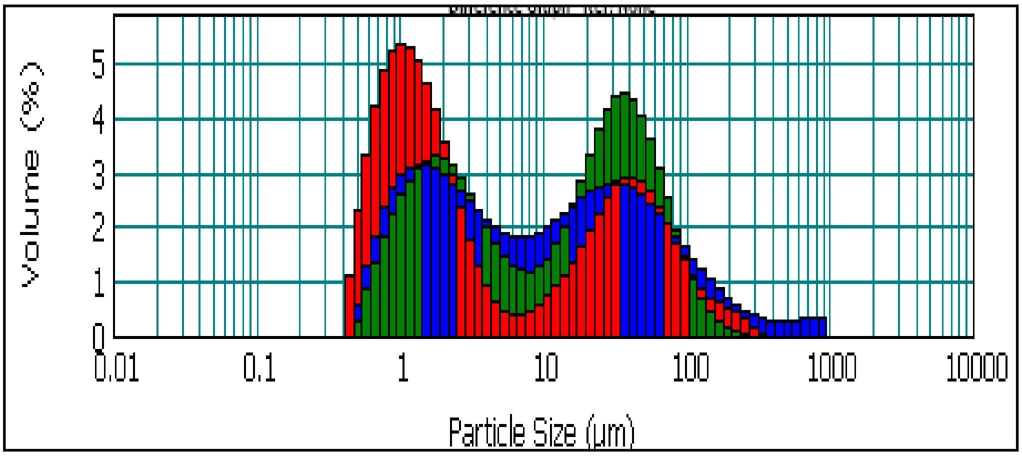


Fig. 5.23: Comparison of Particle Size Distribution using three different concentration of emulsifier at time 200 min. (Blue – 2gm, green-1.5 gm, Red-1 gm).

The essential feature of emulsion polymerization is that polymerization occurs in a large number of isolated particles that normally contain no more than a single polymerizing radical: this permits high molecular weight polymer to be formed at a high rate of polymerization, by contrast with bulk or solution polymerization in which an increase in the rate of polymerization generally results in a decrease in the molecular weight of the polymer produced. Emulsion polymerization without the use of an emulsifier may be achieved even with a monomer with water solubility as low as possible provided one uses an initiator such as potassium persulfate which introduces ionic end groups into the polymer that can stabilize the polymer latex particles produced electrostatically.

Emulsifier-free emulsion polymerization is advantageous some times when the object is to obtain a well-characterized model colloid for use in experiments on colloidal stability, etc.

When an emulsifier is used, its type and concentration primarily affects the number of latex particles formed, which in turn determines the rate of polymerization and, depending also on the rate of initiation, the molecular weight of the polymer formed. Although the physical properties of the polymer are primarily dependent on its molecular weight and their distribution, the properties of the latex depend on its concentration, average particle size, particle size distribution, and the viscosity of the aqueous phase.

The best emulsifiers for stabilizing the monomer emulsion are not only those that are best for stabilizing the polymer latex but remains in dispersion for prolong time even without agitation if required.

The fact that the latex particles are much smaller than the monomer droplets in the original emulsion facilitates stabilization of the latex, but emulsifiers will usually have to be chosen with a view to stabilizing the latex rather than the monomer emulsion.

The effects of emulsifiers in emulsion polymerization systems may be detailed as follows:

(1) Stabilization of the monomer in emulsion,
(2) Solubilization of monomer in micelles,
(3) Stabilization of polymer latex particles,
(4) Solubilization of polymer,
(5) Catalysis of the initiation reaction, and
(6) Action as transfer agents or retarders which leads to chemical binding of emulsifier residues in the polymer obtained.

In the absence of particle coalescence (i.e., when relatively large concentrations of emulsifiers are present sufficient to stabilize all primary particle nuclei formed) the essential condition for the formation of a latex with a very narrow particle size distribution is that the nuclei of all particles should be formed at very nearly the same time and should subsequently grow at equal rates

Low initial surfactant concentration was attributed to homogeneous nucleation where high initial concentration was attributed to micellar nucleation.

Decrease in the flow rate of surfactant causes decrease in the total number of particles nucleated this result in larger growth rate thereby causing the particles to grow in large size.

Increase in the concentration of Surfactant causes multimodal distribution of monomer droplets. Higher the concentration of emulsifier, greater is the number of particles that can be initiated. As the number of particles increases the number of reaction sites also increases, thus faster the rate and lower the reaction time which results in broader particle size distribution. Multimodal distribution is also resulting by considerably coagulation event; increase in the concentration of emulsifier increases the possibility of coagulation.

Occurrence of secondary nucleation as shown in fig 23 can be explained as at the beginning of the reaction micelle nucleation rate is much higher than that of homogeneous nucleation rate therefore micelle nucleation is dominating. After 30-40 minutes the micelle nucleation decreases and homogeneous rate increases and then secondary nucleation is because of homogeneous nucleation.

b) Particle size distribution as a function of *initiator*.

Large initiator concentration will cause rapid particle formation so that all the particles are formed almost simultaneously and will grow to a relatively narrow particle size distribution. Concentration of initiator is used to control the PSD .Higher concentration of initiator favour narrow initial and final distribution by as shown in the Fig 5.24.

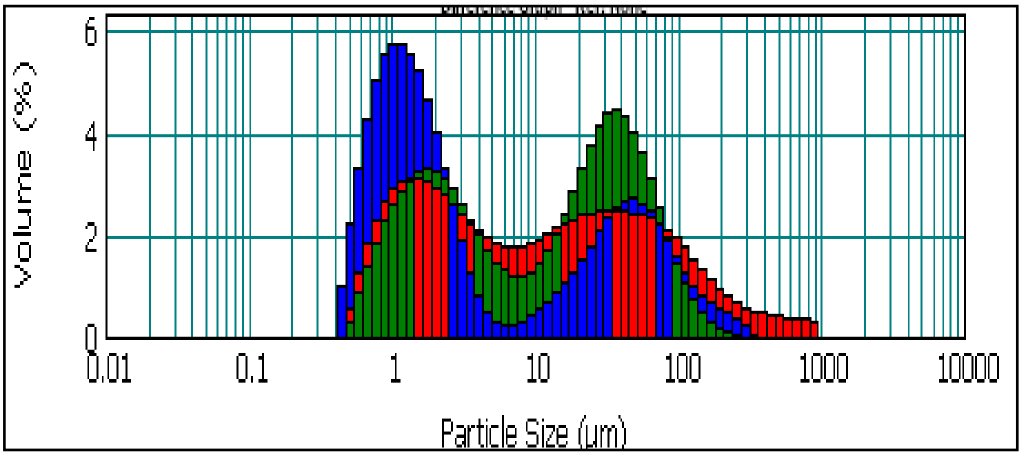


Fig. 5.24: Comparison of Particle Size Distribution using three different concentration of Initiator (Blue – 1.5gm , green -1 gm , Red -2 gm).

Increase in concentration of initiator cause increase in conversion rate, final average polymer size drops ultimately resulting in a narrower distribution.

The effect of the reaction medium on the initiator can be found in literature. In a polymerization process the initiator is inefficiently used. There is wastage of initiator due to normally two reactions. The first one induced decomposition of initiator, this ensue by the hit of propagating radicals on the initiator. This is called chain transfer to initiator.

Concentration during polymerization, as the newly formed radical will initiate a new polymer chain. The second reaction, which will give wastage of initiator, is a reaction involving side reactions of the radicals formed in the primary step of initiator decomposition.

Efficiency factor (f) is defined as the fraction of radicals formed in the initial step of initiator decomposition. This is the nature of the decomposition pathway that controls the efficiency of the primary radicals in initiating new polymer chains. This effect has been called the ”cage” theory. According to cage theory the two dissociated fragments will be surrounded by reaction mass and this reaction mass will form a sort of cage around them. The two fragments will stay inside the cage for a finite amount of time, and during this time they may reassociate to give back the initiator molecule.

Redox systems appear very versatile, permitting polymerization at ambient temperatures and the possibility of control of the rate of radical initiation versus polymerization time. This would thus permit control of heat generation and the minimization of reaction time. The use of potassium persulfate with water forms an effective redox system for PMMA emulsion polymerization. At high conversions, the concentration of monomer in the aqueous phase is very low and water-phase termination of hydrophilic radicals becomes excessive. The rate of radical entry into polymer particles is thus greatly reduced and the polymerization rate falls to a very low.

c) Particle size distribution as a function of *Agitation speed*

Agitation in polymerization reactors play a key role in polymer engineering, since the process is highly non-linear in nature so sufficient mixing is required to control the process. Agitation is notably affected the course of reaction. Increasing stirring speed make the particle size distribution to become narrower.

In multiphase systems like emulsion polymerization it is important to achieve good mixing conditions in order to favour heat and mass transfer, avoiding phase coagulation or segregation.

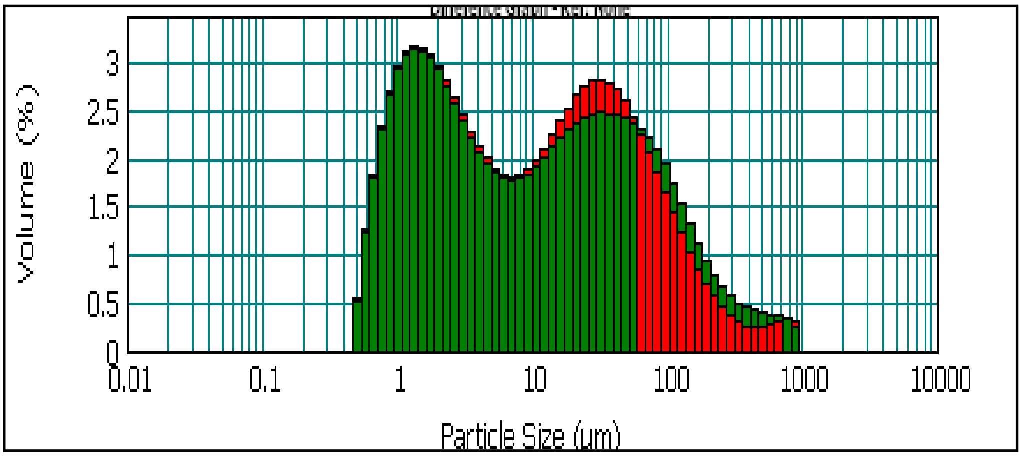


Fig. 5.25: Effect of RPM on PSD (Green shows PSD @ 1500 rpm and red shows 2000).

Monomer droplet and particle size is being influenced by RPM of Malvern mastersizer is proven in the fig 5.25 where the sample was analysed with Malvern agitation i.e. 1500 and 2000.Agitation speed is responsible for the uniform mixture of monomer droplet.

Emulsion droplets are unstable in nature as the time passes the size of droplets may be change so it is required to measure the sample as early as possible Increase in the stirrer speed resulting smaller droplets without significantly changing the distribution.

Data obtained from the Malvern (peak areas of the particles and droplets) has been used in an attempt to quantify this theory. In addition to particle size the Malvern outputs the volume % of the sample below a given size, and thus allows an estimate of the volume of residual monomer, Three distinct peaks were typically observed in the Malvern plots, on below 1 µm, one between 1-100 µm, and beyond 100µm**.** For this analysis it was assumed that the material less than 1 µm was a polymer particle and anything from 1 - 100 µm was monomer droplets. Particle sizes grater than 100 µm were assumed to be either monomer droplets or polymer particles that had coagulated due to the fact the concentration of emulsifier drops significantly. The relative areas of the particle and droplet peaks are then assumed to represent the relative amounts of each.

5.3 Molecular Weight

Polymers contain chains of varying lengths and polymers are characterized by its Molecular weight distribution (MWD). There are some techniques to determine MWD and its averages. The Molecular weight and molecular weight distribution affects the properties of the polymers and one example is the mechanical strength which is improved by increasing the molecular weight. MWD is often characterized by its average molecular weight (Vicente, Leiza et al. 2003).

In some polymerization systems polymer molecular weight is observed to be lower than the predicted value. Chain-breaking can occur with a transfer mechanism. In this mechanism the growing radicals remove a weakly bonded atom, from monomer or other molecules in the system to generate a dead polymer chain as well as a new radical that initiates another polymer chain. This weakly bonded atom is usually hydrogen, and other molecules can be monomer, polymer or chain-transfer agent (CTA). These radical displacement reactions are called chain transfer reactions where chain transfers from a propagating radical to monomer and the polymer.

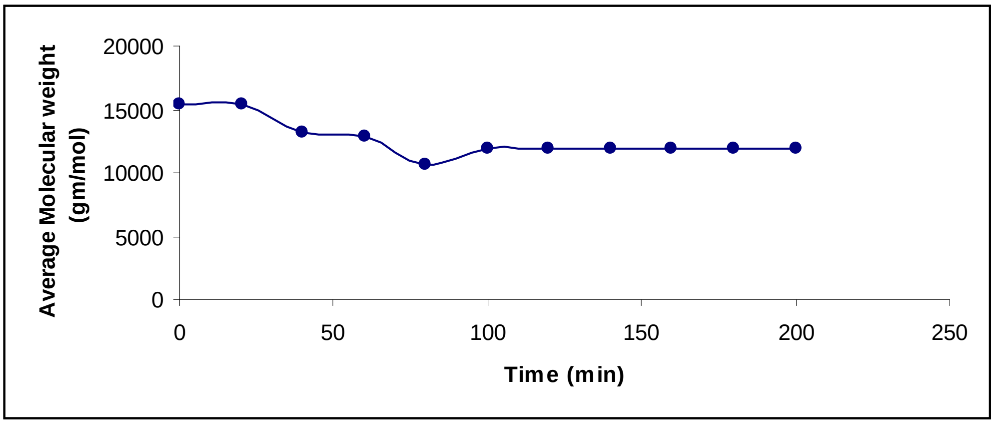


Fig. 5.26 : Average molecular weight using surfactant concentration=1 gm.

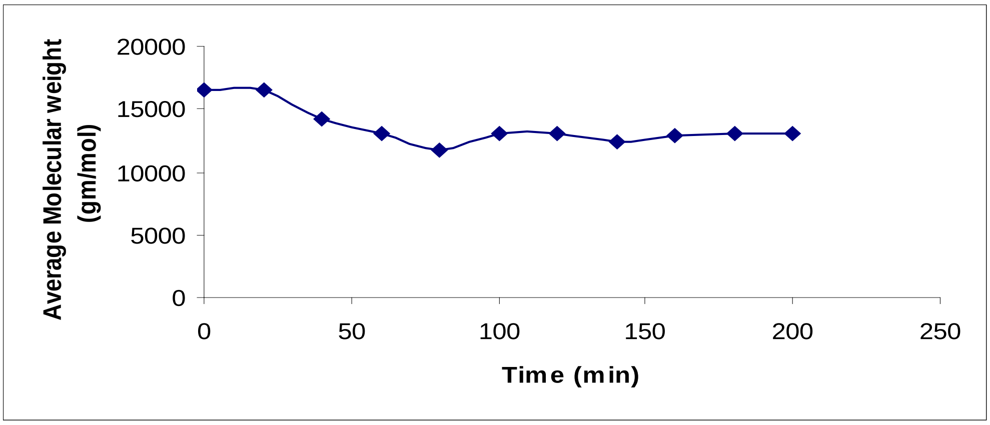


Fig. 5.27: Average molecular weight using surfactant concentration=1.5 gm.

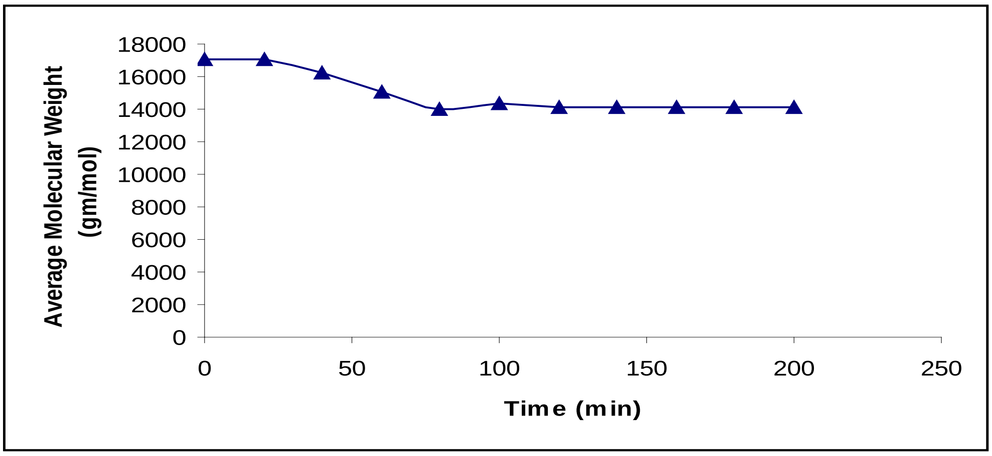


Fig. 5.28: Average molecular weight using surfactant concentration= 2 gm.

Average molecular weight of polymer using three different concentration of emulsifier (sodium oleate) is plotted in figure 5.26, 5.27, 5.28 with 1 gm, 1.5 gm ,2 gm respectively. The graph shows the increasing trend as the concentration of emulsifier were increases as shown in figure 5.29 below.

If molecular weight is too low, the transition temperature and the mechanical properties will be too low for the polymer material to have any useful commercial applications. A polymer having useful application must have transition temperature above the room temperature on the other hand lower the molecular weight, lower will be the strength.

A molecular weight of a polymer is not only a value rather will have a whole distribution of molecular weight and it depends upon the way it produced. Physical properties of any polymer are a function of their molecular weight distribution.

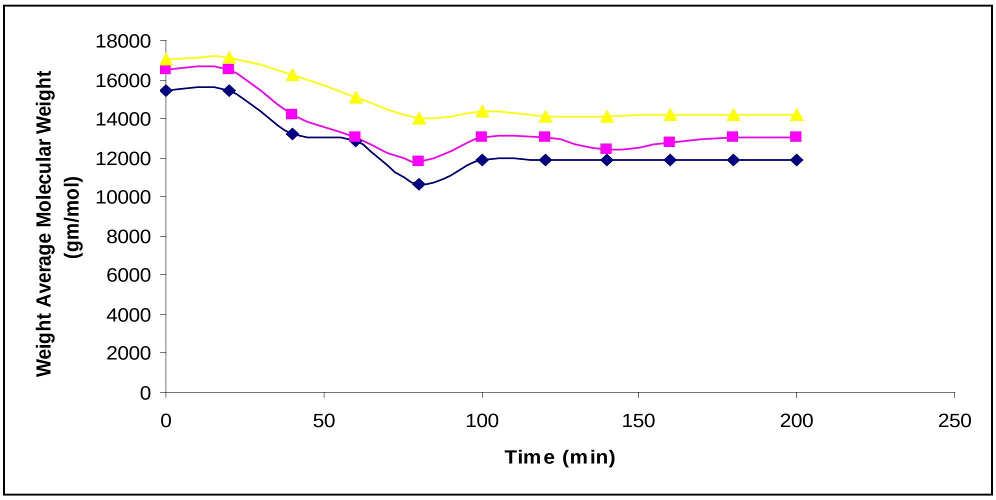


Fig. 5.29: Comparison of Molecular weight using different concentration of emulsifier (yellow line – 2gm, pink – 1.5 gm, black- 1 gm).

There are two limiting kinds of behaviour of the propagation rate coefficient: the chemically controlled and the diffusion-controlled limit. The chemically controlled limit is independent of the weight fraction of polymer in the latex particles, and dependent upon the monomer-polymer system and the reaction conditions. The diffusion-controlled propagation rate coefficient occurs, when the diffusion of monomer to the polymeric radical is slower than the chemical reaction of these two species. The diffusion coefficient depends critically upon the weight fraction of polymer, reaction condition and the monomer-polymer system. Higher weight fractions of polymer (or higher conversions) may cause the diffusion-controlled propagation rate coefficient to decrease by orders of magnitude, thus causing very slow rates of polymerization. Diffusion-controlled propagation normally occurs for systems polymerized below the glass transition temperature of the polymer, but not for systems polymerized above the glass transition temperature of the polymer. If slow diffusion-controlled propagation is to be overcome, the reaction conditions must be changed to favour faster diffusion.

The molecular weight distribution (MWD) of a polymer generated by emulsion polymerizations can be fundamentally different from that generated in solution or bulk. For example, in PMMA emulsion polymerization the MWD of formed polymer has a much higher average molecular weight than may be obtained using other methods. The basic reason for this was the compartmentalization of the polymerization reaction inside the latex particles which leads to the isolation of free radicals. This isolation reduces the probability of bimolecular terminations and hence increases the degree of polymerization.

Since latex particles grow to many times their original volume during the course of polymerization, the component of the MWD produced by nucleation is often negligible (at least, when measured as a weight average).

Polydispersity Index

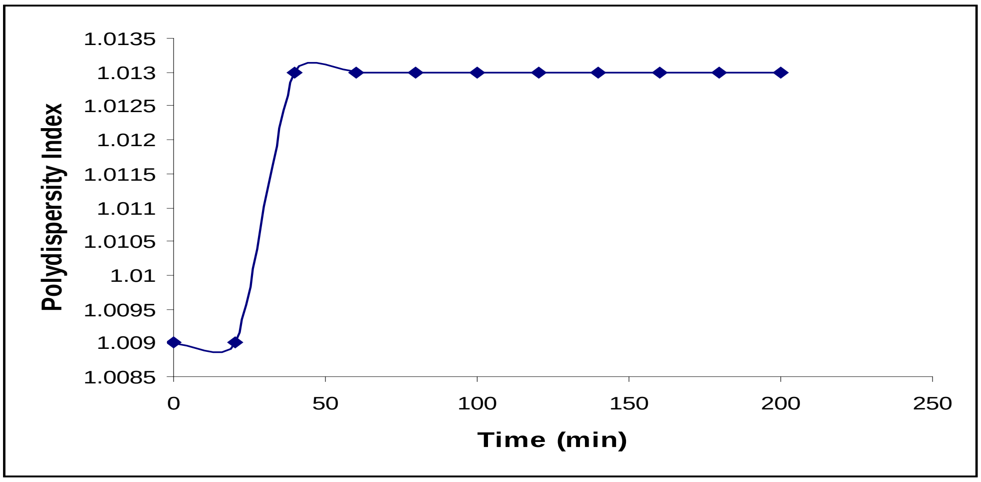


Fig. 5.30: PDI using first formulation.

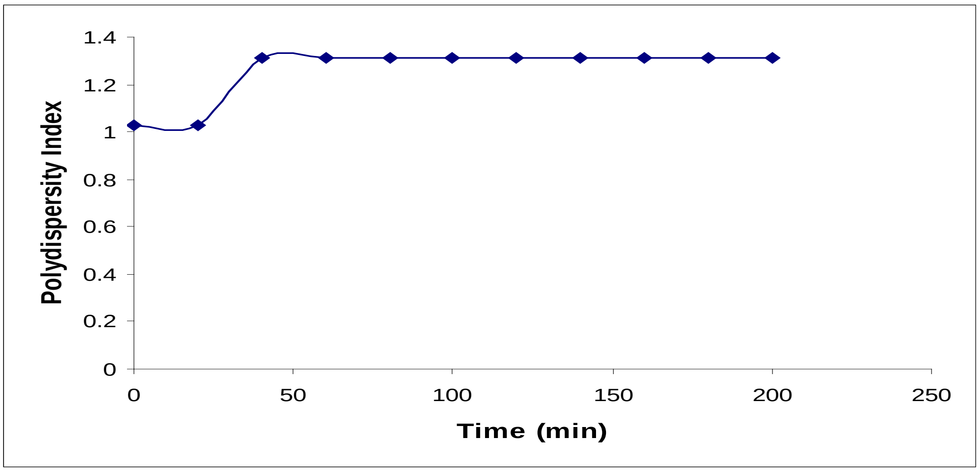


Fig. 5.31: PDI using second formulation.

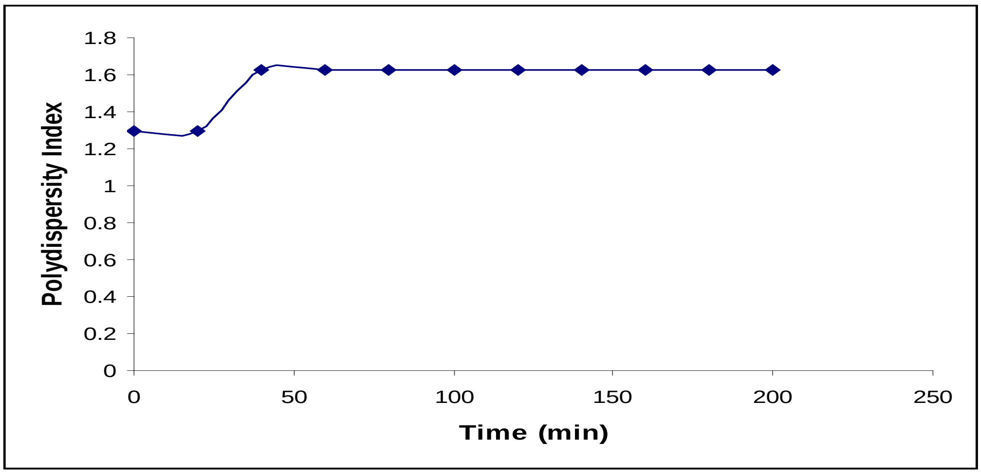


Fig. 5.32: PDI using third formulation.

The Value of polydispersity index may vary from 1- 10.The nature of distribution of molecular weight depends on value of polydispersity index. Polydispersity value 1 means that the polymers are all of the same length, value around 3 means that there is a wide distribution of polymer size. Figure 5.30, 5.31, 5.32 shows the polydispersity of three formulations taken in the study, as the molecular weight increases value of polydispersity index increases in our study.

Chapter-6
Simulation Results (PSD)

6. Simulation Results (PSD)

Particle Size Distribution

A little work is available on control of batch emulsion polymerization reactor due to the complexity and non-linear nature. Many researchers in the area of process control readily acknowledge that there is a wide gap in process control theory and their application to the polymerization system. The reason behind this gap is that the most conventional control is readily available for continuous and semi-batch systems and plenty of work has been already done for these system with measured outputs, and can superimposed on top of an existing system. For the batch process a detailed mechanistic understanding of the process is required for the process control implementation.

Mathematical modeling is a way of summarizing and quantifying our knowledge about polymerization, and is required for process strengthening; beside this, models are powerful tools for improving the understanding of multipart processes, which may result into better product quality. They can also be used to recognize advantageous process conditions and risky situations that must be avoided. Models can also facilitate on-line control of emulsion polymerization reactors and are useful for the education and training of personnel.

The demand of polymer and latexes in the market having special properties and improved performance has led to increase academic interest in advanced modeling and control of polymerization reactors. This chapter includes the control of batch emulsion polymerization reactor which is rarely available in literature.

Heterogeneous polymerization systems like emulsion polymerization having additional difficulties in their modeling. These systems are multiphase system, hence material balance have to used in the modeling and even heat balance is also required for each phase. Additionally their end use properties dependent on concentration of polymer particles and particle size distribution and molecular weight distribution which ultimately increases the complexity.

Emulsion polymerization systems have been discussed in chapter 2 and their detailed modeling in Chapter 3.

Here we emphasise on control of batch reactor using MATLAB. Most polymers and their properties are difficult to measure even off-line in the laboratory and some can be measure with time lagging in case of batch reactor.

Most batch and semi-batch polymerization control systems consist of a pre-programmed recipe addition, a start-up and shut-down scheduler, and temperature control based perhaps on a heat balance and few of them are aimed to optimized polymer properties through using trajectory, here we tried to bridge this gap by optimizing the control system through temperature trajectory and also by applying disturbance in the system during control run of the system.

There is a unique relationship between PSD and rheology, narrow distribution favours high value of rheology property, thus a process model and a rheology model will be needed in the identification of the PSD target. A well known fact is the rate of polymerization increases with increasing temperature. Increase in temperature after a certain temperature, the size of the particle decreases. This inverse dependence between the particle size and the polymerization temperature is due to the increasing decomposition rate of the initiator with increasing monomer solubility in the aqueous phase, which increase the concentration of growing chains and, thus, reduce the latex size. Control of reactor temperature facilitates us to control particle size distribution

Normally batch reactors are extensively used for homopolymerization where only a single monomer is used for the process. In polymerization reactors there are different instabilities and these can be caused by i.e. thermal, viscous, hydrodynamic and kinetics. When system viscosity increases there will be a reduction of heat transfer coefficients and this leads to an increase in the reactor temperature. Exothermic nature can causes serious safety issues, and control schemes have to include tight safety procedures.

On-line measurements of end-use properties of polymer materials are difficult, and the control procedures have to rely frequently in values provided by process models and on measured values provided with long delays by plant off-line measurements. A control methodology has to take into consideration for polymerization system, producing consistent, uniform and in-specification polymer. In order to operate polymer processes safely and in order to set characteristics of the product, a set of process manipulated variables must be kept constant or modified systematically over the duration of the reaction. The keystone of successful control strategy is a good mathematical model, and to perform the modeling knowledge about the process is important. The modeling of a model for a batch emulsion polymerization reaction is already discussed in Chapter 3.

Temperature control in batch reactors can be divided into two phases, one is heating in which the temperature is raised to the target value avoiding overshoot and another is stabilizing phase in which the objective is to maintain the temperature at a set-point through out the process.

In a feedback controller a manipulative variable is used to maintain the control variable. Two type of manipulative variable is used for PID in this thesis. One is flow rates of jacket medium and second is heater power or heat duty of the reactor. Split range is used in the first PID controller when we go through it we found second controller is better to work with further hence, we precede next with second type of controller which is having heat load as manipulative variable. The difficulties come in the way during split range controller is discussed in next section. In this chapter we discuss results of that model with three different controllers i.e. PID, MPC and NNPC. This chapter is divided into two sections one for particle size distribution and second for molecular weight distribution. Each section enfold PID, MPC and NNPC controller separately.

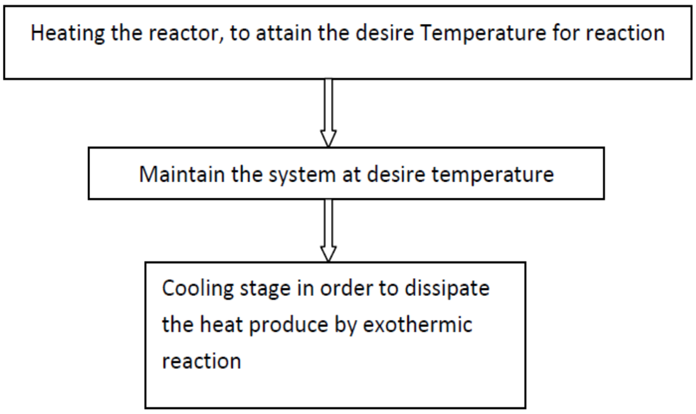
6.1 Proportional-Integral-Derivative (PID)

In general, particle size distribution in batch emulsion polymerization can be controlled through manipulating the temperature of the reactor and flow rates of reactor medium. The bimodal PSD’s obtained in laboratory for PMMA emulsion polymerization were well predicted by their population balance model. The effects of variables on the final latex PSD were investigated and discussed in previous chapter.

In emulsion polymerization rate determining step for the entry of oligomeric particle into latex particle is still to be explored, some researchers presumed that diffusion of soluble oligomers to the particle surface is the rate determining step but other verbalized that displacement of surfactant from particle surface is the rate determining step, more recently researchers postulated a new mechanism in which the propagation of the free radicals in the aqueous phase is the rate determining step. PSD of the emulsion polymer or product is convincingly influence polymer’s rheological, chemical, physical, mechanical, film forming properties.

Batch reactor was used for production of PMMA. A measured amount of MMA, emulsifier and water was charged to the reactor. The reactor was bubbled with nitrogen gas to purge oxygen from the reactor. The reactor was brought to the initial temperature and then required amount of initiator was supplemented to the reactor. Comparison of experimental value of reactor temperature with simulation with on/off controller and with controller was studied and the result found was shown below. PID controller is successfully operated; performance of controller was studied with different parameters. After this we compared two methods which will be explained later.

The temperature profile in batch polymerization reactor follows:-



The prediction of particle number and size distribution has been far less successful than the prediction of conversion time histories and molecular weight development, given these parameters as initial conditions. The nucleation and early growth of polymer particles is even today, after the comprehensive investigations not well understood. There are several reasons for this. First, the measurement of number and size of polymer particles smaller than 100 A° presents rather difficult experimental problems. Many complex processes occur simultaneously including radical capture by micelles and polymer particles, precipitation of growing radicals from the aqueous phase, and finally particle coagulation.

To develop effective control strategies for polymer particle concentration, it is of considerable importance to establish the time scale for micellar nucleation of polymer particles. The effectiveness of any control scheme would of course depend on the nucleation time.

Split-Range PID Control

It is worthy to note that the process model describing the PSD is non-linear, distributed and includes an important number of parameters that are not well known or sensitive to adulterations. This makes the model-based control of PSD more difficult task. Moreover, online measurement of PSD without delay is not available.
Our objective is to control PSD, instead of direct control we control through controlling the temperature of the reactor, Indeed temperature affect the propagation, solubility and entry parameters which affects the nucleation rate, hence temperature ultimately control the PSD.

A split-range-heating/ cooling system is used that adds hot or cold water to a circulating-water system (Lepore, Wouwer et al. 2007), which is assumed to be perfectly mixed at temperature TJ. The set-point of a reactor temperature controller is 343 K .The output signal from the reactor temperature controller positions two control valves, using a split-range setup. Figure 6.1 shows how the flow rates of the hot and cold streams change with the output signal and gives the batch reactor and temperature controller setup when just jacket cooling is used. This cold-stream control valve is usually “air-to-close” (AC) so it will fail wide open, which is the safe position. Using the same logic, the hot-stream control valve is “air-to-open” (AO). The hot-stream temperature is 373 K. The cold stream temperature is 293 K. The maximum flow rate of each of these streams is 0.5 kg/s. If the value of cold water stream is open to its full at the same time value of hot water stream is closed and vice-versa. The range of the output signal is defined between 0-1. Figure 6.1 shows the relationship between flow rates of cold and hot water stream with output signal of the controller. This output signal is the difference between set-point and the actual temperature of the reactor i.e. error calculated by the controller.

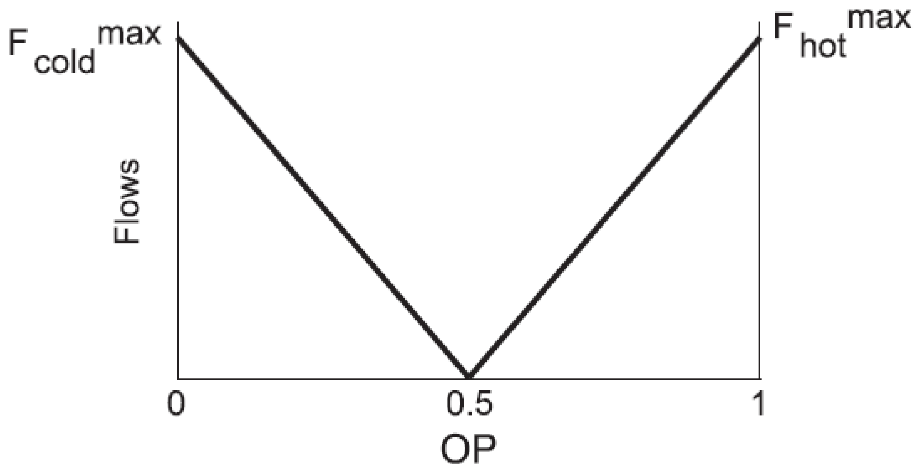


Fig. 6.1: Split range temperature control (Luyben 2007).

The tuning of the controller is another important issue, which is explored in the chapter 4 and their results are discussed here in next few sections of this chapter.

PID Controller (Heater power as manipulative variable)

In our study first PID controller we uses split range controller as explained above and second one uses heater power as a manipulative variable. In this strategy the value of power of a heater is changes accordingly to maintain the temperature of the reactor. Initially the heater increases the temperature of the reactor to its desire value, after attaining the set-point the error is calculated by the controller, with respect to the error the value of the heat load changes. The range of the heat load is defined as 40-140 W. Simulink file is shown in Figure 6.2.

Table 6.1a: Control Parameters.

Parameter	Split range	Heat load
Kc	5.29	10
TauI	0.31	0.01

Table6.1b : Parameters used in the study for PSD.

Parameter	Unit	Value
Kp	lit/mol min	49876.54
Kd	Per min	8.6*10e-5
Kt	Lit/mol-min	1.414*10e9
F	-	0.5
Uc	W/m2-K	55
Tcold	K	275
Cj	J/kg-K	4.183
Thot	K	400

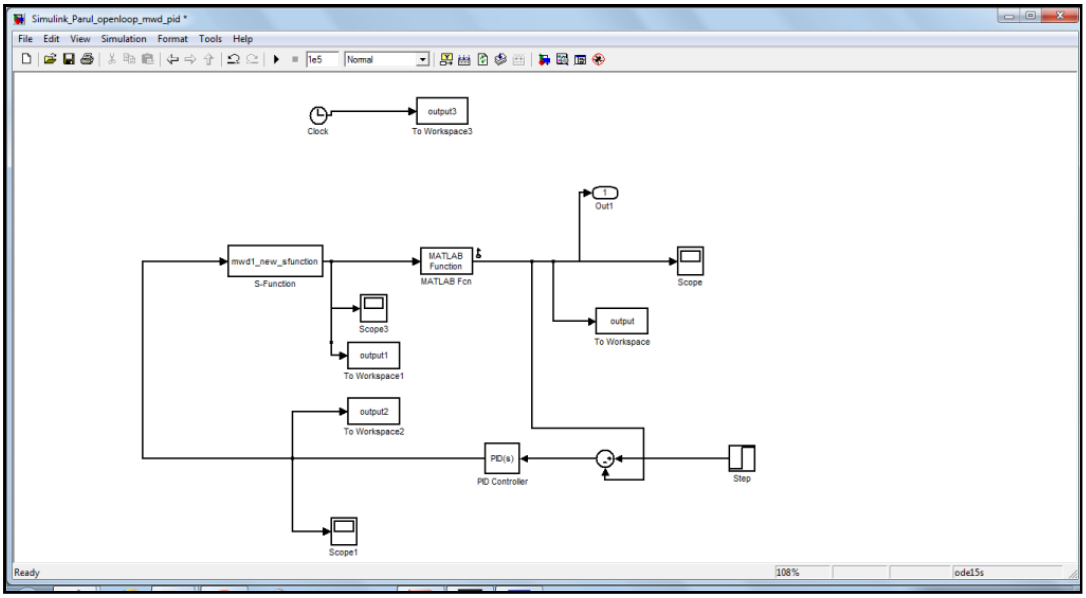


Fig. 6.2: Simulink file for PID

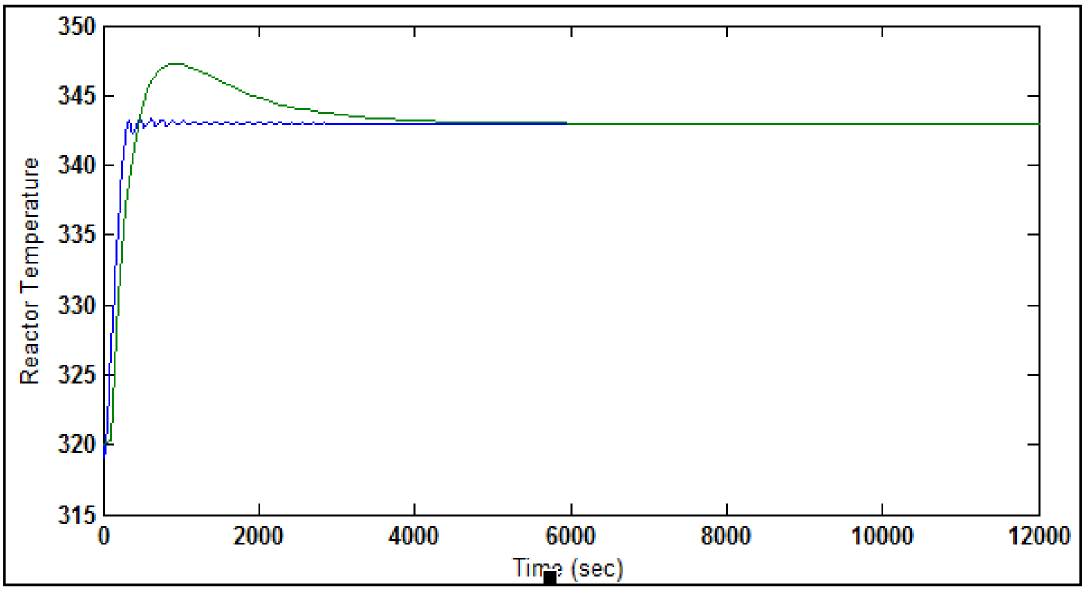


Fig. 6.3: Controlled Variable (split range- blue, Heat load- Green).

The effect of strategy on control variable is shown clearly in the figure 6.3.Green line is showing the PID controller having heater power as manipulative variable and blue shows split range controller. As shown in Fig 6.3 split range controller requires minimum time to settle down at set-point i.e 343 K and heater power takes ample of time (4000 sec) with a small overshoot but there is oscillations occurs in split range controller. The polymerization reaction is an exothermic reaction as the time passes the temperature of the reactor increases along with conversion, hence these controllers maintain the temperature at its target value using there respective control logics. Split range manipulates the flow rates of the steams either hot water or cold water as required where as in second controller the value of heat load of the heater changes with error calculated by the controller. The value of the heat load varies from 40 W to 140 W. Temperature overshoot are noticed in both the controllers at the start of the reaction. The initial overshoot is caused by the fact that for MMA polymerization, most of the heat released at the initial stage of the polymerization when initiation and propagation kinetics are dominating.

Split range controller uses both hot water stream and cold water stream as its manipulative variable (Fig 6.4) and is capable to maintain set-point better than PID using heater power as manipulative variable.

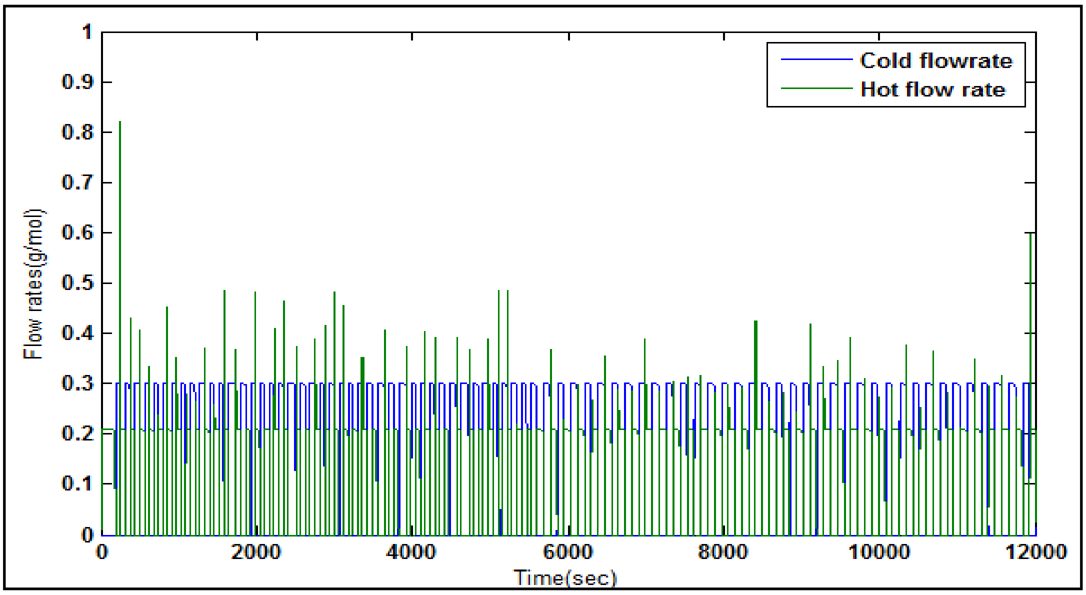


Fig. 6.4: Manipulative variable of split range controller.

The parameters used (Table 6.1a, 6.1b) and performance indexes for both the controller were studied and tabulated in Table 6.2. The data of performance index provide evidence that split range perform better than the heater power.

The value of absolute error for split range is 3.833X10^6 which is enormously lesser than heater power method having value 1.4137X10^7.

As the temperature increases, initial conversion increases significantly. This is expected because the rates of reactions are exponentially temperature dependent functions according to Arrhenius law. At higher temperature, concentration of oligomeric radicals in the aqueous phase and nucleation rate increase and consequently the total number of particles increases. This in turn leads to a smaller final average particle size but run away of the temperature destroys the uniformity of the particles hence a robust control is required to maintain the particle size of the latexes. A better controller is one which handles the load change and set-point change efficiently along with set-point. Figures 6.5 and 6.6 show set-point change in both the controllers. In split range after set point change there are some oscillations before settling down to its target value but in heat load set point change is very smooth.

Both two are capable to maintain the desire reactor temperature with suddenly set point change but there is some noticeable oscillations in split range controller which makes heat duty as manipulative variable as better controller to be used furthur. Performance index is calculated for the system, results are discussed in Table no 6.2.

Performance index were compared in Table 6.3. Performance index shows heater power as manipulative variable is capable to handle load change and set-point change better than split range, which means heat load as manipulative variable is much better strategy to be used since physically or practically there may be disturbance at any time to the controller. The control system for a polymerization reactor must be sufficiently robust to handle unmeasured disturbances, which impact polymer reactor operation. These disturbances typically result either from trace amount of polymerization inhibitors or retarders left over after monomer purification.

The purpose of this test is to see the effect of error on the controller during the process. This error has the effect on the temperature, change in flow rate of the cold water in second strategy is being used to introduce the error in the system, as seen in the figure 6.7 controllers efficiently maintain the temperature by changing the value of manipulative variable.

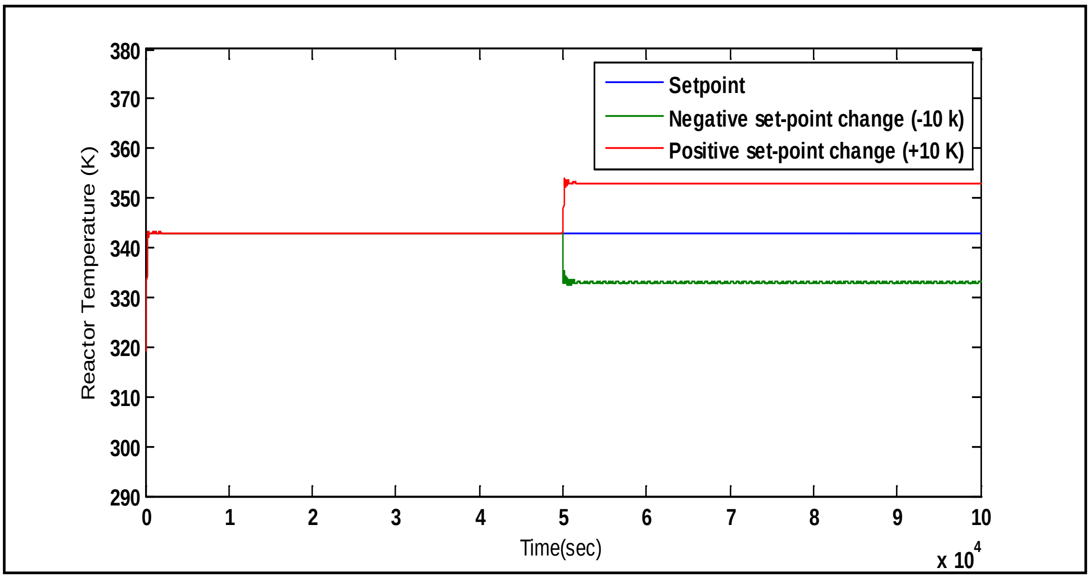


Fig. 6.5: Set point change in split range controller

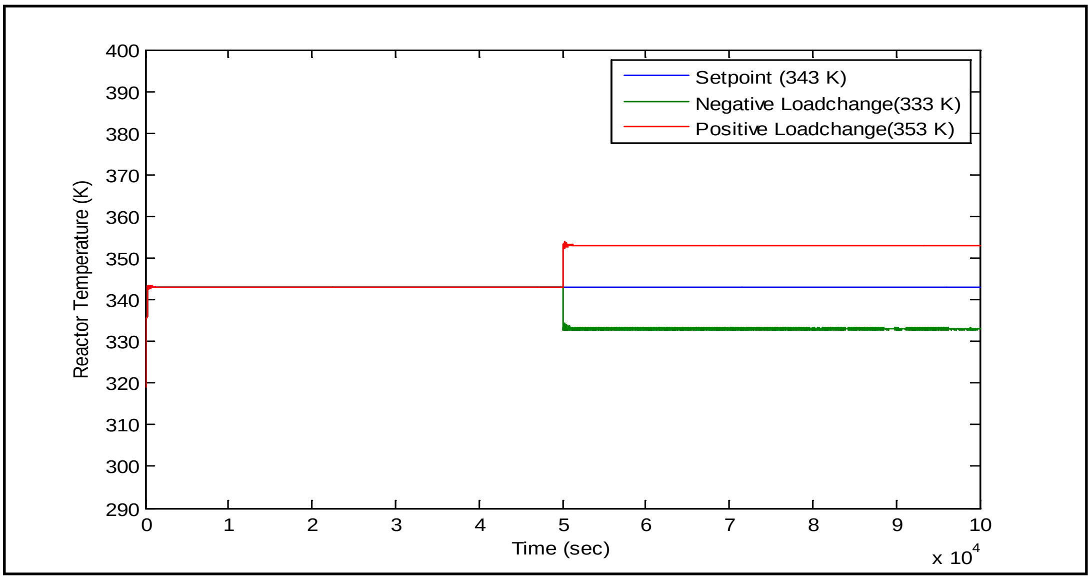


Fig. 6.5: Set point change in split range controller.

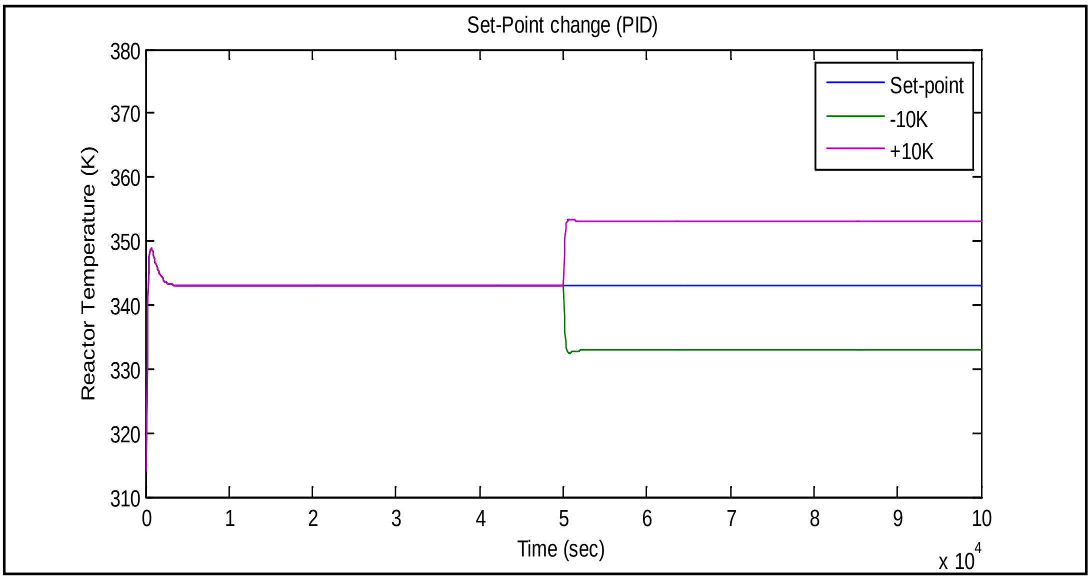


Fig. 6.6: Response of Set point change in controller having heater power as manipulative variable.

We have also studied the load change, in second method it requires 402 seconds to reject the disturbance causes load change in system shown in Fig 6.8 below.

The results explained above point that the PID controller using heater power as its manipulative variable is perform better than the other controller.

After the study of performance of any controller their optimization is the second objective to be studied. Optimization of controller is used to study to optimize the parameters value that a controller used. We have optimized the parameters of the controller for better performance as shown in Fig 6.8 and 6.9.

A common problem in emulsion polymerization is to maximize production of a high quality polymer under safe conditions. Process optimization is an activity is a useful tool to solve this problem.

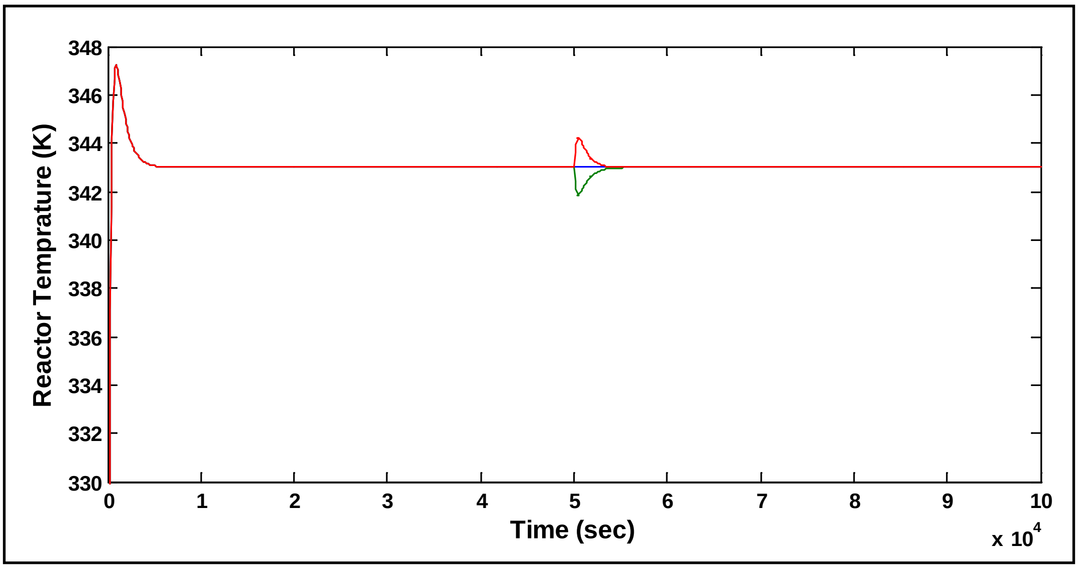


Fig. 6.7: Response of load change in second controller (heater power as manipulative variable).

Parameter Tuning

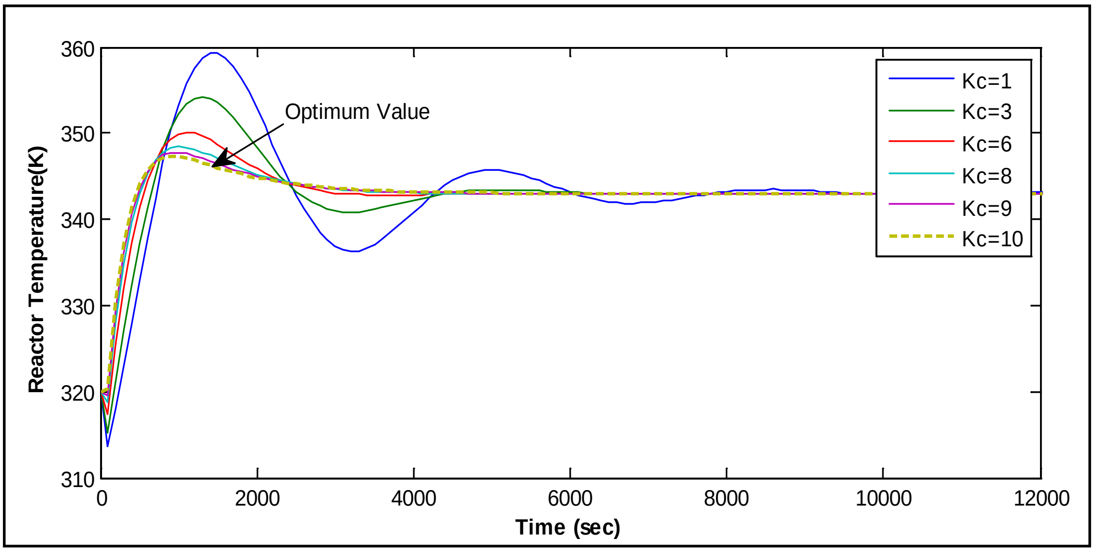


Fig. 6.8: Optimization of controller gain in second controller ($\tau_I = 0.01$).

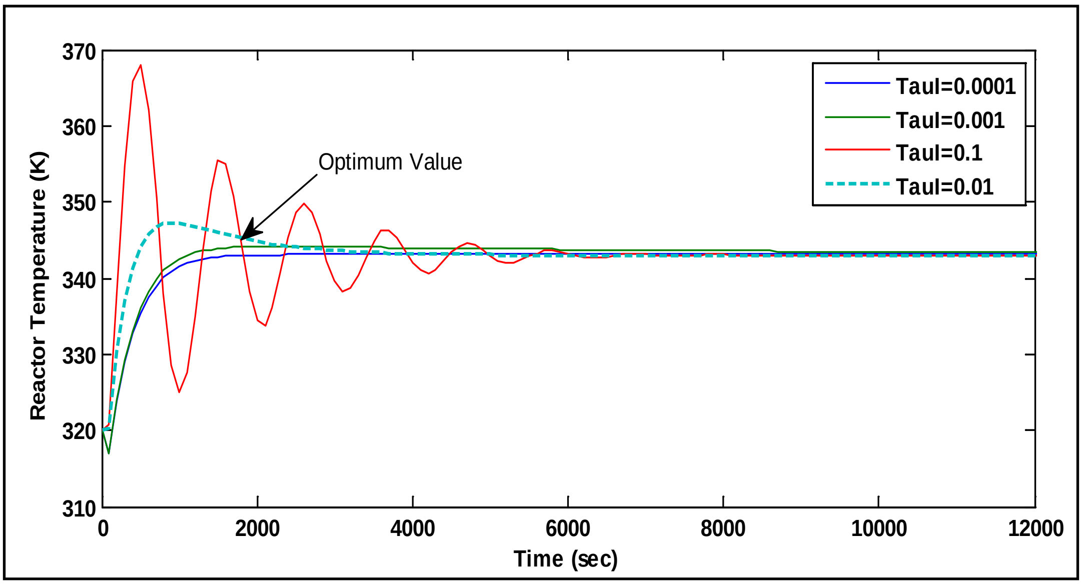


Fig. 6.9: Optimization of τ_I in second controller (K_c=10).

Responses for the change of values of integral time (τ_I), as shown in figure 6.9 for τ_I = 0.0001, 0.001, 0.01 and 0.1 were studied (controller gain, Kc is held constant). It was observed that as the value of integral time decreases, the response becomes less oscillatory but more sluggish, whereas on increasing the value of integral time above 0.01 the system shows some oscillatory behaviour. The effect of various values of controller gain (Kc) were also studied (with constant integral time, τ_I) for Kc = 1, 3, 6, 9 and 10 and is shown in Fig. 6.8. It was observed that at lower value of Kc the controller acts aggressively and oscillatory but finally bringing the response to the desired set point at Kc= 10.

It is found while using split range controller, there is critical zone when switching from heating to cooling. To avoid both heating cooling together is required, there is also a small dead zone where both heating and cooling is absent. Switching between both the modes of control may cause oscillations and difficulties. Comparison of density function of two controllers along with experimental result is shown in fig. 6.10.

Table 6.2: Performance at set-point (343 K) using two different control strategy.

Performance Criteria	Split Range controller	Controller using Heat duty
ITAE	**3.8333e+006**	1.4137e+007
IAE	**3.1993e+002**	1.6120e+004
ISE	**4.2969e+004**	1.8296e+005
ITSE	**5.1468e+007**	7.4853e+007

Table 6.3: Performance of controllers for set-point change and load change.

Controller	Split Range controller				Controller using Heat duty			
Parameter	**ITAE**	**IAE**	**ISE**	**ITSE**	**ITAE**	**IAE**	**ISE**	**ITSE**
Positive Load Change	2.2805 e+008	1.956 e+004	3.5205 e+005	4.2102 e+007	**1.1458 e+007**	1.1949 e+004	1.1505 e+005	1.3816 e+007
Negative Load change	2.7642 e+008	2.311 e+004	4.2346 e+005	5.0635 e+007	**1.0403 e+007**	1.3755 e+004	1.1637 e+005	1.9161 e+007
Positive set-point change	4.8527 e+010	3.643 e+005	5.0364 e+006	6.692 e+010	**3.7422 e+010**	3.1014 e+005	5.0013 e+006	3.7385 e+010
Negative set-point change	1.5279 e+010	5.152 e+005	5.9209 e+006	2.1469 e+010	**1.4722 e+010**	5.1014 e+005	5.9213 e+006	1.7385 e+010

The global minimum of the performance index function for each of the experimental cases was then calculated. Based on the conditions, the performance is optimized when the chosen value of performance index function is minimized. The result of this calculation of performance index indicates which conditions lead to the optimum performance. Line plots, as illustrated in Figure 6.3, provide a graph of these trends. Therefore, a prediction can be made regarding the operating conditions that result in the optimum performance (tabulated in Table 6.2). Table 6.3 shows the performance indexes for set point change from 333 to 353 K. The integral of time absolute error (ITAE) is the popular performance criterion used for control system design. The error is lesser with PID controller using heater power as manipulative variable. Therefore, for further study second control strategy will be used.

Validation

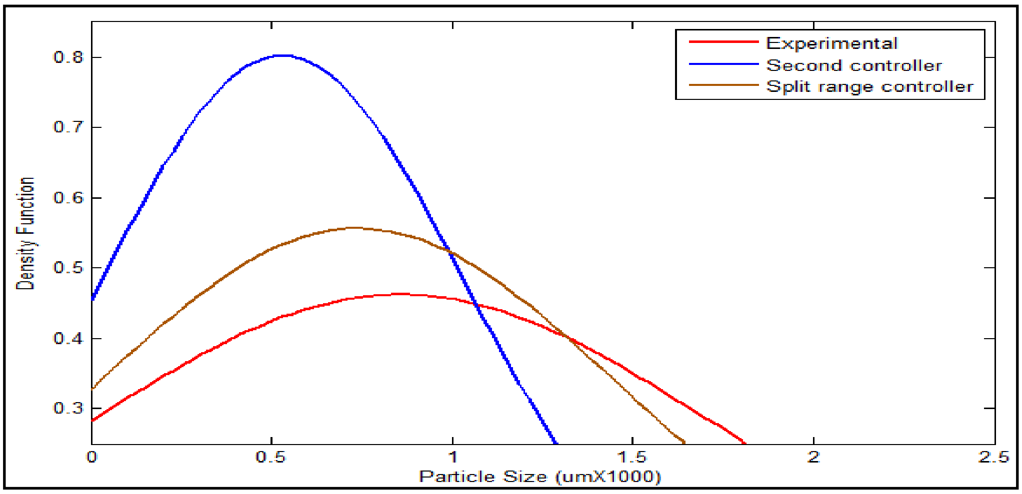


Fig. 6.10: Comparison of density function.

The temperature influences both micelle formation and adsorption of surfactant onto the polymer particles, the rise of temperature causes the increase of CMC in reaction solution, simultaneously with its values.

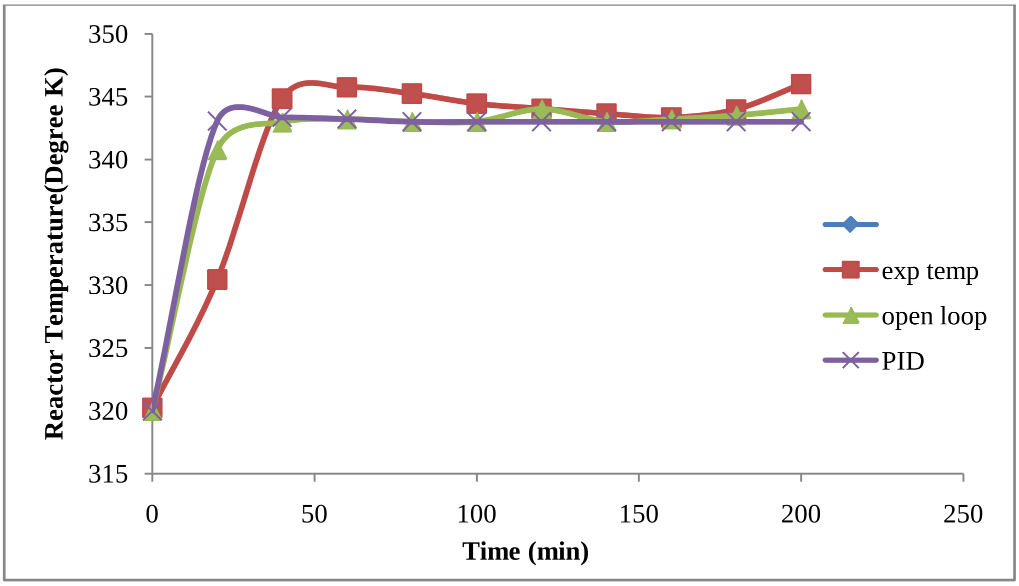


Fig. 6.11: Comparison of Reactor Temperature.

The Figure 6.11 demonstrates the comparison of controlled variable calculated from experiments (on/off controller), open loop run in simulation study and result of PID controller. Experimental result shows some variation from the set-point value of the reactor temperature i.e. 343 k. This variation is the result of exothermic nature of the reaction, during the process temperature increases; effective cooling system is required at the same time to maintain the temperature to its target value. Some times normal cooling system is not capable to maintain the temperature of the reactor hence a robust control system is required. First we run the model in open loop system again the variation was found in the temperature of the reactor. PID controller was implemented to the model using the Toolbox available in the MATLAB; the simulink file is given in figure 6.2. PID controller initially gives a loop and within a few minutes it's settling down to its set-point and is able to maintain the temperature through out the process.

6.2 Model Predictive Control

MPC has attracted many researchers due to its better performance and control of processes including non-minimum phase, long time delay or open loop unstable characteristics (Golshan, MacGregor et al. 2010; Sekia, Ogawab et al. 2001).

The main advantage of the MPC is that constraints (due to: manipulative variables, physical limitations, operating procedures or safety reasons) may be explicitly specified into the problem formulation. The second advantage is its ability to address long time delays, inverse responses, significant non-linearities and multivariable interactions.

During the study of PID controller we came to know that in our case heat load as manipulative variable is better methodology to control the molecular weight and particle size distribution hence we continue with the same, in this section we are going to discuss MPC controller for MWD and PSD followed by NNPC.

The model predictive controller is used for control of PSD of polymer PMMA. Heater power of the heater is used as manipulative variable and temperature as controller variable in this study. The coolant flow rate is kept constant. The design parameters used in the simulation given in Table 6.4, 6.5. The performance of MPC is compared with PID controller. Our next objective is to improve the control performance. Tunning of the controllers were done by trail and error method and tabulated in table 6.6 for MPC and table 6.7 for PID. Figure 6.12 shows the controller profile for MPC and PID. The response shows that PID controller took large time to get closer to the set-point with overshoot. MPC took 2100s where as PID adjusted within 2800s to the set-point with 4 K overshoot which depicts higher overshoot than MPC. In MPC heat duty oscillates in start-up but In PID heater power oscillated at time 50000s with initial start-up also where as MPC gives rest response smoother than PID which will prolong the life of heater.

Absolute Error calculated for the reactors are given in table 6.6 for MPC on the basis of performance index tunning parameters was finalized.

Table 6.4: Tuning parameters for MPC

Parameters	**Value**
Weight Tuning	0.7
Prediction Horizon (Np)	100
Control Horizon (Nc)	10

Table 6.5: Tuning parameters for PID

Parameters	**Value**
Controller Gain	10
TauI	0.01

In industrial practice, some uncertainty and disturbance are normally encountered in the reactor; to explore this we introduce disturbance and set-point change in the reactor. An excitation in the cold flow rate was introduced at the time 50000s. Increasing the flow rate would decrease the temperature of the reactor and decrease in flow rate would increase the temperature because of the heat transfer rate of the reactor shown in fig 6.13 for MPC and PID simultaneously. Similarly set-point was also introduced into the system at time 50000s shown in figure 6.14 for MPC and PID. MPC took less time as compared to PID for getting closer to the set-point in load-change, and gave less oscillation in set-point change with small overshoot. This evidence that advance controllers are promising than traditional controllers in terms of there robustness for non-linear control. Comparison of particle density function is given in figure 6.18.

Table 6.6 :MPC Performance Index for PSD (Lowest ITAE value is the significant digit).

Parameter	ITAE	IAE	ISE	ITSE
Weight Tunning-0.7	**1.7150e+012**	**3.4315e+007**	**1.1775e+010**	**5.8825e+014**
Weight tunning-0.8	1.8158e+012	2.8626e+007	6.7263e+010	2.6668e+014
Nc-10	1.7190e+007	3.4355e+007	1.1776e+010	5.8826e+014
Nc-20	**1.7150e+012**	**3.4315e+007**	**1.1775e+010**	**5.8825e+014**
Nc-50	1.7550e+012	3.4395e+007	1.1795e+010	5.8828e+014
Np-500	**1.7150e+012**	**3.4315e+007**	**1.1775e+010**	**5.8825e+014**
Np-1000	2.1150e+012	2.1315e+007	1.7715e+010	6.6825e+014

Table 6.7: Performance Index PID for PSD

Parameter	ITAE	IAE	ISE	ITSE
Kc-10	**1.1458e+007**	**1.1949e+004**	**1.1505e+005**	**3.1816e+007**
Kc-9	1.1657e+007	1.2715e+004	1.2730e+005	3.8286e+007
Kc-8	1.1871e+007	1.3540e+004	1.4205e+005	4.6841e+007
Kc-6	1.4137e+007	1.6120e+004	1.8296e+005	7.4853e+007
Kc-3	3.1867e+007	2.5277e+004	3.0668e+005	1.9843e+008
TauI-0.1	5.0679e+007	3.3373e+004	4.2574e+005	3.6435e+008
TauI-0.01	**1.4137e+007**	**1.6120e+004**	**1.8296e+005**	**7.4853e+007**
TauI-0.001	1.0293e+008	2.0597e+004	1.7498e+005	6.7183e+007
TauI-0.0001	2.4418e+008	1.6576e+004	1.7379e+005	4.4335e+007

As already mentioned, performance index is calculated to optimize the parameter by minimizing the error by using the ITAE performance criterion. The integral of the absolute magnitude of error (ITAE) criterion is defined as

$$\mathrm{ITAE}=\int_0^T \left| t\, e(t) \right| dt \tag{6.1}$$

The ITAE performance index has the advantages of producing smaller overshoots and oscillations than the IAE (integral of the absolute error) or the ISE (integral square error) performance indices. In addition, it is the most sensitive of the three, i.e. it has the best selectivity. The ITSE (integral time-square error) index is somewhat less sensitive. Since it is not practicable to integrate up to infinity, the convention is to choose a value of T sufficiently large so that e(t) for t > T is negligible.

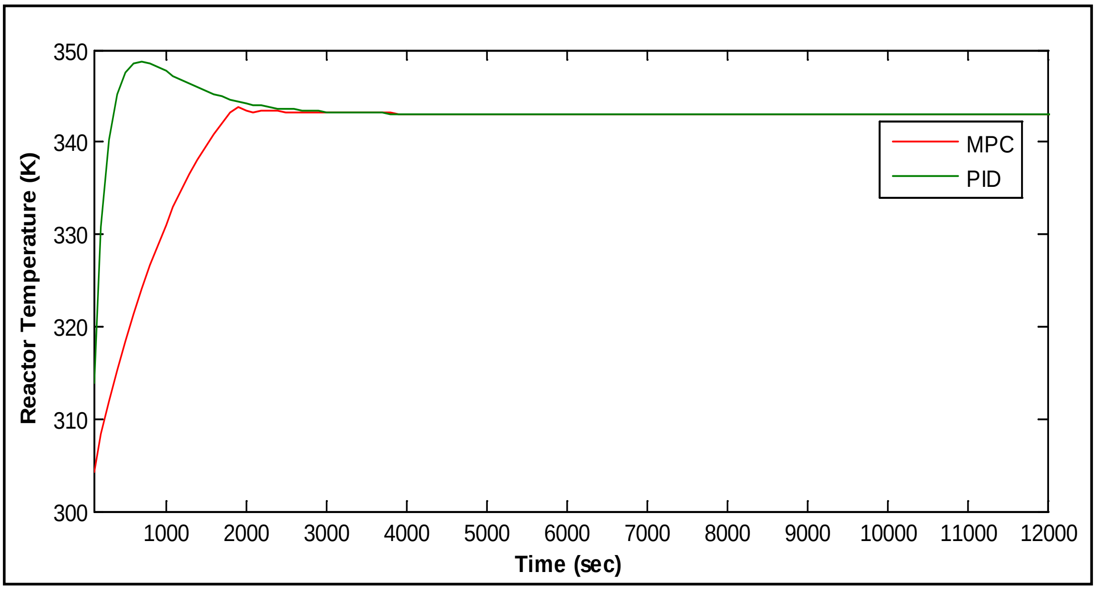


Fig. 6.12: Compariosion of Control variable results of MPC and PID controller.

It is observed in figure 12, in MPC the peak of temperature does not occur, because the MPC strategy is enough to maintain the temperature sufficient to slow down the process dynamics. Thus the controllability of the process is better, even at set-point trajectory (figure 14) and load change shown in figure 13.

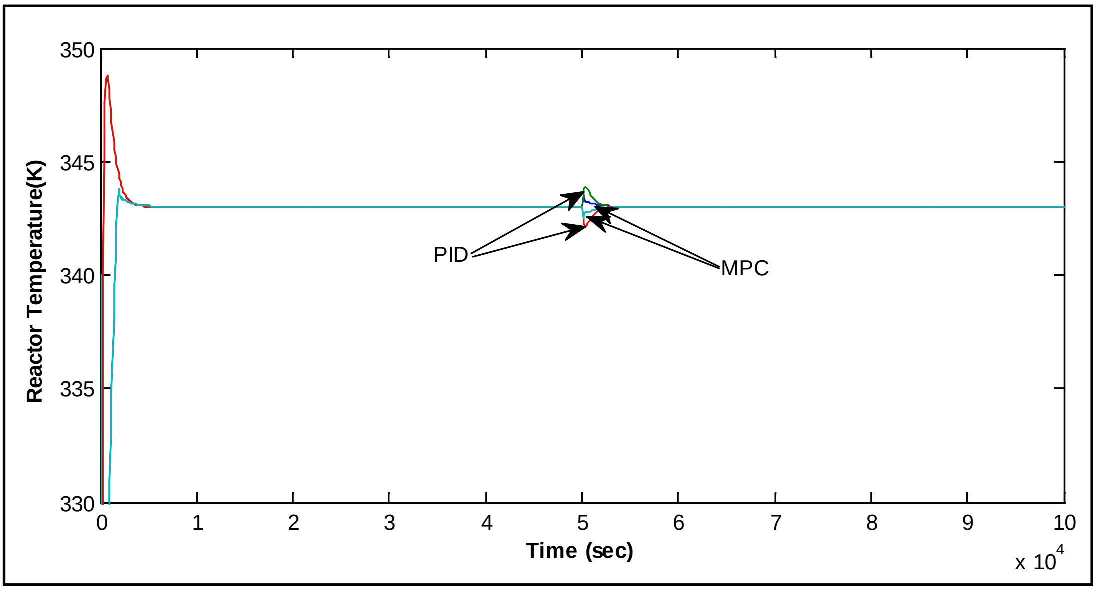


Fig. 6.13: Response of Load change in PID and MPC

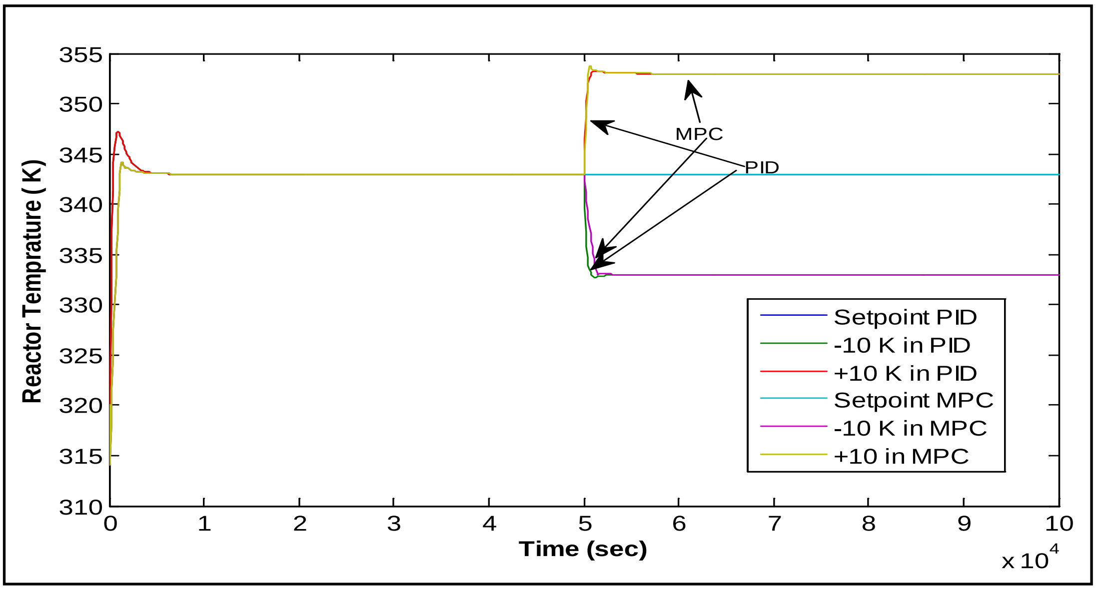


Fig. 6.14: Response of set-point change in PID and MPC

After simulation time 50000 sec, error is introduced in flow rate of water stream in jacket, the impact of this uncertainty on the reactor temperature is shown in the Figure 6.13. As the flow rate of cold water stream decreases to its value 0.4 kg/sec the temperature start rising at the same time as expected MPC takes about 2000 seconds to settle down the control variable to its set-point value. Similarly if introduced flow rate of 0.6 kg/sec causes negative load change as the Figure 6.13 shows.

With MPC algorithm the operation with better control of the process even with disturbance is possible. The main disadvantage of this algorithm is that the time for obtaining the control movement is much larger than PID.

Parameter Tuning

Tuning of parameters in batch reactor is always difficult as compared to continuous reactor. Trial and error method was using for tuning of both the controllers. In MPC as the value of weight tuning decreases number of oscillations increases, Change in control horizon and prediction horizon makes little difference (fig 6.15, 6.16, 6.17) but the best value was taken after the study of performance index.

The quality of control of any controller is strongly depends upon their parameters, simmilarly quality of MPC depends on weight tuning factor, control horizona nd prediction horizon. In figure 6.16 one can see the fact that value of weight tuning factor strongly affects the quality of control of MPC. Increase in the value of weight factor causes ossilatory behaviour, the best quality being obtained for weight tuning= 0.7.

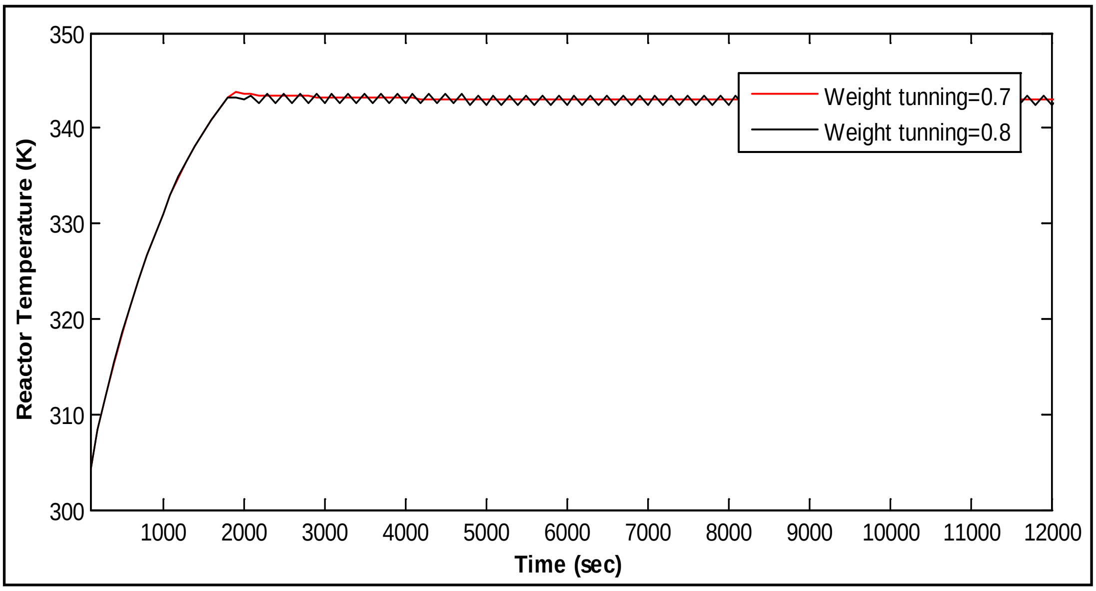


Fig. 6.15: Parameter analysis (weight tuning) of MPC (Nc= 10, Np=20)

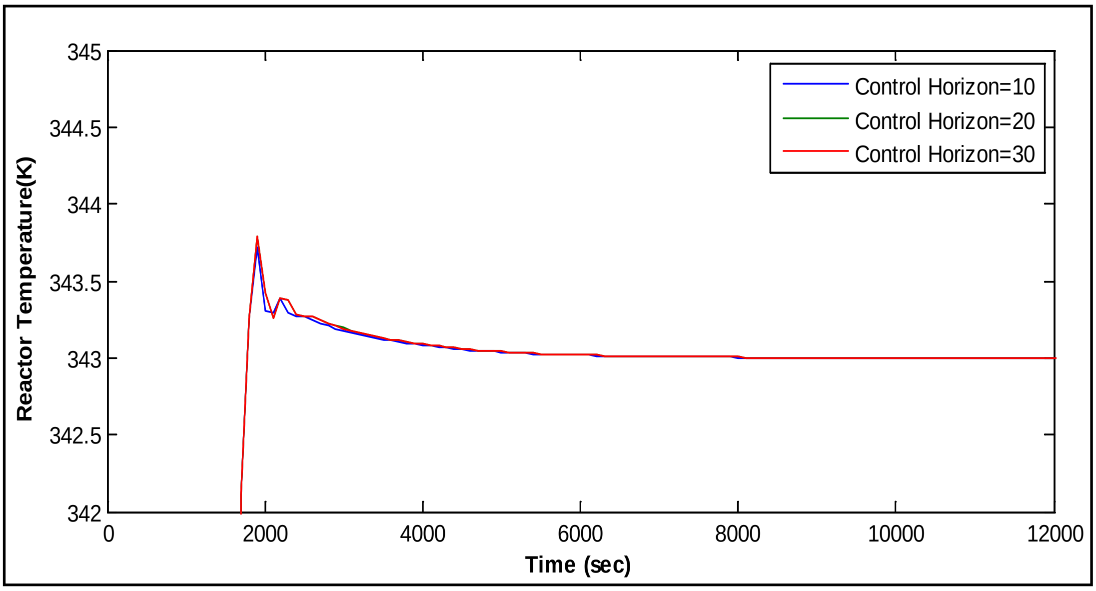


Fig. 6.16: Parameter analysis (control horizon) of MPC.(wt= 0.7, Np=500)

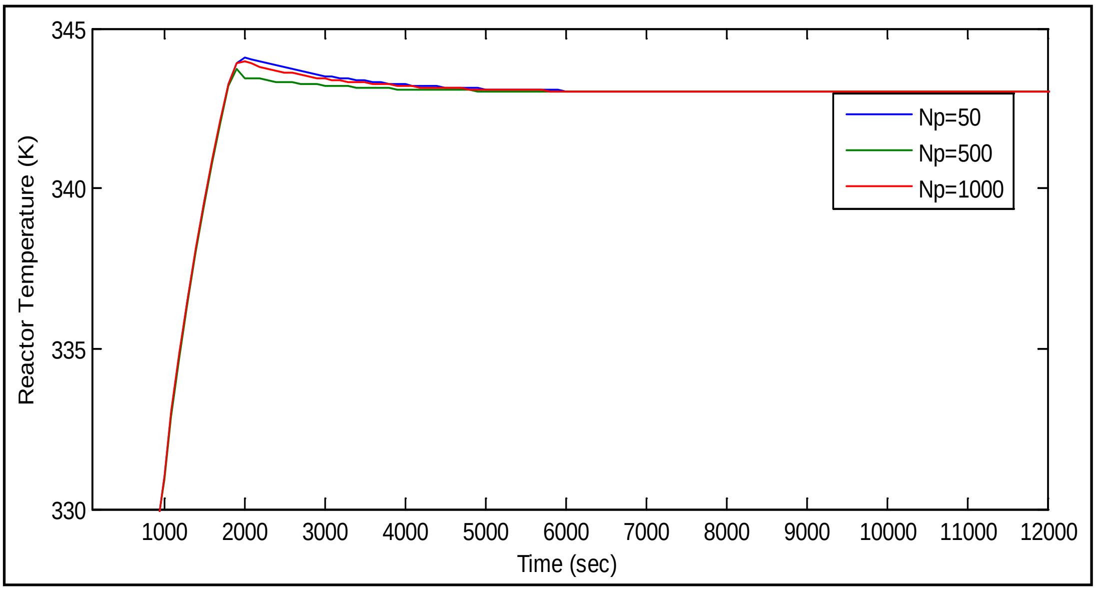


Fig. 6.17: Parameter analysis (prediction horizon) of MPC (wt=0.7,Nc =20)

The best result for prediction horizon is obtained for the value 500 (figure 6.17), the quality of control decreases either P exceeds or decrease from the value P= 500.A bump were found in the starting after changing the value of prediction horizon. The value of control horizon does not influence the nature of control (figure 6.16). After analysing performance index we found best results for value 20.

Validation

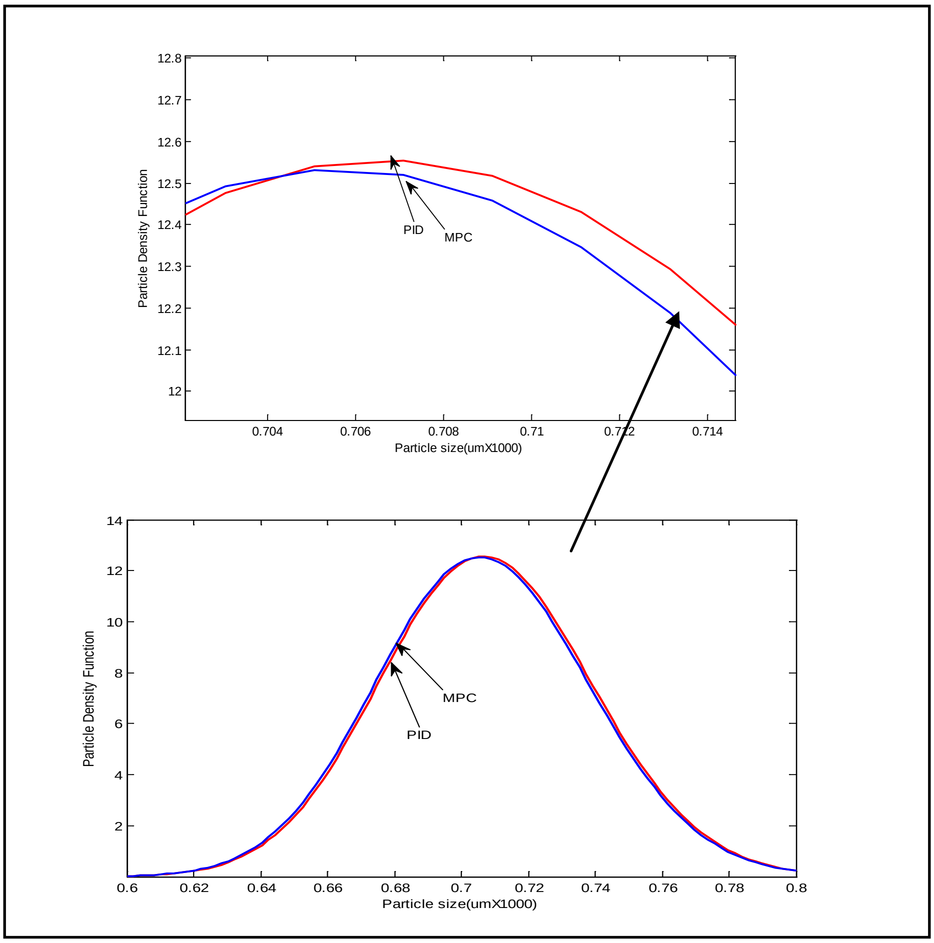


Fig. 6.18: Comparison of particle density function (Red- PID, Blue- MPC).

Figure 6.18 shows the effect of type of controller used on particle density in terms of its function. By increasing the reactor temperature the free surfactant concentration reduces more quickly, therefore its concentration reaches below the critical micelle concentration (CMC) sooner. As micellar nucleation occurs as long as free surfactant concentration is above the CMC, increasing the reactor temperature reduces the nucleation period. On the other hand, the increase of reactor temperature results in a higher rate of production of oligomeric radicals, which leads to formation of more particles in a shorter time. Consequently, increase of the reactor temperature leads to production of higher number of particles in a shorter time and therefore PSD becomes narrower with a smaller average particle size; it is required to maintain the temperature through out the process for uniform narrow distribution.

The main advantage of MPC over PID controllers are its ability to handle constraints, non-minimum phase processes, changes in system parameters and its straightforward applicability to large, multivariable processes.

6.3 Neural Network Predictive Control

Ideally a large amount of data covering process operating conditions should be used in neural network model, but in batch processes neural network models are usually not abundant due to limited runs.

Neural network predictive control is basically a model based predictive control, where the neural network is used for model predictions. It offers an alternative approach to modeling process behaviour as they do not necessarily require a previous knowledge of the process phenomena. They are trained to follow a process by ‘training’ them, were they are open to the sets of input–output data and a least-squares optimization is performed. Throughout this optimization, the neural network forms its own model of the process which can be used to predict output(s) for a given set of inputs. Neural network predictive control uses a neural network model of the process, a history of past control moves and an optimization cost function over the receding prediction horizon to calculate the optimal control moves (Ng and Hussain 2004; Vasickaninova and Bakosova 2009; Zhang, Morris et al. 1998).

In the neural network model Heater power is used as manipulative variable. Performance of manipulative variable is given in figure 6.19; the value of the heater power (M) may vary from 40 W – 140 W. The value of heater power initially increases to reach the desire value of the reactor temperature and after that remains at the value 90 W to maintain the set- pint of the control variable.

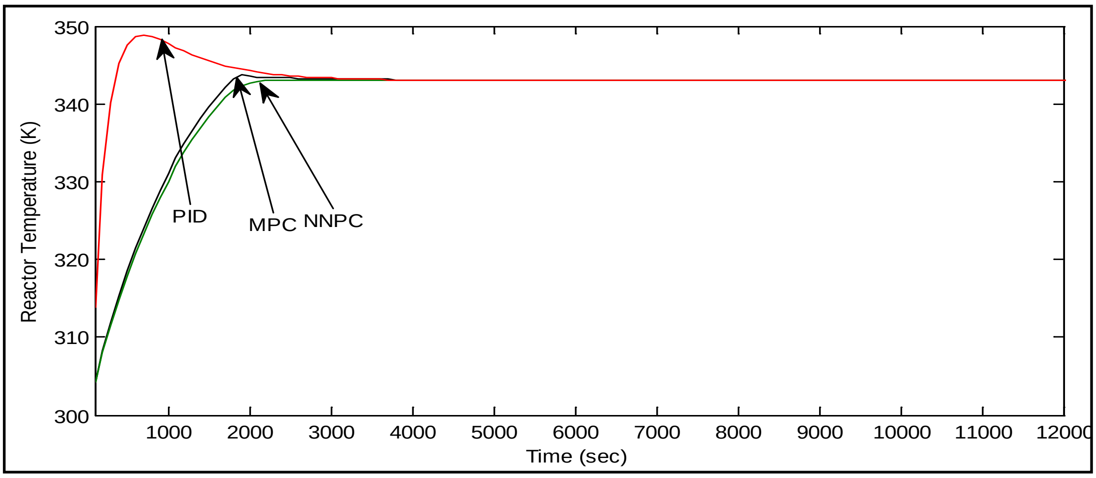


Fig. 6.19: Comparison of Response of Controllers.

Set point trajectory and error were also introduced in the process run as same as discussed for the other controllers to see the performance of the neural network shown in figure 6.20 and 6.21 respectively.

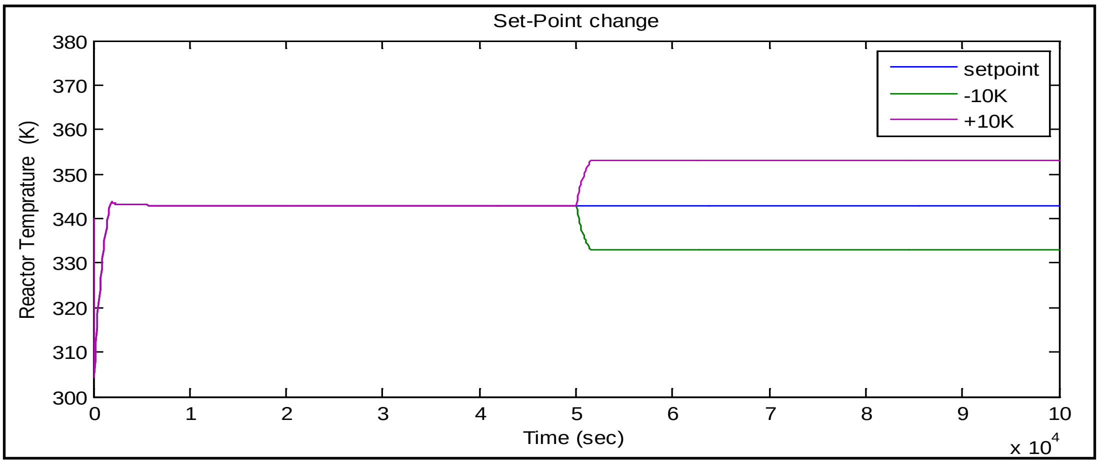


Fig. 6.20: Response of set-point change in control variable

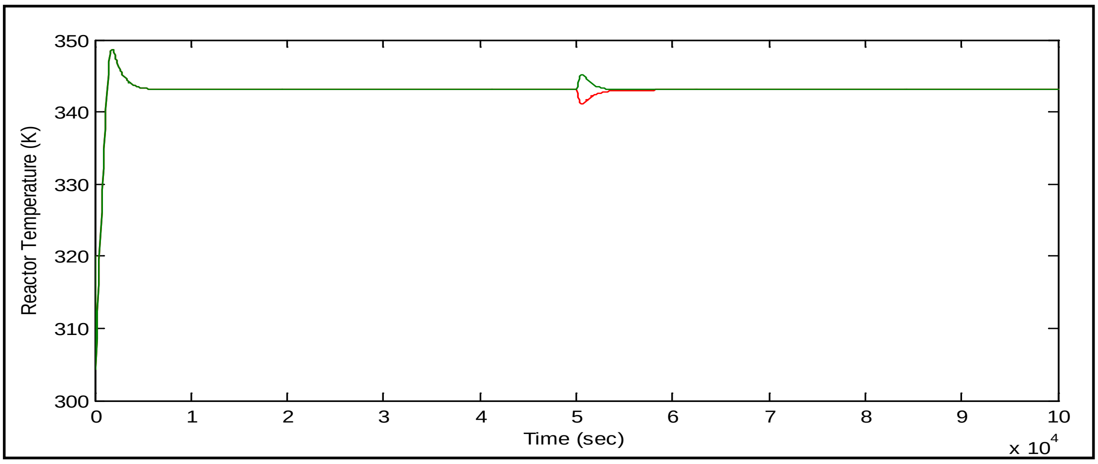


Fig. 6.21: Response of load change in control variable

Tuning

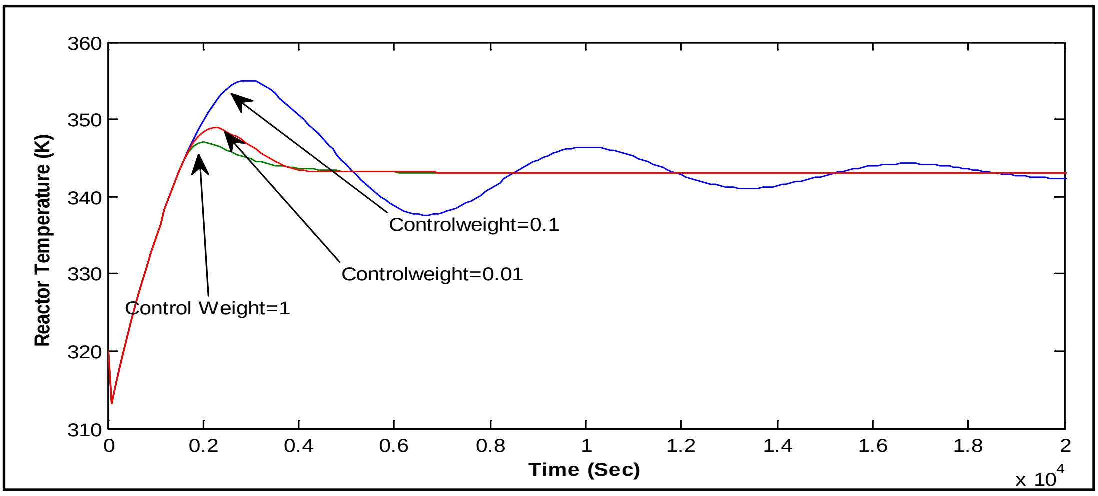


Fig. 6.22: Effect of control weight factor on control variable (Nu =4, H=9)

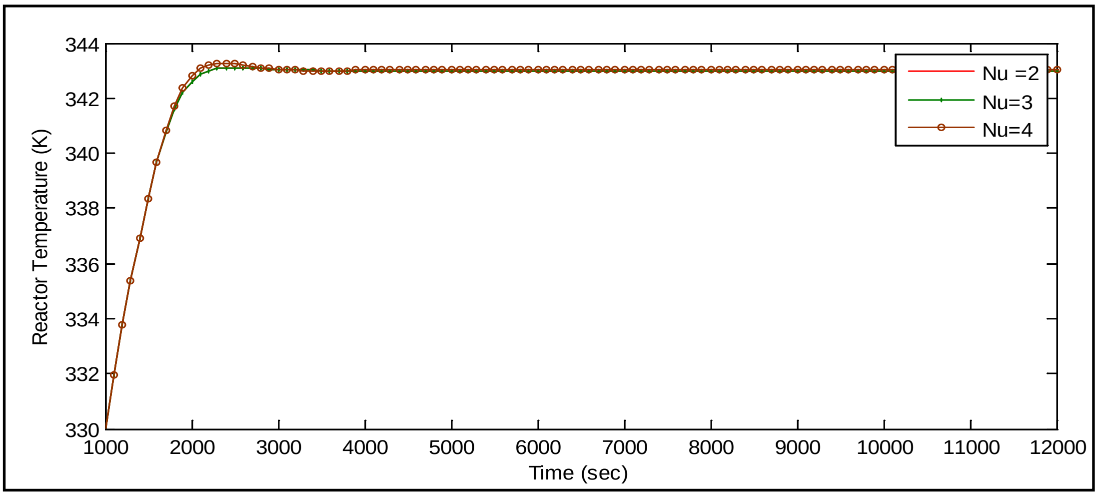


Fig. 6.23: Effect of Nu on control variable (Nc= 0.01, H=9)

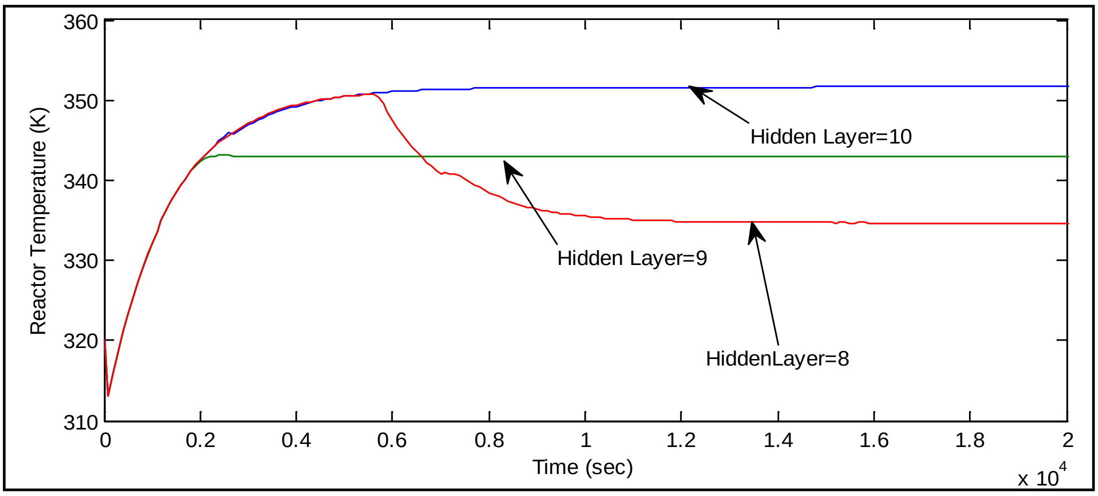


Fig. 6.24: Effect of hidden layer on control variable (Nu=3, Wt=0.1)

Table 6.8: Performance Index NNPC for PSD

Parameter	**ITAE**	**IAE**	**ISE**	**ITSE**
Nu-2	1.7607e+010	2.6725e+005	1.5591e+006	8.2064e+010
Nu-3	**1.7566e+010**	**2.6824e+005**	**1.5665e+006**	**8.1701e+010**
Nu-4	1.7959e+010	2.7307e+005	1.6094e+006	8.5332e+010
Control Weighting factor-1	1.7939e+010	3.1572e+005	1.8872e+006	8.4228e+010
Control Weighting factor-0.1	**1.7566e+010**	**2.6824e+005**	**1.5665e+006**	**8.1701e+010**
Control Weighting factor-0.01	1.5767e+010	2.3927e+005	1.3208e+006	6.5892e+010
Hidden Layer-10	1.5790e+010	2.3951e+005	1.3241e+006	6.6118e+010
Hidden Layer-9	**1.8767e+08**	**2.3927e+004**	**1.3208e+004**	**5.5892e+010**
Hidden Layer-8	2.4878e+012	3.7346e+007	1.8570e+010	1.3869e+015

The quality of any controller can be improved by optimizing there parameters. The effect of parameters on the control quality of the controller are analysed here. The control parameters which have been optimized in this study are Control weight, Nu and neurons of hidden layer in the neural network.

Increase in control weight causes oscillatory behaviour in the control variable. The optimum value found is 0.01 for the control weight (Figure 6.22). A single Hidden layer was used in the neural network, the number of neurons highly affect the control ability of the controller. The optimum value of neurons found is 9, increase in the number of neurons cause controller sluggish in nature (Figure 6.23). Nu does not affect the quality of NNPC strongly but during performance analysis, we found optimum value is 4 for this study; the zoom in view of effect of Nu on control variable is given in Figure 6.24. At the same time, an increased Nu increases the computation time. The choice of control horizon Nu has serious impact on the computational results

Training of Neural Network

Initially, the fundamental model was used as the real process and simulated open-loop in order to obtain two sets of random number data, namely training and test sets. Training datasets contained 5001 samples and test dataset contained 1001 samples with 100 s sampling interval. These datasets were used to generate an input matrix consisting of output variable and manipulated variable.

Figure 6.25 represents our structure of NNPC. Levenberg Marquardt algorithm is used for the training. NNPC first trained using random data collected from the open loop using same model. The procedure for selecting the network parameters is called training the network. The Levenberg-Marquardt (LM) algorithm is very efficient for training. The LM algorithm is an iterative technique that locates the minimum of a function that is expressed as the sum of squares of nonlinear functions. It has become a standard technique for nonlinear least-squares problems and can be thought of as a combination of steepest descent and the Gauss-Newton method.

Number of neurons used in the NNPC is 9, 1000 data sets were used for training and 25% of the training data sets were used for testing and validation purpose.

In this study Feed-forward back propagation neural network was created which consist of number of layers using the input function, weight function and the specified transfer functions. Each consequent layer has a weight coming from the previous layer. The last layer is the network output. For creating a feed-forward back propagation network, first we define the number of hidden layers and number of neurons in the hidden layer. In this study we specified 9 neurons in single hidden layer and used a ‘tan-sigmoid’ transfer function for hidden layer. Figure 6.26 shows the resulting network. The training performance and training state is given in the Figures 6.27 and 6.28 respectively.

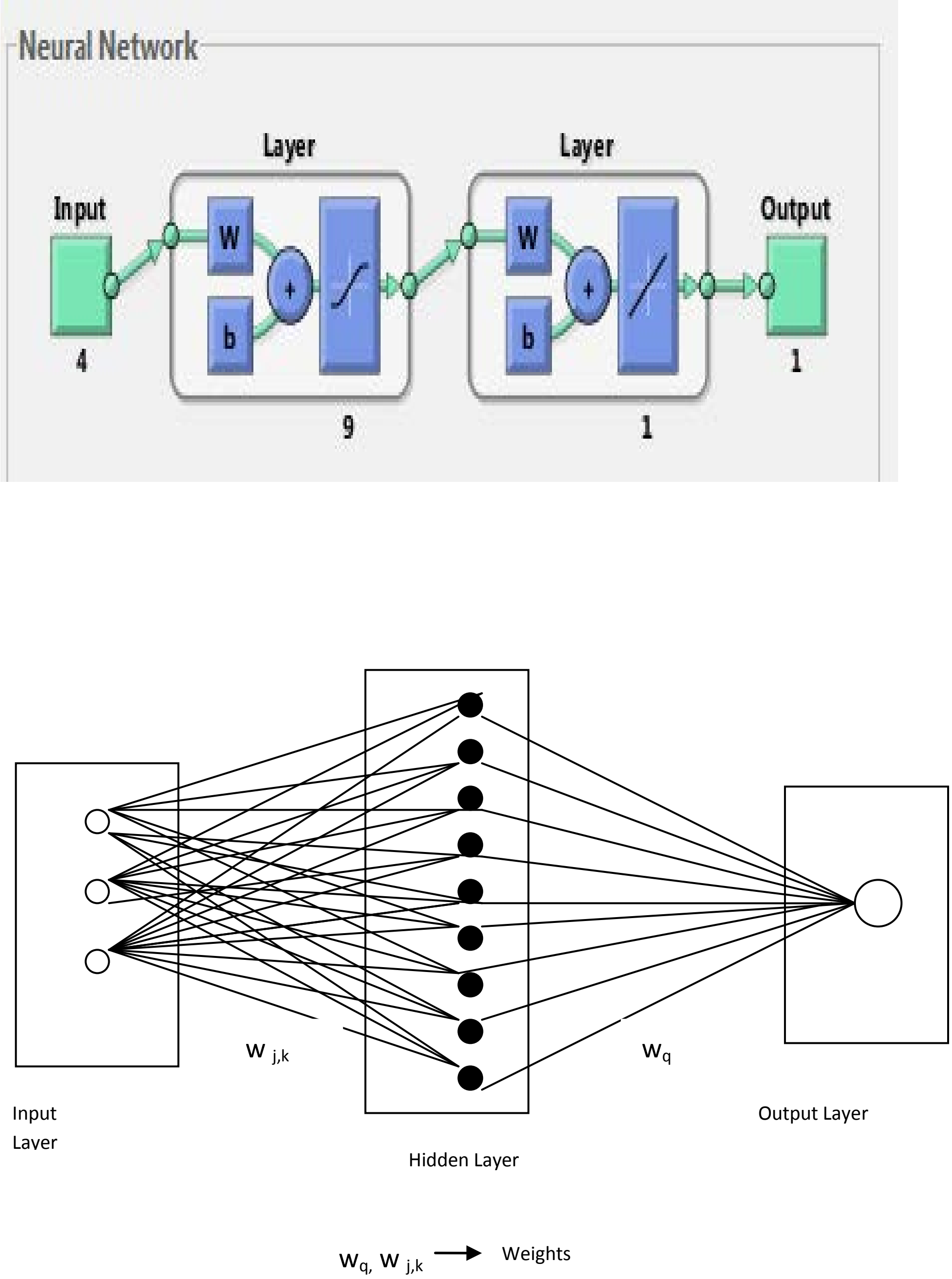
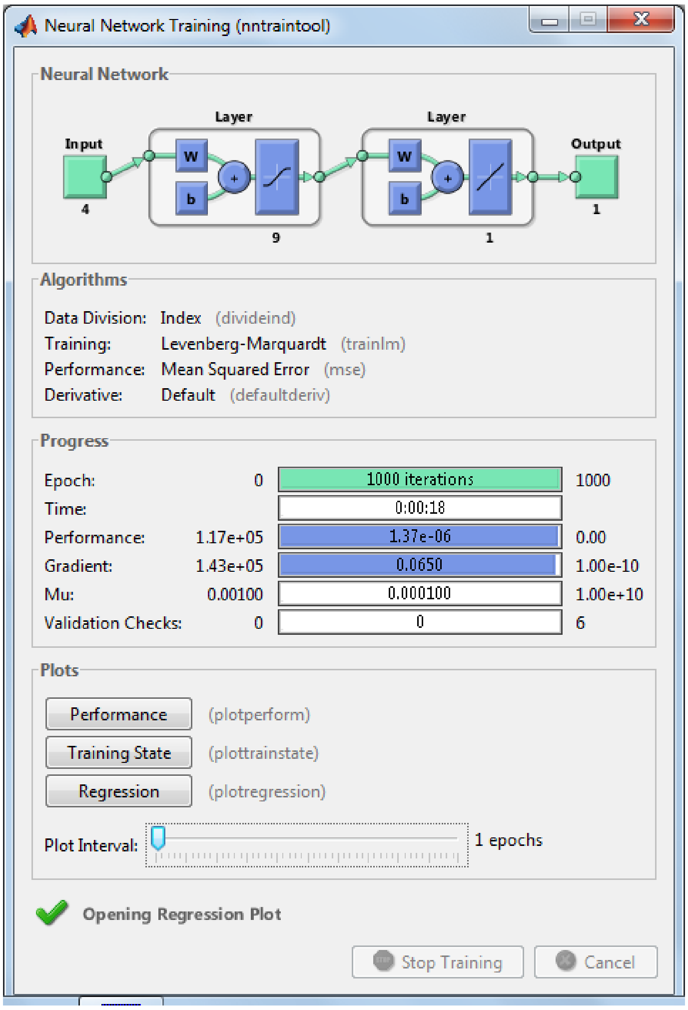


Fig. 6.25: Neural Network



Algorithms

Data Division: Index (divideind)
Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Derivative: Default (defaultderiv)

Progress

Epoch:	0	1000 iterations	1000
Time:		0:00:18	
Performance:	1.17e+05	1.37e-06	0.00
Gradient:	1.43e+05	0.0650	1.00e-10
Mu:	0.00100	0.000100	1.00e+10
Validation Checks:	0	0	6

Plots

Performance (plotperform)
Training State (plottrainstate)
Regression (plotregression)

Plot Interval: 1 epochs

Opening Regression Plot

Fig. 6.26: Neural Network Training

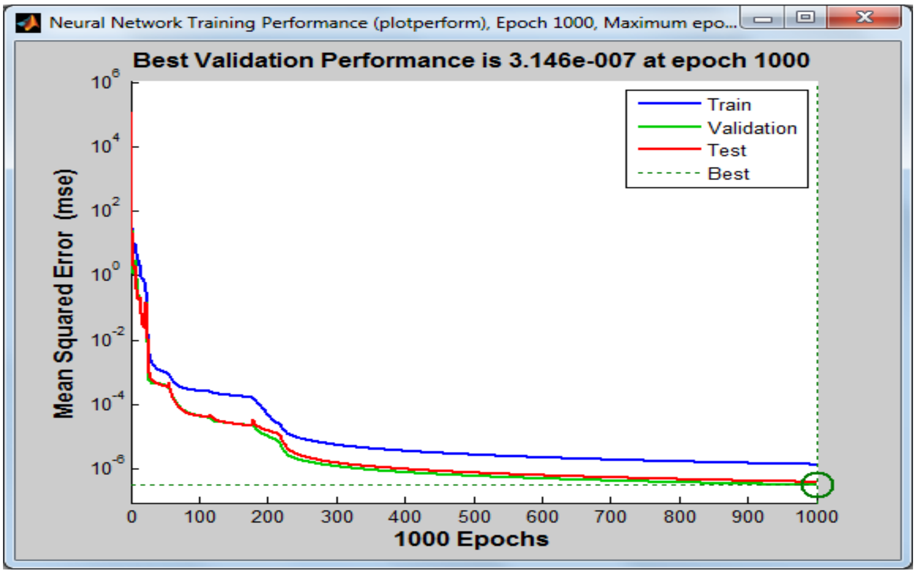


Fig. 6.27: Neural Network training performance

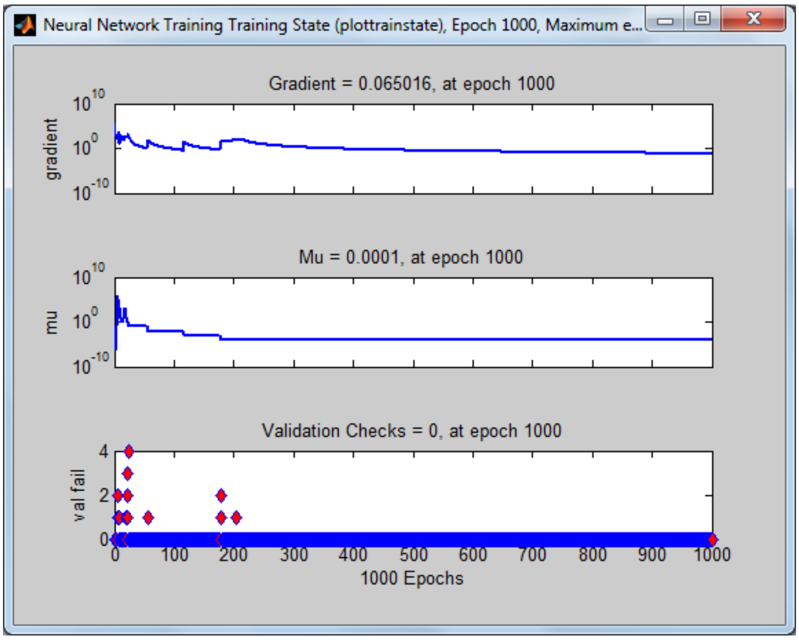


Fig. 6.28: Training state of Neural Network Training

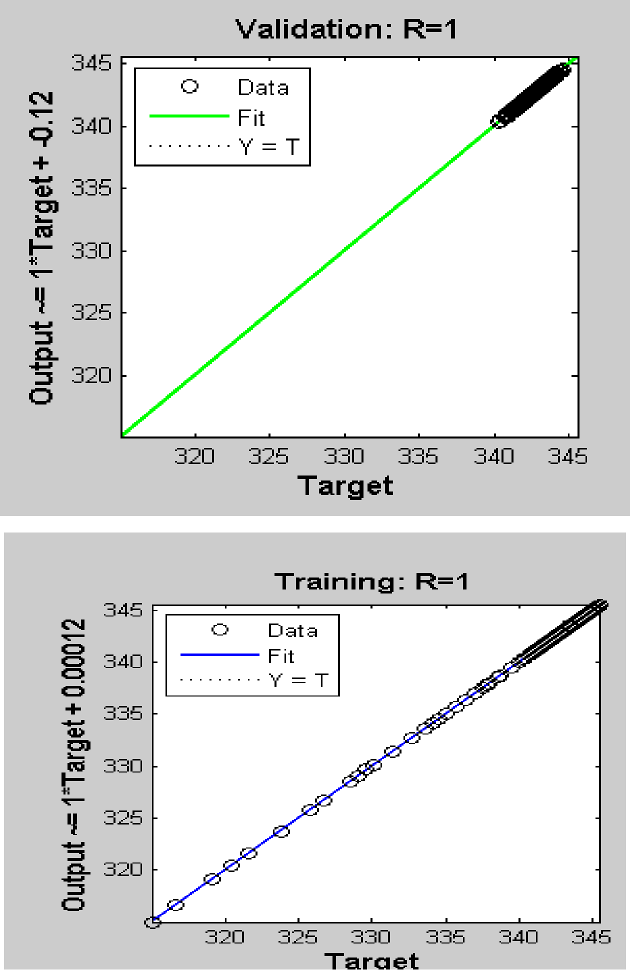
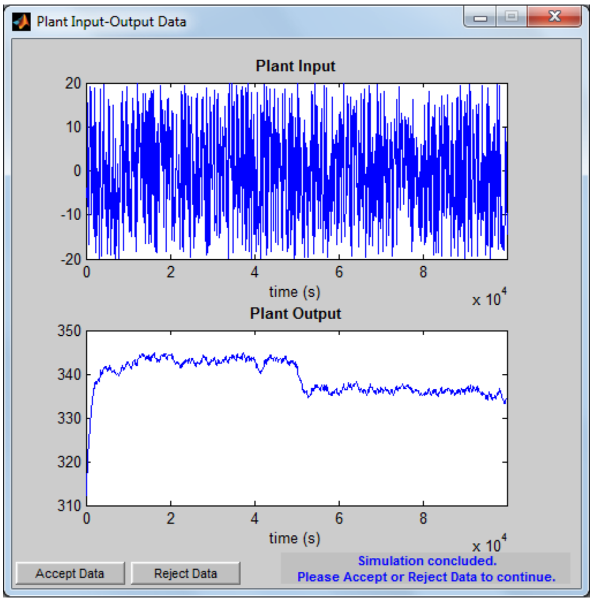


Fig. 6.29: Regression analysis for training and validation of Neural Network.



Simulation concluded.
Please Accept or Reject Data to continue.

Fig. 6.30: Input/output data produced during training

The neural network was trained using Levenberg- Marquardt backpropagation (trainlm) method the training output data produced during the training is shown fig 6.30. The regression shows that the training is perfect as shown in Figure 6.29 having R^2 value as 1 for training and Validation. Test dataset were validated with the trained neural network. The mean square error is also calculated and presented in the figure 0.00125. Minimum mean squared error (MSE) is used as the criterion for the network selection and also for the stopping of weights and bias adjustment. These results indicate that neural network was trained perfectly.

Validation

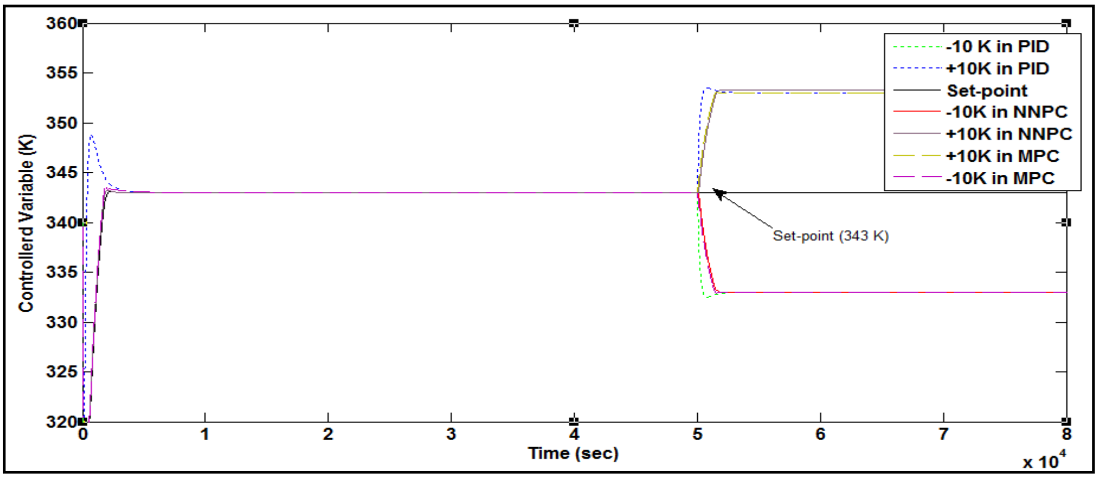


Fig. 6.31: Responses of controllers to set-point change (dotted line- Response of PID, dashed line- response of MPC and solid line- response of NNPC).

Figure 6.31 presents the comparison of controller's ability to handle set-point change during the process. Black sold line shows the set-point of the process i.e. 343 K and other lines represents- Dotted line shows response of PID, dashed and solid lines portray the response of MPC and NNPC respectively. PID shows a bump in there response where as MPC and NNPC show good tracking of the set-point change. Neural network more closely following the set-point trajectory as seen in the figure. Figure 6.32 gives the comparison of response of the controllers along with experimental value obtained from the experiments done in the laboratory.

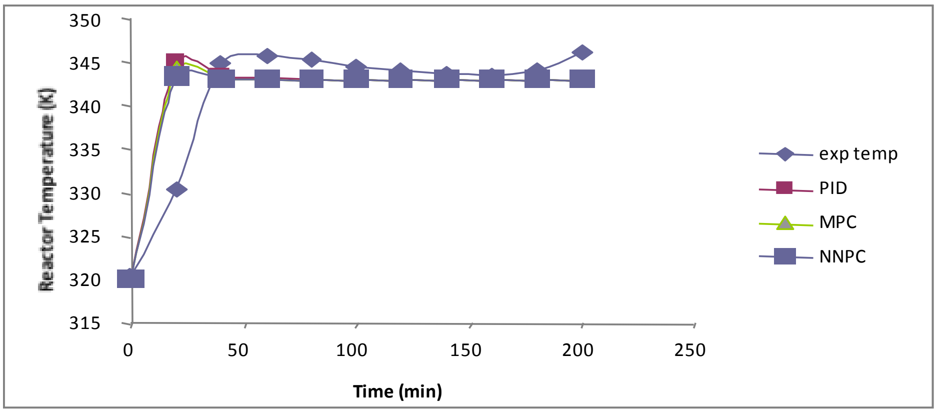


Fig. 6.32: Comparison of control variable (Experimental value using on/off controller)

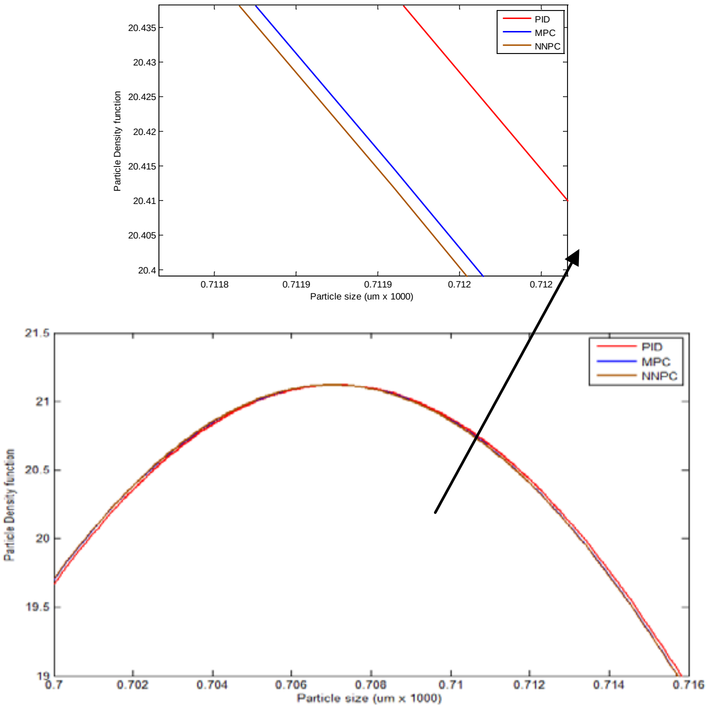
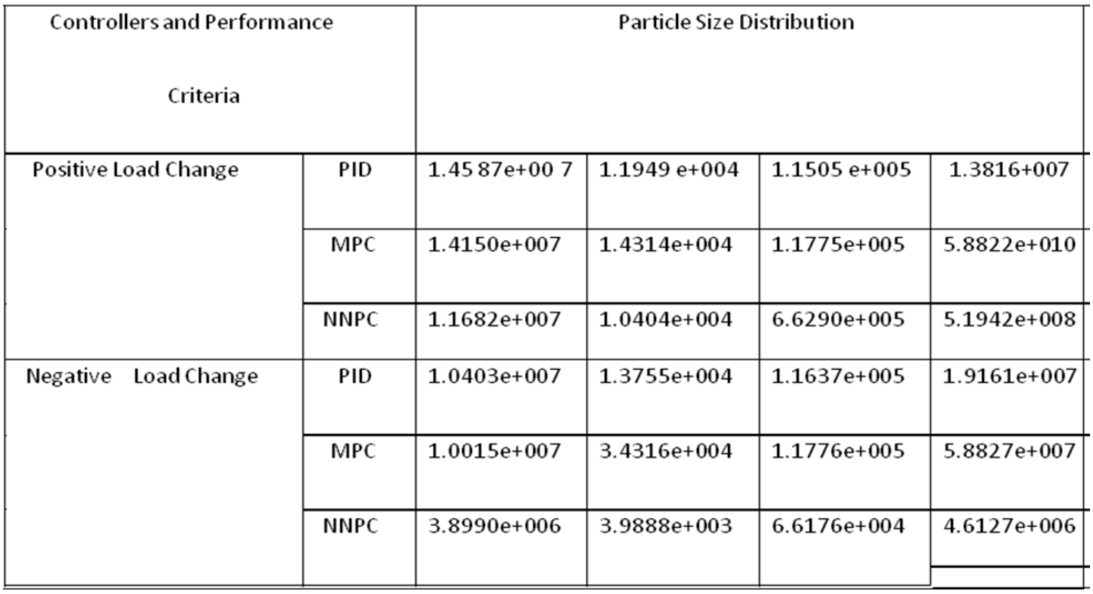


Fig. 6.33: Comparison of Particle density functions as a result of PID, MPC and NNPC.

Table 6.9: Performance Criteria for Set-point change in the controllers.

Controllers and Performance Criteria		**Particle Size Distribution**			
		ITAE	**IAE**	**ISE**	**ITSE**
Positive Set-point Change	PID	3.7422e+010	3.1014e+005	5.0013e+006	3.7385e+010
	MPC	1.6776e+010	3.0817e+005	1.1439e+007	3.6295e+010
	NNPC	**1.2301e+010**	**2.5064e+005**	**4.1452e+006**	**2.8109e+010**
Negative Set-point Change	PID	3.7422e+010	5.1014e+005	5.0913e+006	3.7385e+010
	MPC	1.7522e+010	4.8009e+005	1.2119e+008	6.1412e+010
	NNPC	**1.3279e+010**	**4.6355e+005**	**4.3718e+006**	**2.9836e+010**

Table 6.10: Performance Criteria for load change in the controllers.



Controllers and Performance Criteria		Particle Size Distribution			
Positive Load Change	PID	1.45 87e+00 7	1.1949 e+004	1.1505 e+005	1.3816+007
	MPC	1.4150e+007	1.4314e+004	1.1775e+005	5.8822e+010
	NNPC	1.1682e+007	1.0404e+004	6.6290e+005	5.1942e+008
Negative Load Change	PID	1.0403e+007	1.3755e+004	1.1637e+005	1.9161e+007
	MPC	1.0015e+007	3.4316e+004	1.1776e+005	5.8827e+007
	NNPC	3.8990e+006	3.9888e+003	6.6176e+004	4.6127e+006

The core objective of this whole study is to control the end use properties (particle size distribution and molecular weight) of the final polymer product for this aim a robust control system is required. In this study we found NNPC works better than PID and MPC although there is little difference in the response of MPC and NNPC but still it is proved in this study that NNPC controlled our system better than else two. Figure 6.33 presents the comparison of density function of three controllers and table 6.9, 6.10 tabulated the comparison of performance of all three controllers viz. PID, MPC and NNPC for set-point change and load change through which we had made decisions. PID gives broader density than the others.

Chapter-7
Molecular Weight

7. Molecular Weight

Molecular Weight

Molecular weight averages are a convenient measure of polymer molecular weight; these molecular weight averages do not describe the complete characteristics of polymer MWD. Furthermore, for some polymers such as PMMA, knowing the full MWD may not be always sufficient for many practical applications. It is possible that two polymer samples of different chain length distribution can have identical number and weight average molecular weights. Bimodal or multi-modal MWD curves cannot be represented by molecular weight averages and polydispersity.

The major limitation in using the molecular weight moment technique is that only molecular weight averages are calculated and a complete MWD is not obtainable. Certain functions, such as distributions are often adopted and fitted with molecular weight average. Certainly, such methods are no more than curve fittings, lacking any physical implications.

But now a technique of moments fully utilizes the convenience at the same time it enables the computation of full chain length distribution. We use six moments' equations in which three for live polymer and three for dead polymer.

The molecular weight and MWD affects the mechanical properties of the final latex, whereas the PSD affects the rheological and optical properties of the final polymer product and their stability, in previous chapter we discussed PSD and here we are going to discuss MW.

A major simplification in the modeling of molecular weight and branching development results when it can be assumed that a negligible amount of polymer is produced via termination reactions but actually a polymer can be produced via the following reactions: transfer to monomer to chain transfer agent and to polymer, termination reactions, and terminal double bond reactions. Transfer to polymer and terminal double bond reactions produce long-chain branches. Transfer to small molecules and termination reactions produce linear polymer chains. Fortunately, in most emulsion polymerizations, transfer reactions are relatively more important than termination reactions in the production of polymer. When the amount of polymer produced by termination reactions is negligible, molecular weight and branching development is independent of initiator and emulsifier levels (or number and size of the polymer partic1es) and when polymer produced by termination reactions is appreciable, molecular weight and branching development depend on the initiation rate and emulsifier concentration (number of particles and their size distribution).

7.1 Proportional-Integral-Derivative (PID)

The reactor was brought to the initial temperature having on/off controller and then required amount of initiator was supplemented to the reactor. On/off controller is successfully operated experimentally; performance of controllers here was studied with different parameters. After this we compared two methods which will be explained later.

In our study first PID controller uses split range controller as explained in previous chapter for particle size distribution and second PID controller uses heater power as a manipulative variable. In the split range controller, the reactor is initially heated with hot water until the reaction begins to generate heat. Then cold water is used. The control methodology used is as same explain above for particle size distribution. To avoid repetition we skip the discussion of strategies as they explained already in previous chapter and jump directly to results for molecular weight.

Split range controller uses flow rates of hot and cold water as manipulative variable, Figure 7.1 shows how the flow rates of cold and hot streams change with output signal of the controller.

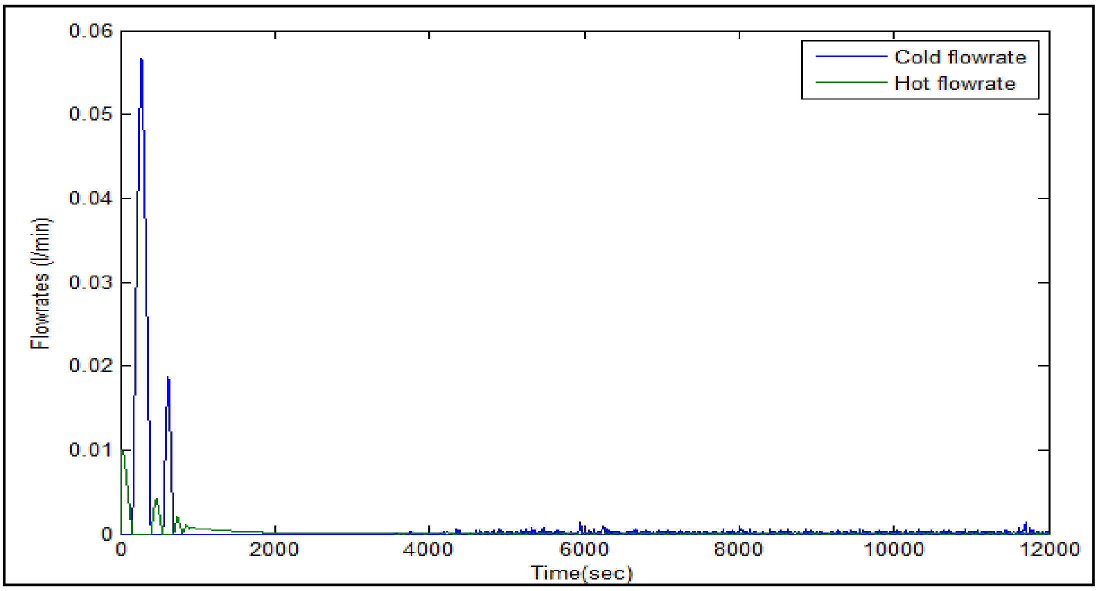


Fig. 7.1: Hot and cold stream for split range controller.

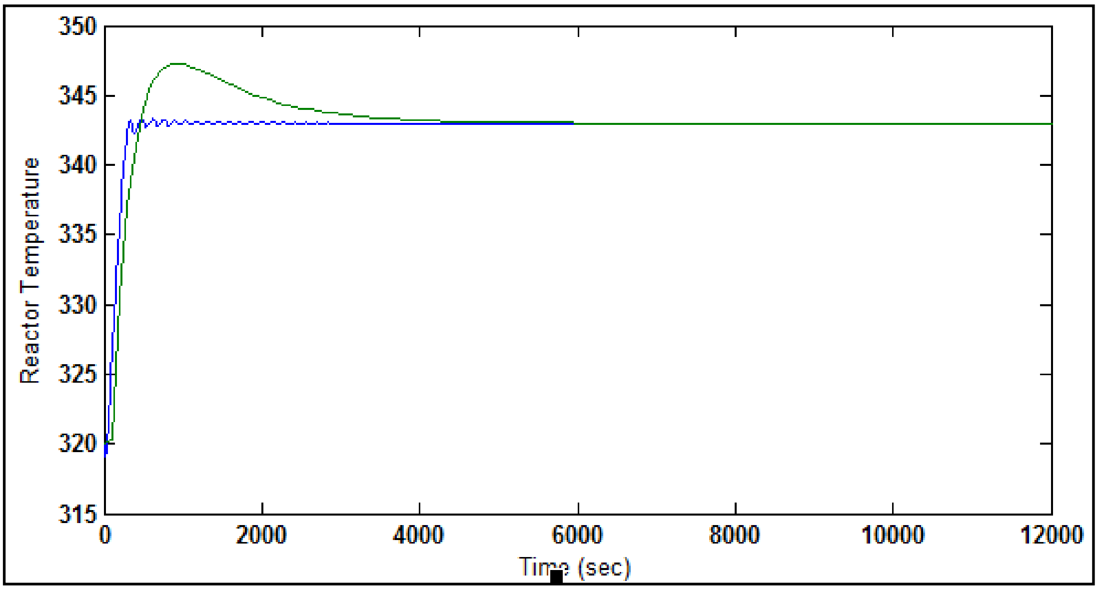


Fig. 7.2: Control Variable (split range- blue, Heat load- Green).

The Green line is showing the heat load method and blue shows split range. As clearly shown in Fig 7.2 split range controller requires minimum time to settle down at set-point i.e 343K and heater power takes ample of time (4000 sec) but there are small oscillations in split range controller. Split range controller uses both hot water stream and cold water stream as its manipulative variable (Fig 7.1) and is not capable to maintain set-point better than heat load. The hot stream temperature is 380 K and temperature of cold stream used is 294K. The maximum flow rates of the streams are 0.5 kg/s. The value of Absolute error for split range is 3.7613e+007 which is enormously higher than the heat load method having value 8.9167e+006. Both the controllers behave well at load change and set-point change in system. Table 7.1 gives the value of parameters used in simulation studies. Performance index were compared in Table 7.2. Contradictory results were found. Performance index shows heater power as manipulative variable is capable to handle set-point change better than split range, which means heat load as manipulative variable is much better strategy to be used since physically or practically there may be load at any time to the controller.

Both two are capable to maintain the desire reactor temperature with load changes and suddenly set point changes.

Figure 7.3 and 7.4 presented set-point change in both the controllers and Figure 7.5 represent load change. In split range after set point change there are some oscillations before settling down on change but in heat load set point change is very smooth.

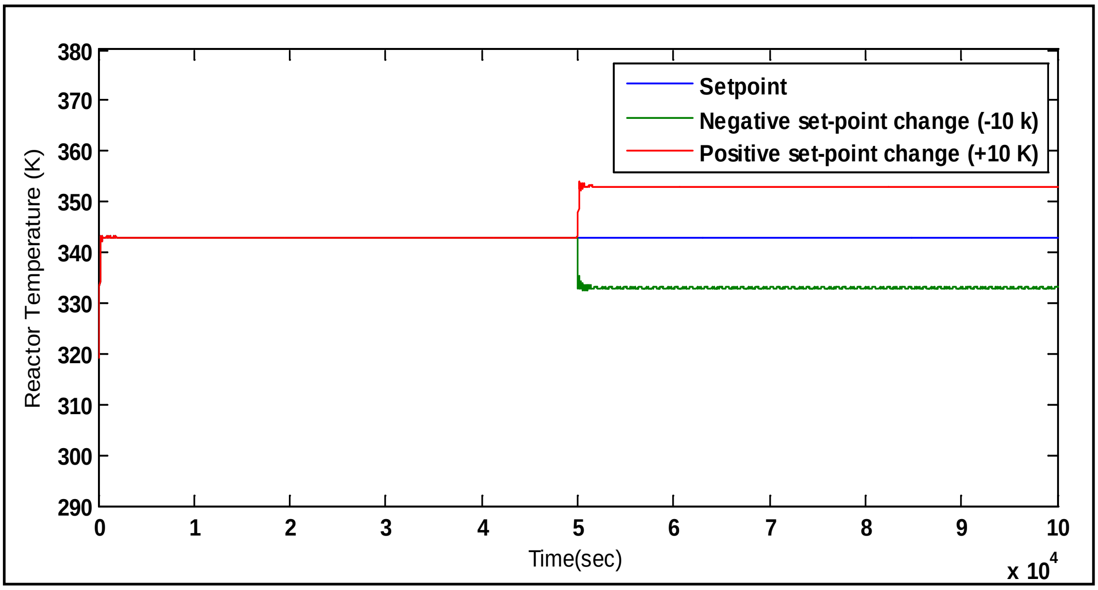


Fig. 7.3: Set point change in split range controller.

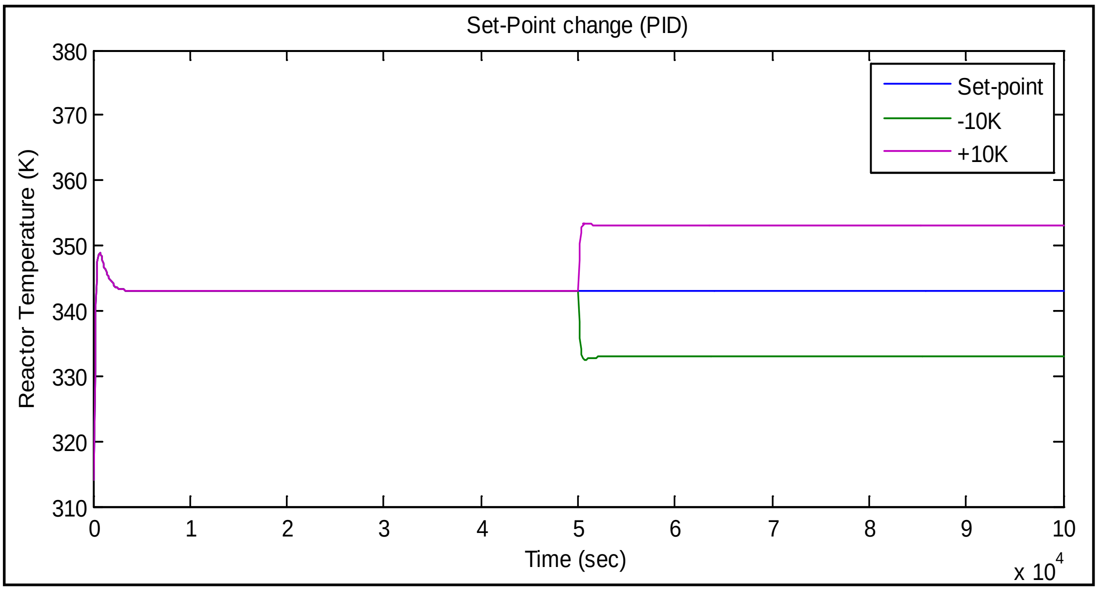


Fig. 7.4: Response of Set point change in controller having heater power as manipulative variable.

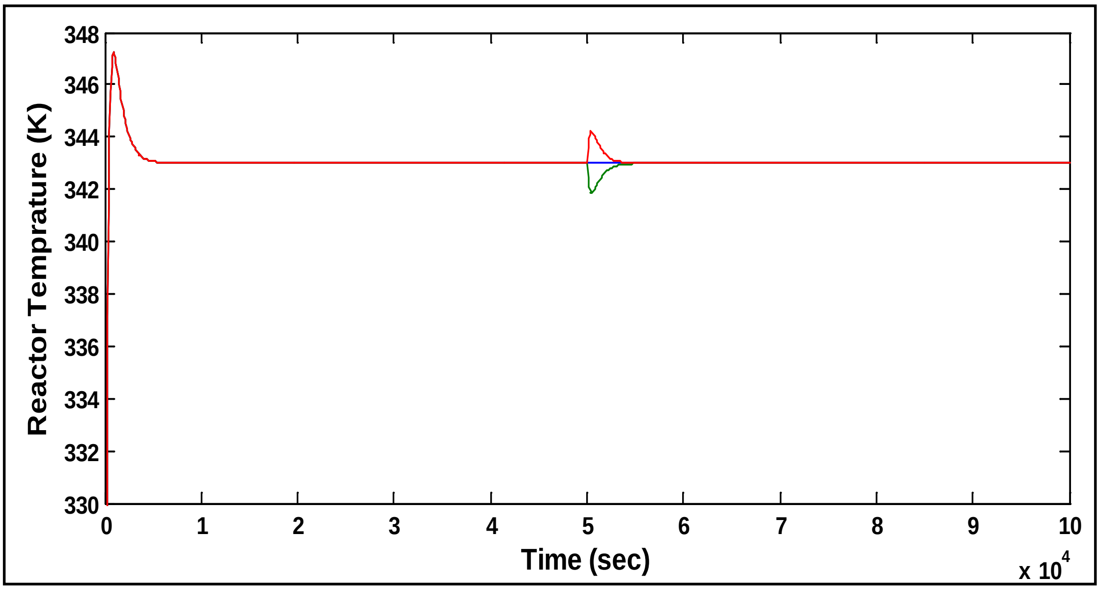


Fig. 7.5: Response of load change in second PID controller (heater power as manipulative variable).

The disturbance is scheduled at time 50000 sec, flow rate of the cold water increases by 0.1 kg/sec to its optimum value in negative load change which resultant in decrease in the reactor temperature, where as in positive load change the value of flow rate decreased by 0.1 kg/sec to its optimum value. The controller is active enough to maintain the set-point within 3000 seconds.

Parameter Tuning

The tuning of the temperature controller is an important issue (Table 7.3), Low controller gain leads to overshoot, Kc=1 leads to 8K overshoot and at Kc=3 leads to 3K overshoot as shown in Figure 7.7 because lower value of controller gain makes the Controller vary unstable in nature. Higher the value of TauI leads to oscillatory response of the controller as shown below in the Figure 7.8.

In this study we calculate error with adjustable parameters then select the optimum value of parameter with minimum error. These set of parameters are tabulated in Table 7.2.

Table 7.1 : Parameters used in the study for MW.

Parameter	Unit	Value
Kp	lit/mol min	49876.54
Kd	Per min	8.6*10e-5
Kt	Lit/mol-min	1.414*10e9
F	-	0.5
uc	W/m2-K	55
T_{cold}	K	275
C_j	J/kg-K	4.183
T_{hot}	K	400

Table 7.2: Performance of controller using heat duty as manipulative variable.

Parameters	ITAE	IAE	ISE	ITSE
Kc-9	**7.7540e+007**	**1.4355e+004**	**1.4409e+005**	**3.1997e+007**
Kc-6	7.9275e+007	1.8180e+004	1.9122e+005	5.2891e+007
Kc-3	8.4318e+007	2.8848e+004	3.4146e+005	1.5403e+008
Kc-1	9.6242e+007	4.5368e+004	6.5680e+005	5.3608e+008
TauI-0.0001	1.6711e+008	1.1272e+004	1.4334e+005	2.2589e+007
TauI-0.001	7.7540e+007	1.4355e+004	1.4409e+005	3.1997e+007
TauI-0.01	**8.9167e+006**	**1.2244e+004**	**1.5136e+005**	**3.5224e+007**
TauI-0.1	1.3334e+007	1.9443e+004	3.0616e+005	1.2576e+008

Table 7.3 Control parameters.

Parameter	Split range	Heat load
Kc	0.1	9
TauI	0.0009	0.01

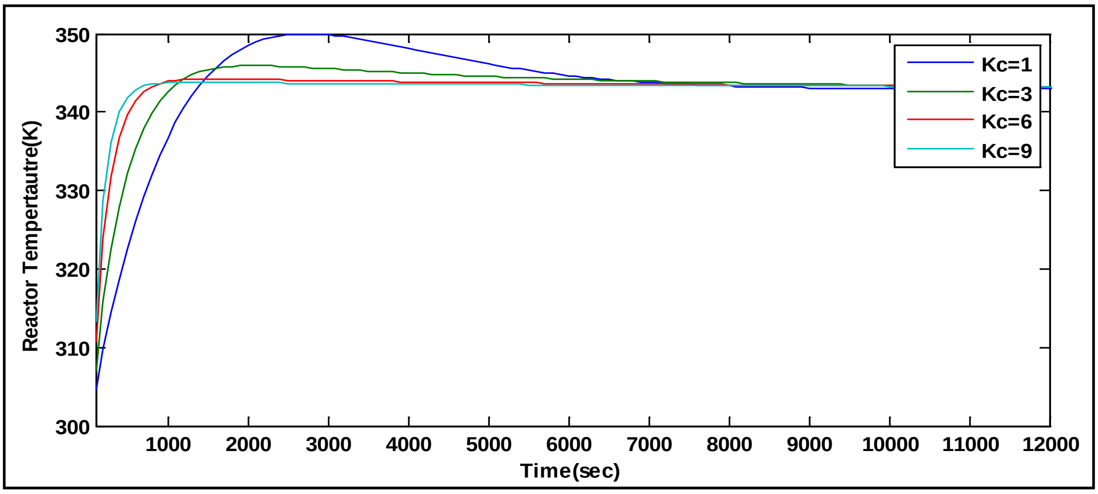


Fig. 7.6: Analysis of controller gain in second controller. (0.01)

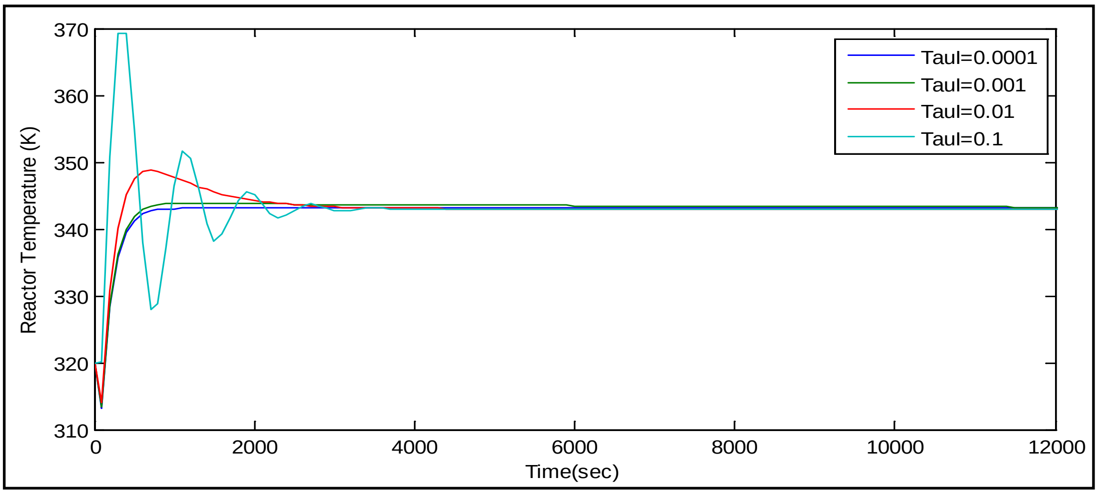


Fig. 7.7: Analysis of TauI in second controller (kc=9)

Performance index is calculated for the system, results are discussed in Table 7.4 and 7.5.The comparison of result of the controller and experimental result with on/off controller is given in Figure 7.9.

The performance index for both the controller were studied and discussed in Table 7.5. As the data of Performance index provide evidence that heat load perform better than the split range.

Table 7.4: Performance at set-point (343 K) using two different control strategy.

Performance Criteria	ITAE	IAE	ISE	ITSE
Split range controller	3.7613e+007	4.6035e+003	6.1616e+004	4.6702e+006
Controller using heat duty	8.9167e+006	1.2244e+004	1.5136e+005	3.5224e+007

Table 7.5: Performance of controllers for set-point change and load change.

Controller	Split Range controller				Controller using Heat duty			
Parameter	**ITAE**	**IAE**	**ISE**	**ITSE**	**ITAE**	**IAE**	**ISE**	**ITSE**
Positive Load Change	2.2805 e+0010	1.9063 e+006	3.5205 e+007	4.2102 e+012	**1.7292 e+0010**	1.3246 e+006	1.5194 e+007	6.4684 e+012
Negative Load change	2.7642 e+0010	2.3111 e+005	4.2346 e+007	5.0635 e+012	**1.9942 e+0010**	1.3246 e+005	1.5191 e+007	6.2928 e+012
Positive set-point change	4.8527 e+010	5.6430 e+005	5.0364 e+003	6.6920 e+011	**3.7366 e+010**	5.1037 e+005	5.1328 e+006	3.7362 e+011
Negative set-point change	1.5279 e+010	5.3152 e+005	2.09 e+003	2.1469 e+011	**1.1736 e+010**	5.1037 e+005	5.1328 e+006	3.7362 e+011

Validation

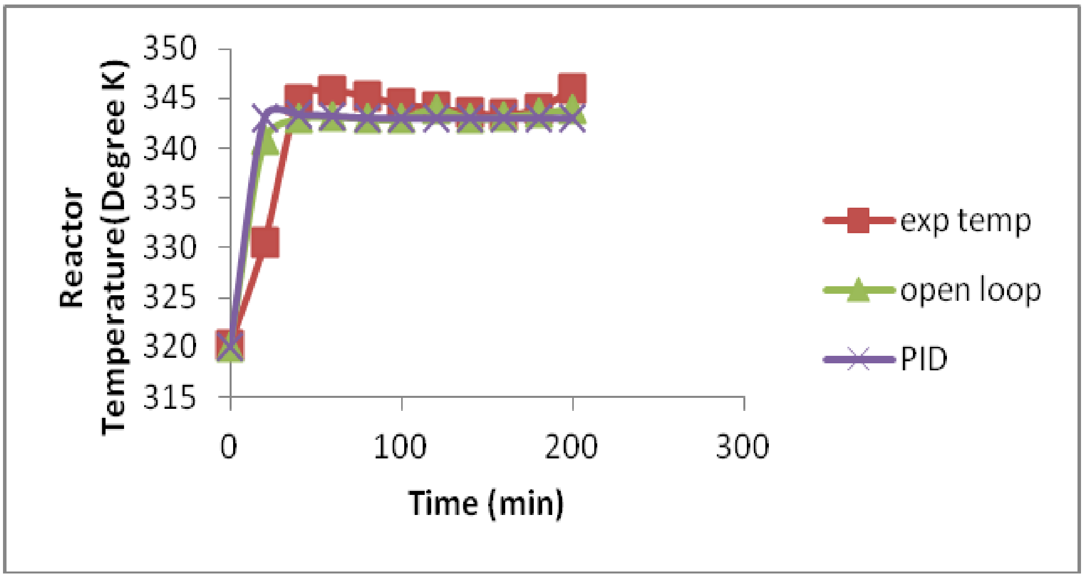


Fig. 7.8: Comparison of Reactor Temperature.

Comparison of experimental value of reactor temperature with open loop simulation controller and with on-off controller (experimental result) was studied and the result found was shown below in Fig 7.8.

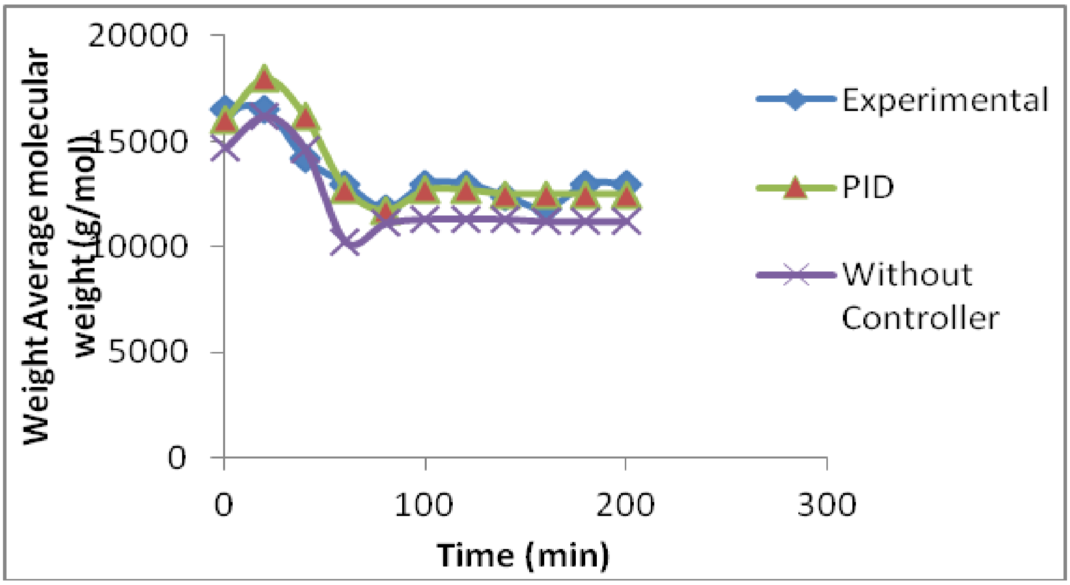


Fig. 7.9: Comparison of experimental data with controller.

A comparison of molecular weight is given in Figure 7.9 which demonstrate that molecular weight (Crowley and Choi 1998) of polymer is maintained at the value 12500 gm/mol with the help of controller rather than of without controller. In I interval the number of particles increases, monomer droplets are also present in the system which act as a supplier, in interval II when all the monomer droplets disappeared from the system the average molecular weight decreases because of diminish of monomer droplets and remains nearly constant through out the process.

7.2 Model Predictive Controller

The model predictive controller is used for control of the molecular weight of polymer PMMA. Again we used the same strategy i.e. power of the heater is used as manipulative variable and temperature as controller variable. The coolant flow rate is kept constant. The design parameters used in the simulation given in table 7.6, 7.7.

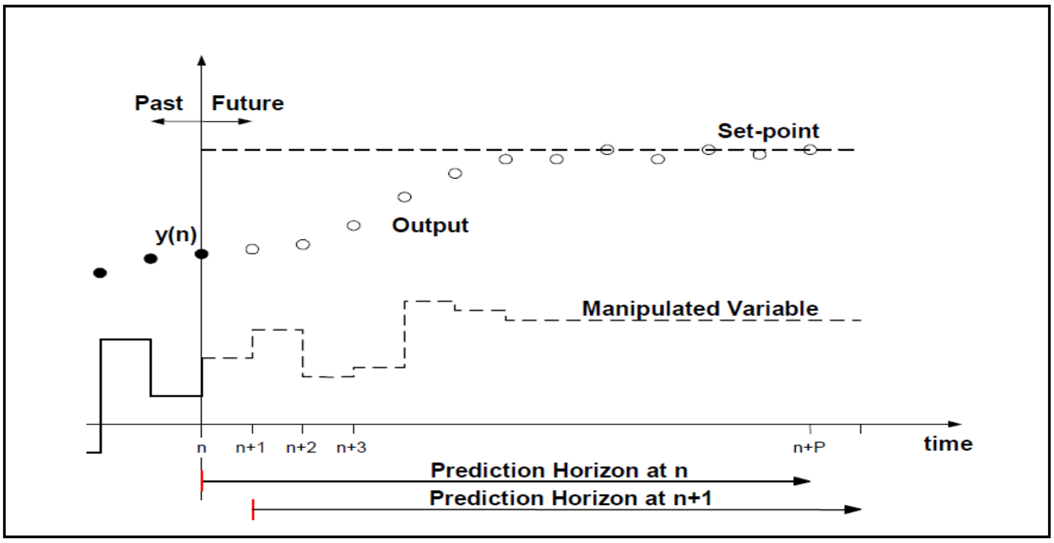


Fig. 7.10: MPC strategy

Model predictive strategy involves the following steps:

1. The process model calculates the predicted future outputs for the prediction horizon (N) at each sampling time t. Theses depends upon past inputs and outputs, including the current output y(t) (initial condition).
2. The sequence of future control signals is computed to optimize a performance criterion. Usually the control effort is included in the performance criterion.
3. Only the current output signal u(t) is send to the process. Step 1 is repeated for all the sequence to bring the process up to date.
4. The future moves of the manipulated variables are determined by minimizing the predicted error or the objective function

The performance of MPC is compared with PID controller and presented in Figure 7.12 and MPC flow chart is given in Figure 7.11. Our objective is to improve the control performance using different controllers. The response shows that PID controller took large time to get closer to the set-point with overshoot. MPC took 2000s where as PID adjusted within 2800s to the set-point with 5.5 K overshoot which depicts higher overshoot than MPC. The behaviour of heat duty as manipulative variable is shown in Figure 7.13 and 7.14 for MPC and PID respectively. In MPC heat duty oscillates in start-up but In PID heater power oscillated at time 50000s with initial start-up also where as MPC gives rest response smoother than PID which will prolong the life of heater.

In industrial practice, some uncertainty and disturbance are normally encountered in the reactor; to explore this we introduce disturbance and set-point change in the reactor. An excitation in the cold flow rate was introduced at the time 50000s. Increasing the flow rate would decrease the temperature of the reactor and decrease in flow rate would increase the temperature because of the heat transfer rate of the reactor shown in Fig 7.15 and 7.16 for MPC and PID simultaneously. Simulink file used in Matlab for MPC is given in Fig 7.17. Similarly set-point was also introduced into the system at time 50000s shown in Fig 7.18 for MPC and 7.19 for PID. MPC took less time as compared to PID for getting closer to the set-point in load-change, and gave less oscillation in set-point change with small overshoot. This is evidence that advance controllers are promising than traditional controllers in terms of there robustness for non-linear systems control. Control variable obtain from MPC and PID compared with experiment result, these experiments were performed in laboratory, we found overshoot in PID is greater than MPC thus MPC performs well in our case.

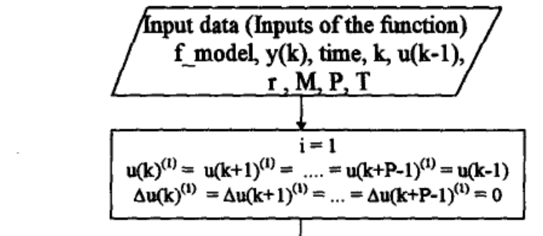


Fig. 7.11: Flowchart for MPC

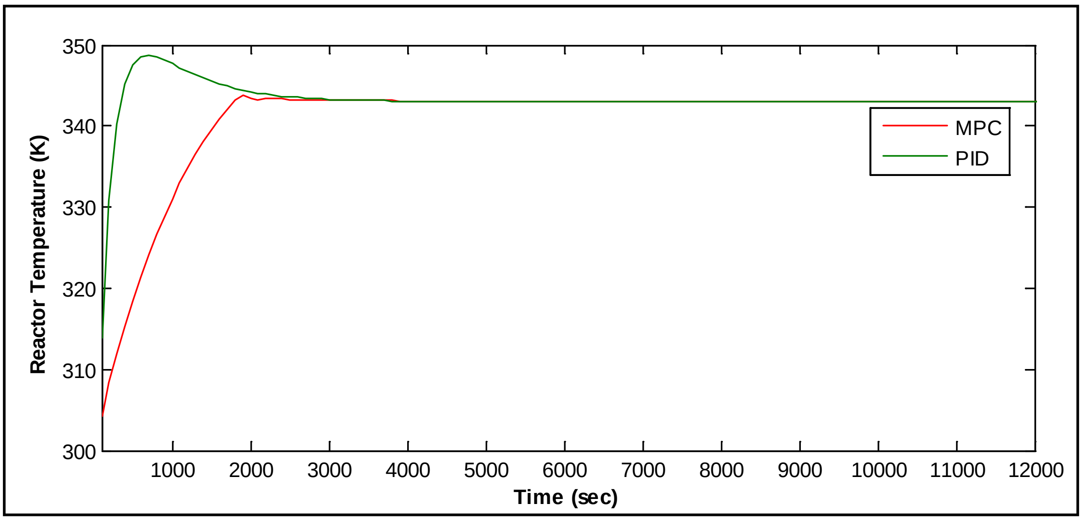


Fig. 7.12: Comparison of control variable using MPC and PID

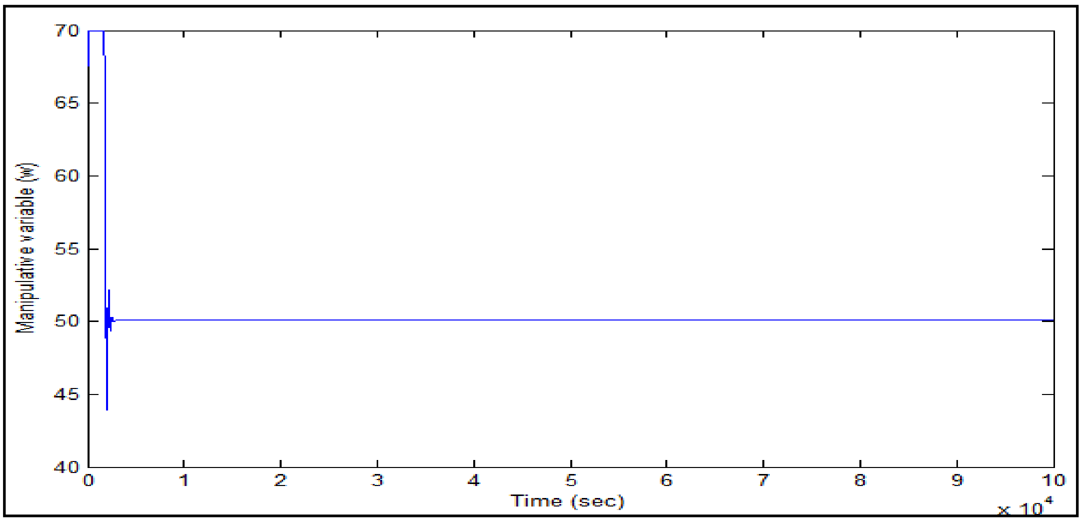


Fig. 7.13: Manipulative variable (MPC heat duty as manipulative variable).

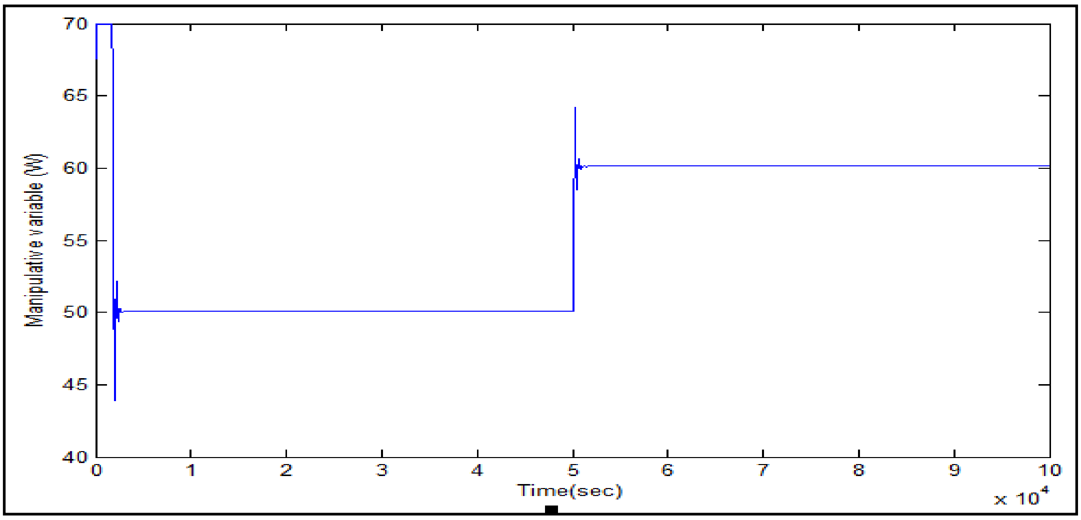


Fig. 7.14: Manipulative variable (PID heat duty as manipulative varable).

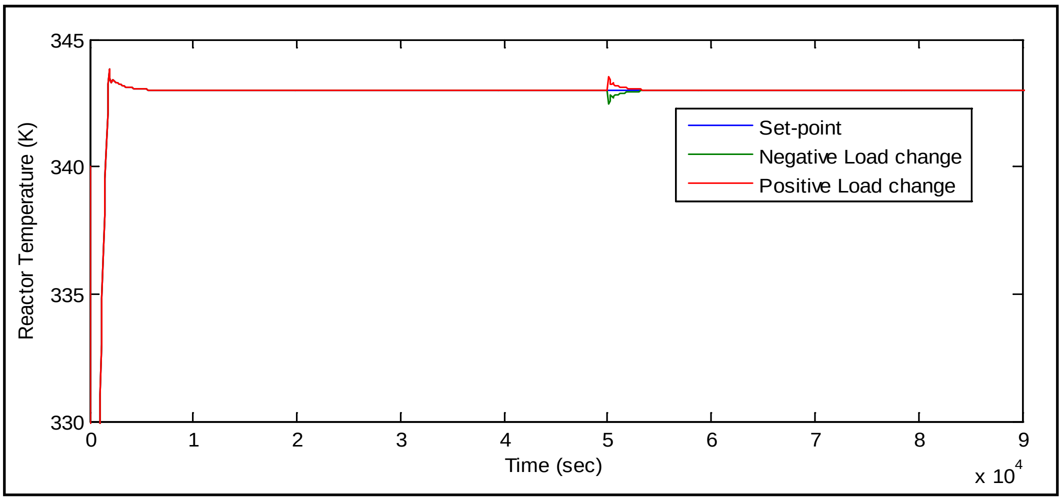


Fig. 7.15: Load change in MPC.

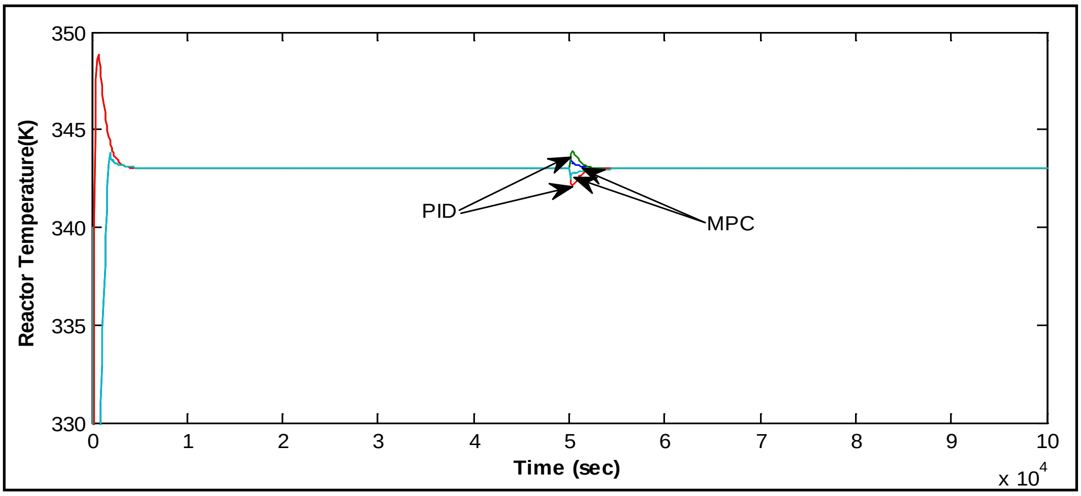


Fig. 7.16: Load change in PID and MPC.

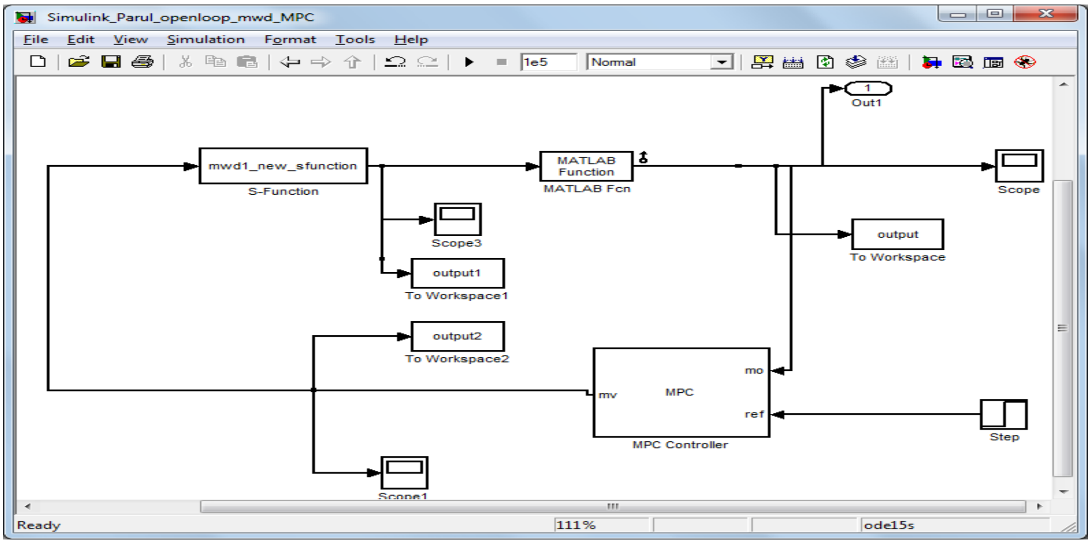


Fig. 7.17: Simulink file for MPC.

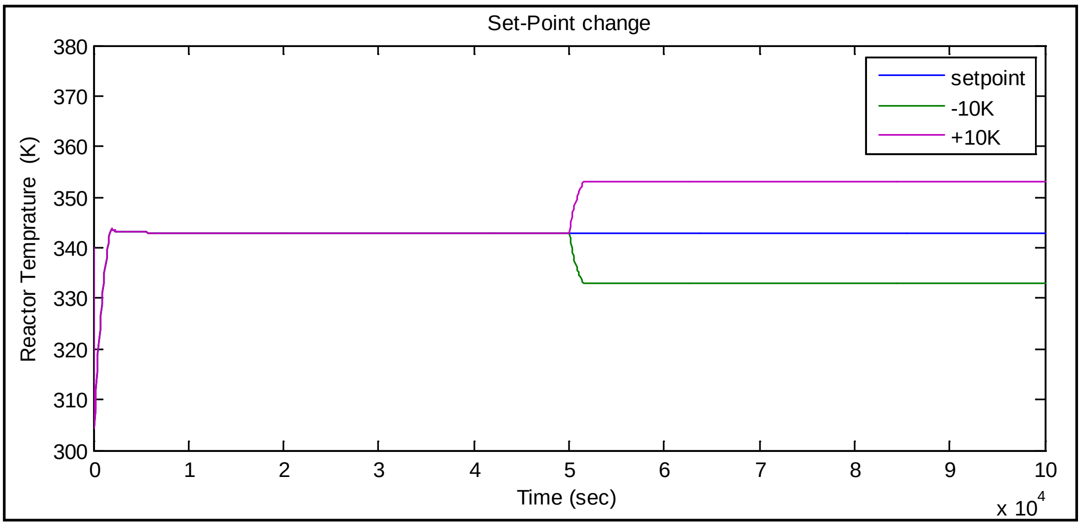


Fig. 7.18: Response to set-point change in MPC.

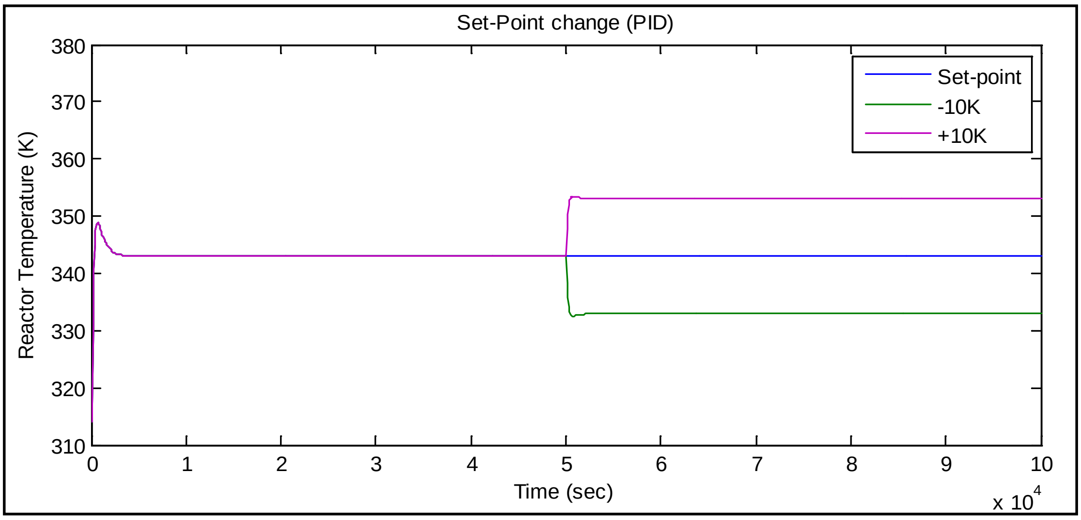


Fig. 7.19: Response to set-point change in PID.

In this work we have formulated non-linear model predictive control for the control of batch emulsion polymerization within target points i.e. temperature of the reactor at 373 K and compared with PID controller. This is to cover the gap between theoretical and real control and also to provide better controller. MPC was able to track the optimum reactor temperature profile efficiently and without a noticeable overshoot as in the case of PID, better disturbance rejection and smoother control move were also shown by MPC (Sheibat-Othman, Othman et al. 2011). This study shows advanced controllers are more robust and faster than traditional controller.

Tuning

Tuning of the controllers were done by trail and error method and tabulated in Table 7.6 for MPC and Table 7.7 for PID.

Table 7.6: Tuning parameters for MPC

Parameters	**Value**
Weight Tunning	0.8
Prediction Horizon (Np)	500
Control Horizon (Nc)	10

Table 7.7: Tuning parameters for PID

Parameters	**Value**
Controller Gain	9
TauI	0.01

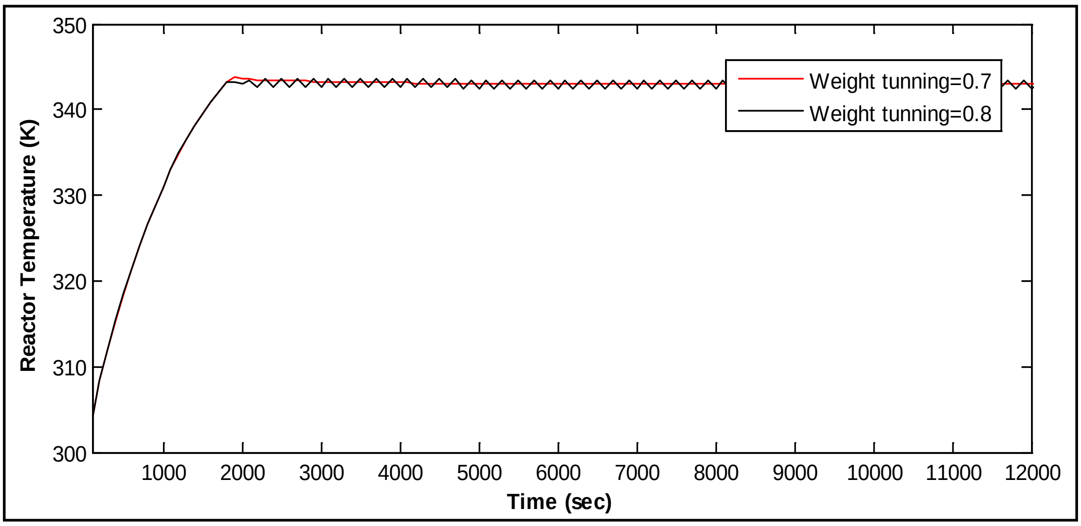


Fig. 7.20: Effect of weight tuning(Nc=20,Np=1000).

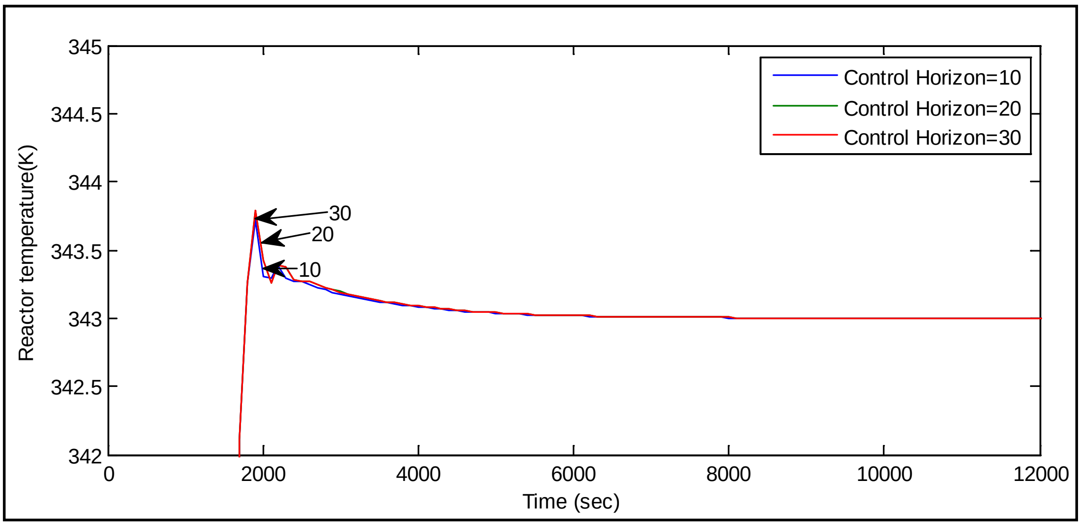


Fig. 7.21: Effect of Control horizon of MPC(wt=0.8,Np=1000)

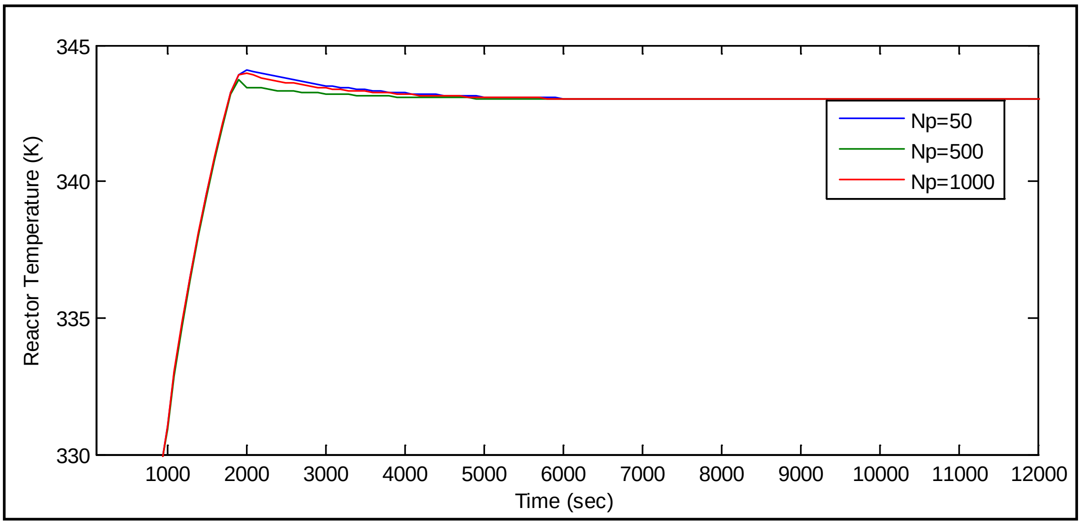


Fig. 7.22: Effect of prediction horizon of MPC (Nc=20, Wt=0.7)

Tuning of parameters in batch reactor is always difficult as compared to continuous reactor. Trial and error method was using for tuning of both the controllers. In MPC as the value of weight tuning decreases number of oscillations increases (Figure 7.20), Change in control horizon (Figure 7.21) and prediction horizon (Figure 7.22) makes little difference in our case but the best value was taken after the study of performance index, the same procedure is repeated for the PID controller, decrease in the value of controller gain causes higher the value of overshoot on control variable as shown in Figure 7.6, at Kc=1 highest overshoot was obtained, as the value of tauI increases oscillations in the control variable increases as in Figure 7.7.

Table 7.8: MPC Performance Index for MWD

Parameters	**ITAE**	**IAE**	**ISE**	**ITSE**
Weight tunning 0.7	**1.8158e+007**	**2.8626e+004**	**6.7263e+005**	**2.6668e+008**
Wt tunning 0.8	6.2645e+007	3.3623e+004	6.7436e+005	2.8880e+008
Nc -10	**1.7193e+007**	**2.8313e+004**	**6.7193e+005**	**2.6620e+008**
Nc-20	1.7351e+007	2.8364e+004	6.7190e+005	2.6624e+008
Nc-30	1.7346e+007	2.8363e+004	6.7192e+005	2.6624e+008
Np-100	2.0476e+007	2.9342e+004	6.7304e+005	2.6841e+008
Np-500	1.7753e+007	2.8673e+004	6.8195e+005	2.7088e+008
Np-1000	**1.7558e+007**	**2.8631e+004**	**6.8299e+005**	**2.7129e+008**

Absolute Error calculated for the reactors are given in Table 7.5 and 7.8 for PID and MPC respectively. On the basis of performance index tuning parameters was finalized. The value of parameter having minimum absolute error is used as optimum parameters for the controller (Table 7.8). Significant digit is the lowest value of ITAE i.e. weight tuning is 0.8, Nc is 10 and Np is 1000.

Validation

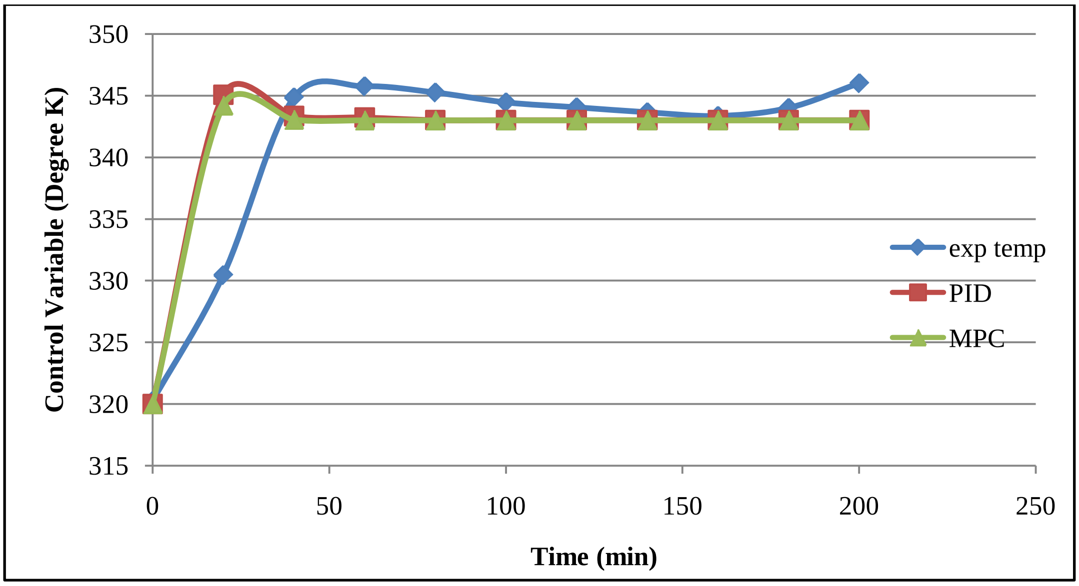


Fig. 7.23:Comparision of MPC, PID control variable with experiment result.

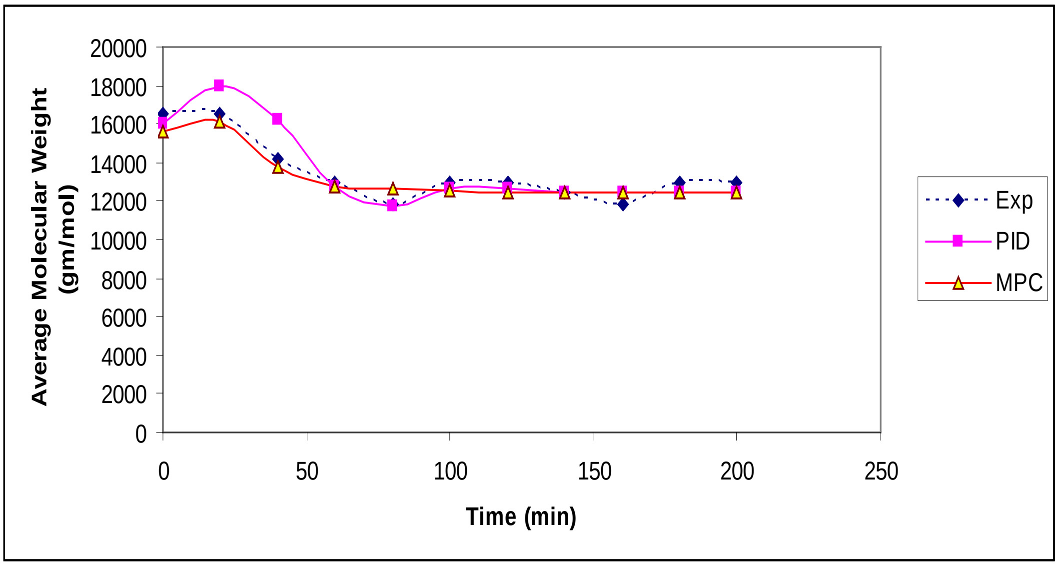


Fig. 7.24: Comparison of Average molecular weight.

The effect of temperature on MWD has been investigated well in the literature (Shahrokhi and Fanaei 2002). Increasing the reactor temperature, shifts MWD towards shorter chain length or lower weighted average molecular weight. It is well known that MWD is highly dependent on the ratio of chain transfer rate coefficient to propagation rate coefficient. In the absence of CTA, the chain transfer to monomer is dominant and therefore temperature determines temperature effect on MWD. Derivative of the above ratio respect to temperature is positive and therefore MWD is decreased as temperature is increased. Finally, according to the results of the above analysis, it can be concluded that MPC is the best candidates for controlling MWD and PSD, respectively, with minimal overshoot, presented in Figure 7.23. To overcome with this minimal overshoot present in MPC we studied another advance controller which is discussed below. Figure 7.24 illustrate the average molecular weight by PID MPC and on-off controller in experiments.

It can be concluded that synthesizing an optimal open loop assuming perfect modeling would leads to important errors between real and desired molecular weights, due to impurities, changes in raw materials or due to degradation of the process components. Meanwhile, the closed-loop SISO MPC strategy is a much batter than PID since it reduces the impact of error.

7.3 Neural Network Predictive Control

The molecular weight of the polymer is most important element to the properties if the product. However it is difficult to measure the molecular weight in real time. Therefore, the control of the molecular weight is often carried out by controlling the reaction temperature which influences the monomer conversion and molecular weight significantly. As NNPC is already discussed in previous chapters.

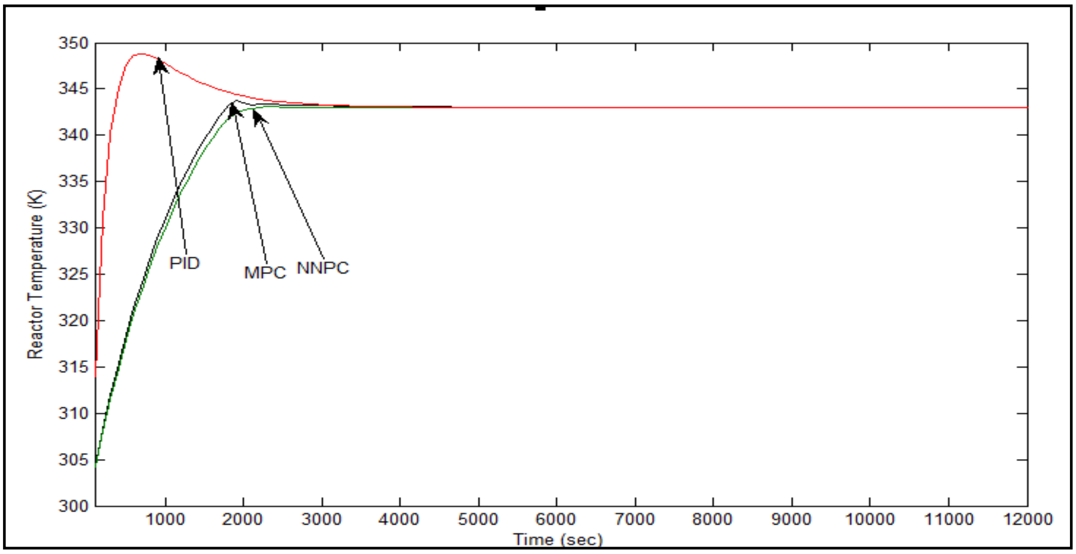


Fig. 7.25: Comparison of Control variable.

The main control objective of our study is to bring the reactor temperature to its target value as rapidly as possible with minimal temperature overshoot. It has been observed in the figure that temperature overshoot can be minimized by this proposed method.

The PID control shows a little delay in action which causes the overshoot from the set-point and NNPC gives faster response this is due to the fact that NNPC and MPC uses the prior information which is lacking in the case of PID. It can be seen in the Figure 7.25 that NNPC is more active and faster than the other two without any overshoot.

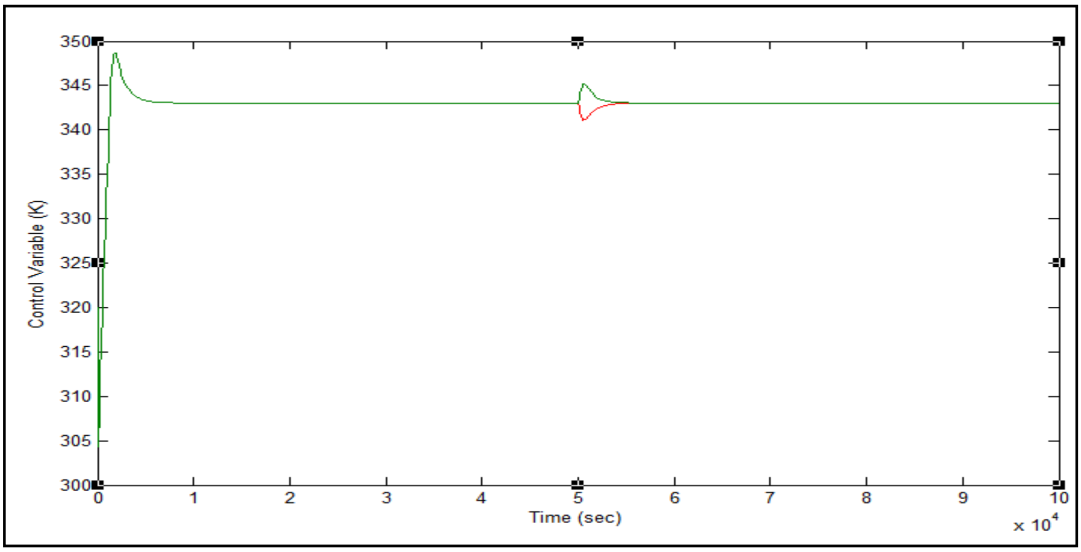


Fig. 7.26: Response to Load change in NNPC

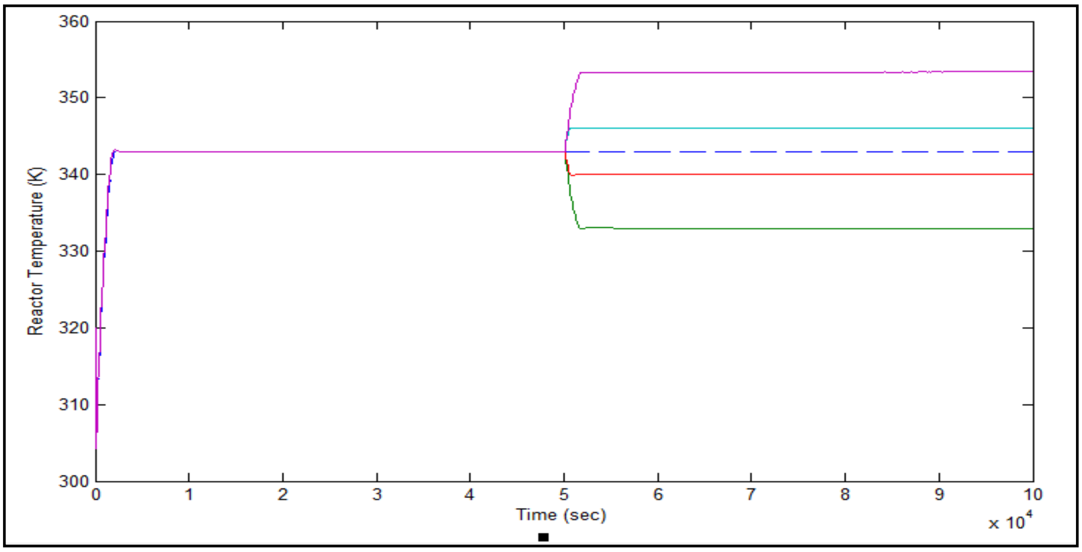


Fig. 7.27: set-point change in the control variable (dotted line shows set-point).

Tracking of set-point changes in control variable is presented in Figure 7.27 .Set-point of the reactor temperature is represented by dotted line in the figure. Negative and positive set-pint changes are introduced in the process and the NNPC handle the changes more satisfactorily. This is because the NNPC takes into account the changes caused in the processes and thus it changes the manipulative variable accordingly.

Load change is also introduced in the process at run time 50,000 sec by changing the flow rate of cold water by +_ 0.1 kg/sec. Positive and negative effect of load change in presented in the figure 7.26.

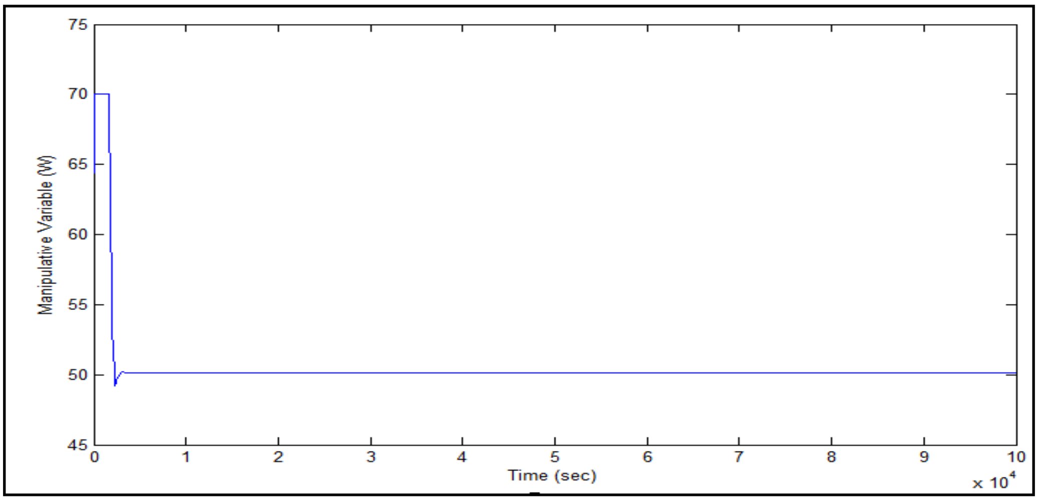
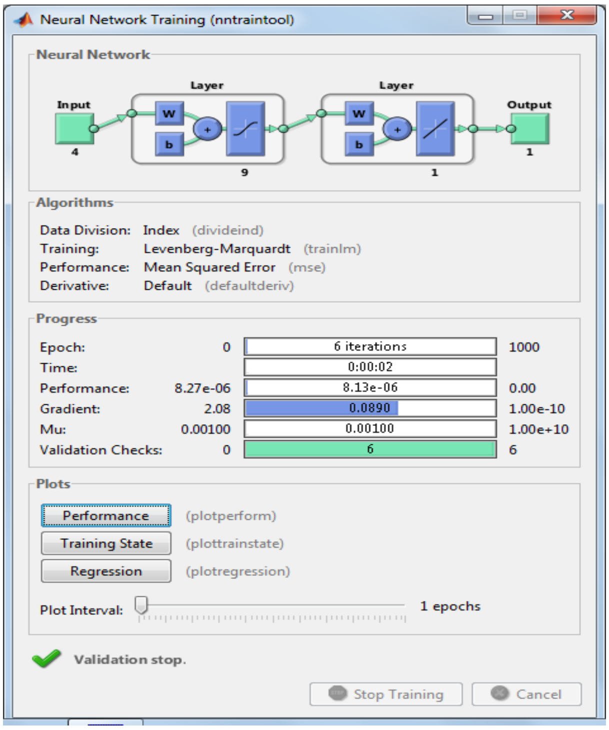


Fig. 7.28: Manipulative Variable during the process without any disturbance.

Heater power is used as manipulative variable in the process as explained previously. The trend of the manipulative variable during the process is shown in Figure 7.28 without any disturbance the manipulative variable is maintained at its optimum value 50W through out the process.

Neural Network Training



Algorithms

Data Division: Index (divideind)
Training: Levenberg-Marquardt (trainlm)
Performance: Mean Squared Error (mse)
Derivative: Default (defaultderiv)

Progress

Epoch:	0	6 iterations	1000
Time:		0:00:02	
Performance:	8.27e-06	8.13e-06	0.00
Gradient:	2.08	0.0890	1.00e-10
Mu:	0.00100	0.00100	1.00e+10
Validation Checks:	0	6	6

(plotperform)
(plottrainstate)
(plotregression)

Plot Interval: 1 epochs

✓ Validation stop.

Fig. 7.30: Neural Network Training

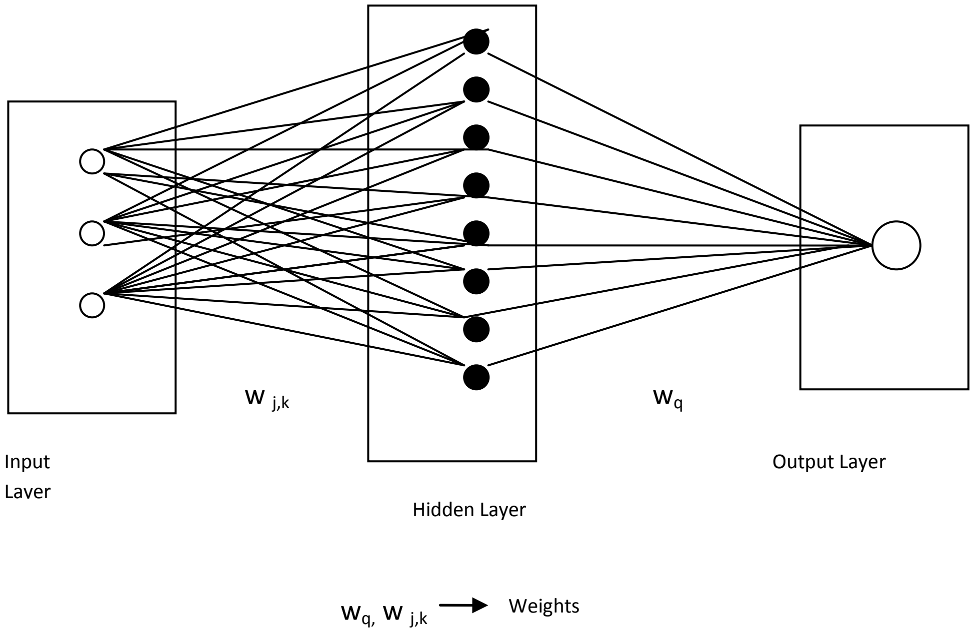
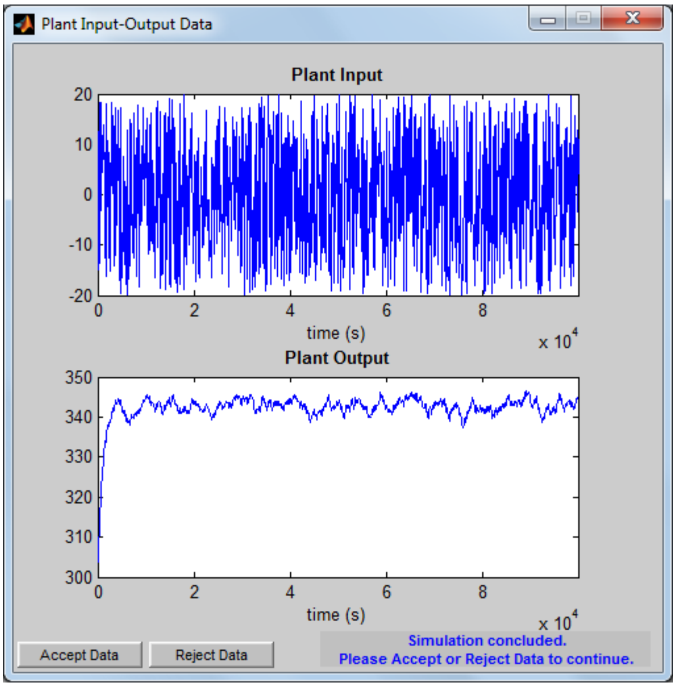


Fig. 7.30: Architecture of NNPC used in our model

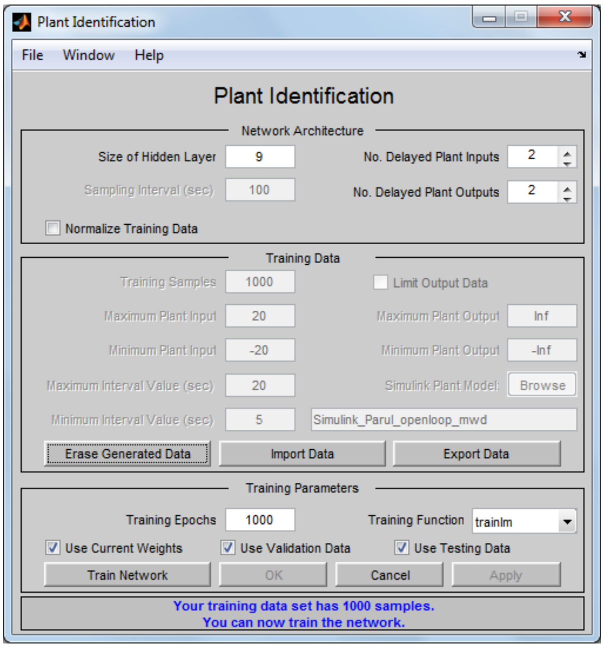
Neural network has proven to be accurate and a fast dynamic estimators. The architecture of multilayered feed-forward neural network can be seen in Figure 7.29. The network consist of an eight number of nodes arranged in a layers (Figure 7.30). Through these nodes in the layer signals propagate in feed-forward direction. The output of nodes transmitted signals to the next.



Simulation concluded.
Please Accept or Reject Data to continue.

Fig. 7.31: Data generated during training in NNPC.

Since the reactor is dynamic in nature. It is necessary to feed the network with past historical data. The necessary data are generated from simulation the open loop detailed model. Data generated during the training is presented in the Figure 7.31. The training of the neural network is done by using backpropagation algorithm. Also mean square error (MSE) (Figure 7.32, 33 and 34) performance function was used to determine overall error for training and validation. Regression analysis is also done for training and validation and found R=1 (Figure 7.35).



Size of Hidden Layer 9
No. Delayed Plant Inputs 2
Sampling Interval (sec) 100
No. Delayed Plant Outputs 2
☐ Normalize Training Data
Training Samples 1000
☐ Limit Output Data
Maximum Plant Input 20
Maximum Plant Output Inf
Minimum Plant Input -20
Minimum Plant Output -Inf
Maximum Interval Value (sec) 20
Simulink Plant Model: Simulink_Parul_openloop_mwd
Minimum Interval Value (sec) 5
Training Epochs 1000
Training Function trainlm
☑ Use Current Weights
☑ Use Validation Data
☑ Use Testing Data

Your training data set has 1000 samples.
You can now train the network.

Fig. 7.32: Network Architecture

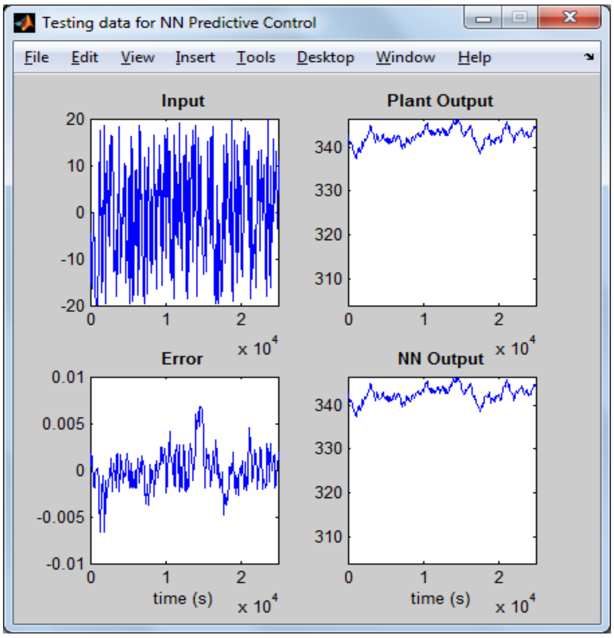


Fig. 7.33: Testing data

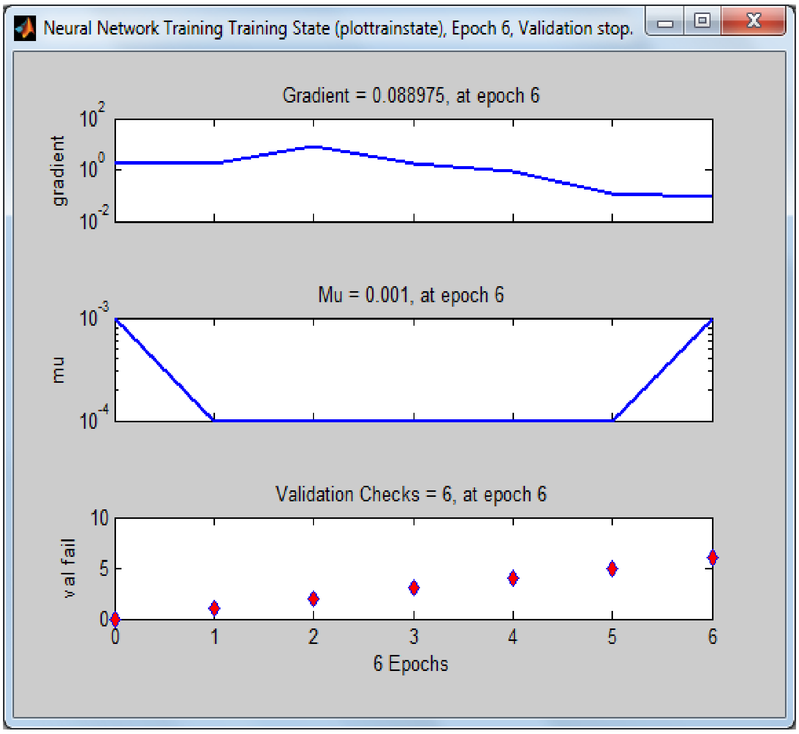


Fig. 7.34: Training state of neural network training

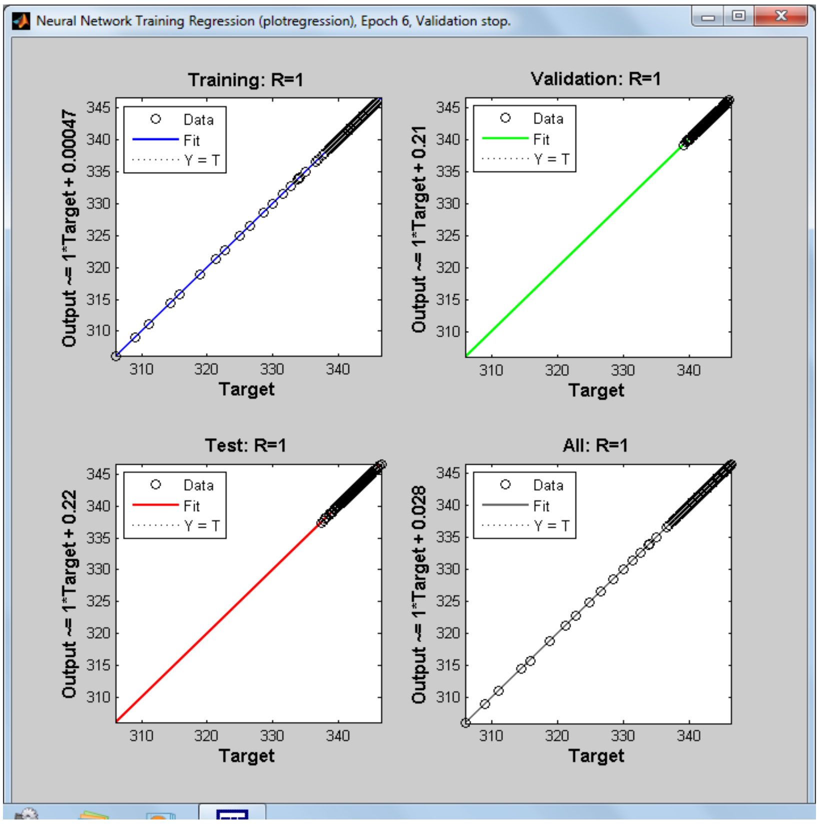


Fig. 7.35: Regression Analysis

Parameter Tuning

The quality of any controller can be improved by optimizing there parameters (Table 7.9). The effect of parameters on the control quality of the controller are analysed here. The control parameters which have been optimized in this study are Control weight, Nu and neurons of hidden layer in the neural network. Increase in control weight causes a bump in the control variable in the starting of the process. The optimum value found is 0.01 for the control weight. A single Hidden layer was used in the neural network, the number of neurons highly affect the control ability of the controller. The optimum value of neurons found is 8, increase in the number of neurons cause controller sluggish in nature. Nu does not affect the quality of NNPC strongly but during performance analysis, we found optimum value is 4 for this study (figure 7.36, 37 and 38).

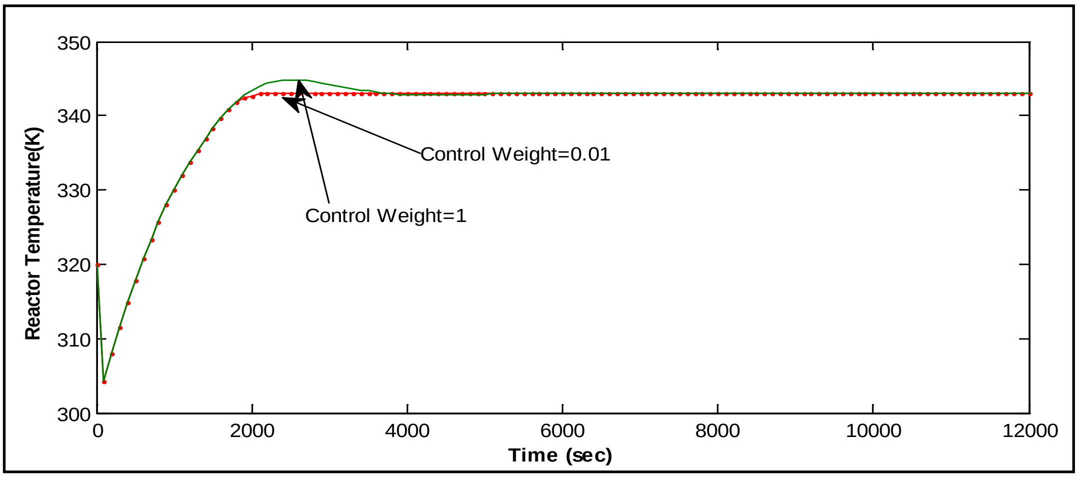


Fig. 7.36: Effect of control weight on control variable (H=8,Nu=4)

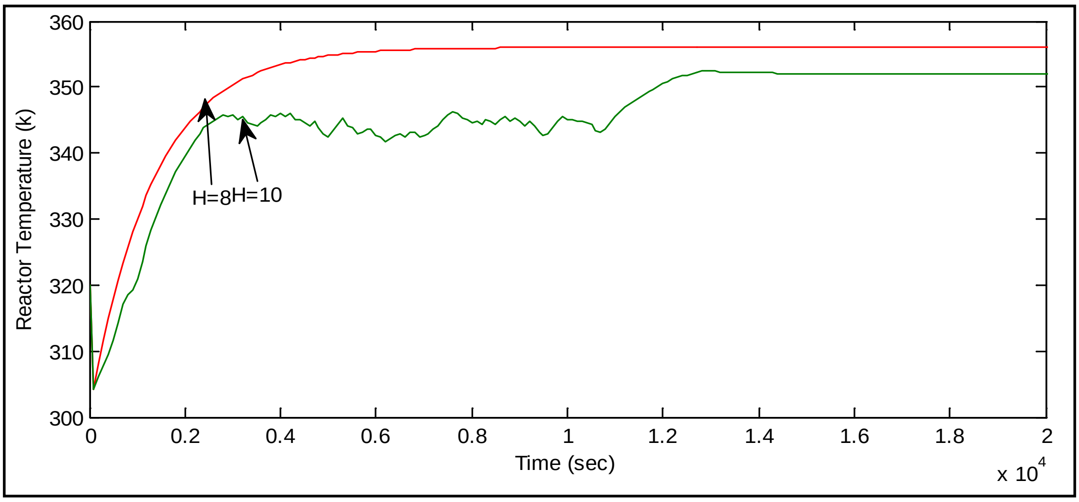


Fig. 7.37: Effect of neurons of the hidden layer on control variable (Nu=4, controlwt=0.01)

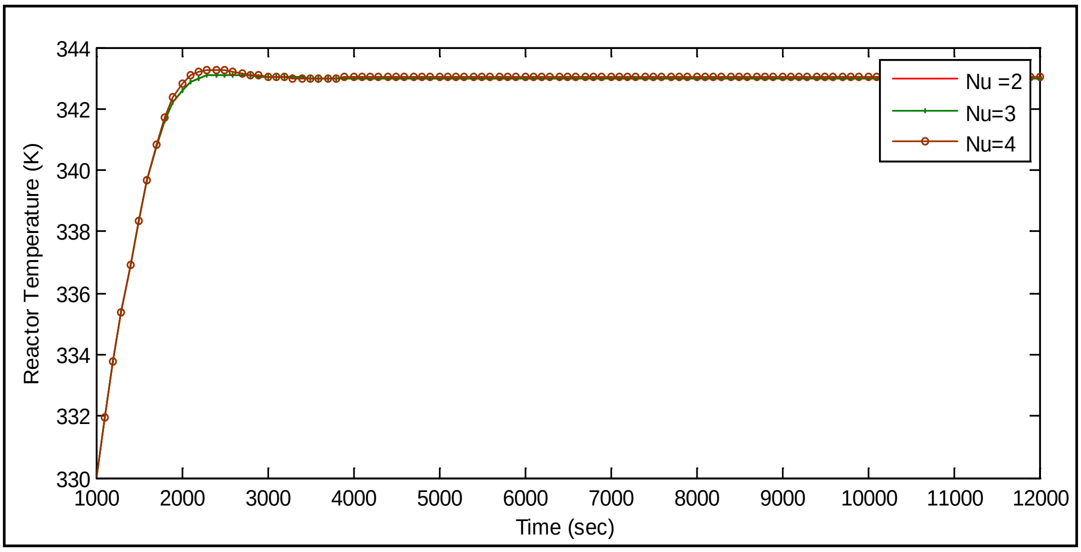


Fig. 7.38: Effect of Nu on control variable(H=8,controlwt=0.01)

Table 7.9: Performance Index NNPC for MWD

Parameters	ITAE	IAE	ISE	ITSE
Nu-2	5.3760e+007	3.1182e+004	7.3247e+005	2.9333e+008
Nu-3	5.3636e+007	3.1184e+004	7.3243e+005	2.9327e+008
Nu-4	**1.9997e+007**	**3.0696e+004**	**7.3239e+005**	**2.9298e+008**
Control Weight-0.01	**1.9997e+007**	**3.0696e+004**	**7.3239e+005**	**2.9298e+008**
Control Weight-0.001	4.7853e+007	3.0976e+004	7.3234e+005	2.9303e+008
Control Weight-1	6.6236e+007	3.3347e+004	7.3520e+005	3.0082e+008
Hidden Layer-10	4.4430e+010	8.5020e+005	8.2611e+006	3.9938e+011
Hidden Layer-8	**1.5303e+010**	**1.2947e+006**	**1.7158e+007**	**8.5505e+011**

Validation

A model aims to predict the future behaviour of the process and the best one is chosen by a correct optimal control of the manipulated variables.

The advantage of NNPC is Constraints (such as manipulated variables physical limitations, constraints due to operating procedures or safety reasons) may be specified and the disadvantage is Computational time needed may limit on line use Suboptimal solutions.

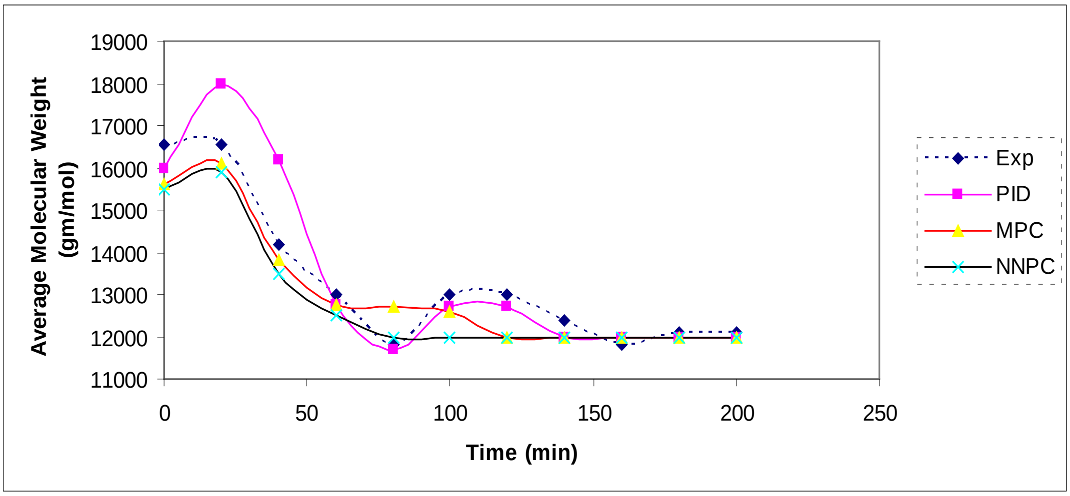


Fig. 7.39: Comparison of average molecular weight.

The ultimate goal of the polymerization reactor temperature control is to obtain polymer product having desire properties. Therefore, the batch operation is carried out to control the molecular weight of the product through tracking the temperature trajectory. Molecular weight is very sensitive to the reaction temperature unlike the monomer conversion, so small changes in the reaction temperature may induce large deviation in molecular weight. The initial temperature was 343 K and the total reaction time is 200 min. The desire average molecular weight obtained is 12000 kg/mol (figure 7.39). PID shows the highest deviation from the experimental result. This implies that the polymer product having desire properties can be obtained by the controlling the reactor temperature with robust controller.

To make the quantitative comparison of the controllers, Different criteria for good control action were applied. These are the integral of time weighted absolute error (ITAE), integral of the square of the error (ISE), the integral of the absolute of the error. The results are presented in the table for PID, MPC and NNPC respectively. All the criteria tested carefully and concluded that NNPC is superior to the others (Table 7.10 and 7.11). It is evident that the end-use properties of the product can be controlled more efficiently by using Neural Network predictive controller.

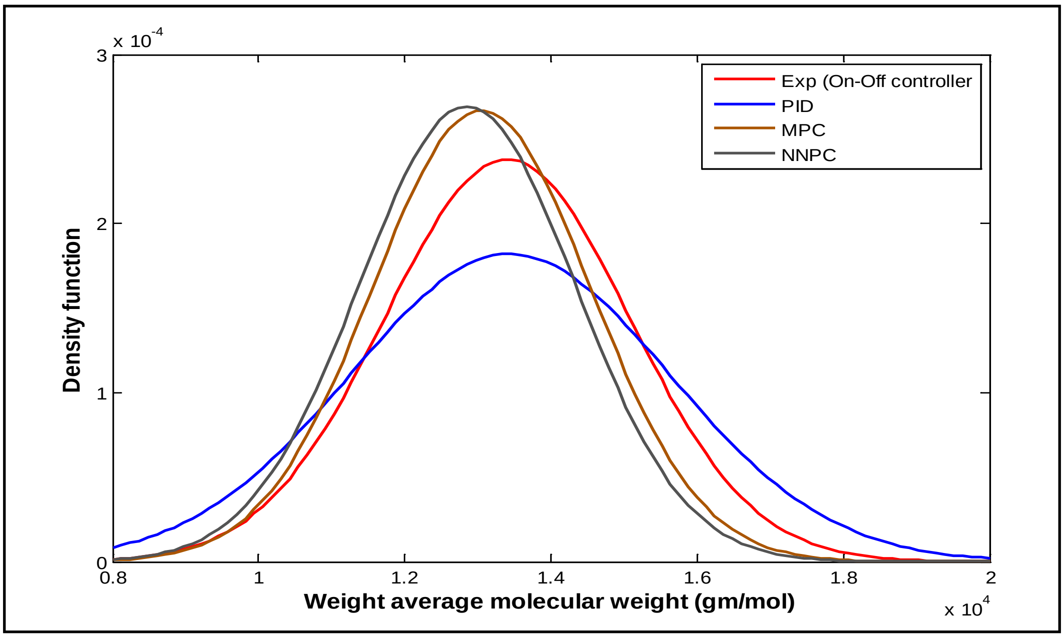


Fig. 7.40: Comparison of density functions for average molecular weight.

In figure 7.40 it is clearly shown that NNPC gives narrow distribution of density function. NNPC is the only controller able to produce particles having same or nearly same molecular weight.

Table7.10: Performance Criteria for Set-point change in the controllers viz PID, MPC and NNPC.

Controllers and Performance Criteria		**Molecular Weight Distribution**			
		ITAE	**IAE**	**ISE**	**ITSE**
Positive Set-point Change	PID	3.7366e+010	5.1037e+005	5.1328e+006	3.7362e+011
	MPC	3.7209e+010	5.2232e+005	5.5874e+006	3.7097e+011
	NNPC	**1.1458e+007**	**1.1949e+004**	**1.1505e+005**	**3.1816e+007**
Negative Set-point Change	PID	1.1736e+010	5.1037e+005	5.1328e+006	3.7362e+011
	MPC	2.1212e+010	5.2237e+005	5.5884e+006	3.7102e+011
	NNPC	**1.7284e+007**	**5.2418e+004**	**5.6478e+005**	**3.7361e+007**

Table 7.11: Performance Criteria of all the controllers for Load change in jacket fluid flow rate

Controllers and Performance Criteria		**Molecular Weight Distribution**			
		ITAE	**IAE**	**ISE**	**ITSE**
Positive Load Change	PID	1.7292e+010	1.3246e+005	1.5194e+007	6.4684e+0012
	MPC	2.8212e+010	6.3297e+004	3.7744e+007	5.5543e+011
	NNPC	**0.041682e+010**	**4.0404e+004**	**6.6290e+005**	**5.1942e+008**
Negative Load Change	PID	5.9942e+010	1.3246e+005	1.5191e+007	6.2928e+0012
	MPC	2.5694e+010	5.3396e+004	0.0714e+007	1.0453e+011
	NNPC	**0.038990e+010**	**3.9888e+004**	**6.6176e+005**	**4.6127e+008**

As shown in above analysis MPC takes more settling time than PID in disturbance rejection the reason being is MPC takes large computation time and using time consuming algorithm, Where is gives the best result for disturbance rejection than others.

7.4 Bubble Entrapment

Entrapment of bubbles is a function of viscosity of the reaction liquid. Rate of entrapment of bubbles are tend to change as the viscosity of the reaction mass changes. It is observed that as the viscosity increases number of entrapped bubbles increases and the diameter of the bubble is also increases. At low viscosity the high percentage of bubble entrapped having small diameter and vice-versa. The first term in the equation 3.64 (term in first bracket) dominates at low viscosity of reaction mass and tends to entrapment of bubbles of low size range. Parameter p_1 is represents rate of instantaneous breakage of big bubbles of gas; parameter p_2 is used for the inverse of the overall rate at which large bubbles are getting entrapped at the surface. As the viscosity increases the effect of second term increase and this term became dominating. The third term (exponential term) gives log normal distribution effect at the value of parameter p_5.The value of parameters are p1= 690.01,p2= 2.14, p3= $3.20X10^{-4}$, p4= 334.31, p5= -8.76

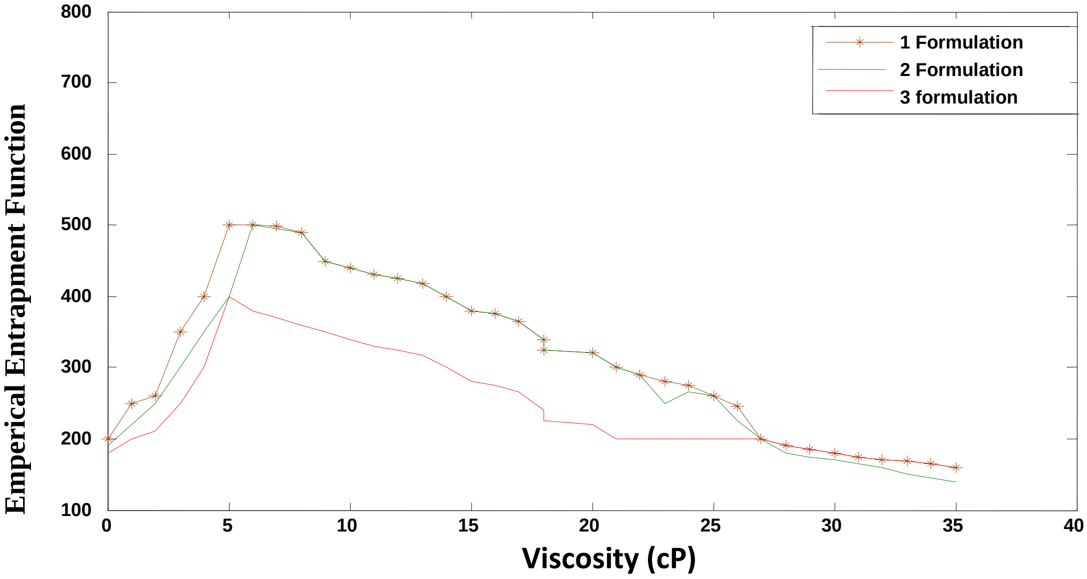


Fig. 7.41: Comparison of entrapment functions of all three formulations.

Presented in figure 7.41 as viscosity of the reaction mass increases the number of bubbles entrapped increases formulation 1 having the higher number of bubbles entrapped into the reaction mass.

Chapter-8
Conclusions

8. Conclusions

Problems encountered during experiments and control of batch reactor

The primary objective of reactor control in industrial polymerization processes is to maintain stable reactor operations and product quality at their target values. For an existing plant, improved reactor controls are needed to increase the polymer yield and to reduce production cost. Process knowledge, sensors, transmitters, and analysers are the prerequisites for the design of basic control system to regulate pressure, temperature, level, and flow rate. With the regulatory control system in place, one can design advanced regulatory control, model based control and intelligent scheduling and optimization system.

There have been a large number of publications on the control of polymerization reactors in the past two decades. Many of these publications dealt mainly with reactor temperature control and polymer property control problems of semi-batch and continuous reactors.

Exothermic polymerization processes often exhibit strongly nonlinear dynamic behaviours (e.g., multiple steady states, autonomous oscillations, limit cycles, parametric sensitivity and thermal runaway), particularly when continuous stirred tank reactors are used. Some polymerization processes are open loop unstable and susceptible to unmeasured disturbances, even with a feedback controller in place.

Since many of the polymer properties are hard to monitor online, first-level process variables are controlled to follow a certain process recipe. Polymerization rate and polymer properties are non-linearly correlated and hence a polymerization process control system is inherently a multivariable control system. In presence of unexpected process disturbances, or load change, little can be done to correct the damages made on the product properties but in a batch process, the consequence of not being able to handle load change and disturbance is a heavy economical loss.

Control objectives include the direct control of polymer properties using on-line measurements or estimates of polymer properties. Any variations in the product quality can be corrected if such quality parameters are known available during the polymerization.

Here are some issues concerning batch polymerization reactor control. A batch polymerization process is a multivariate and non-stationary or dynamic process. Quite often, direct on-line control of polymer properties is not feasible, or very difficult in batch polymerization processes. For example, sampling from a reactor can be quite a challenge in some high-pressure batch reactor systems. For short batch reaction time, there is simply no time to analyze polymer samples off-line and use the result to make appropriate corrective control actions before the batch operation is terminated. A batch polymerization reactor should also be operated to maintain consistent batch-to-batch product quality and to maximize the product yield by increasing monomer conversion and/or reducing batch reaction time.

During this study we encounter with some difficulties and those are:

1. The product is characterized by its end use properties like molecular weight and particle size which is strongly depend upon temperature. A proper temperature policy would keep these parameters within range.
2. In batch polymerization, physico- chemical properties are changing with time and important mass and heat transfer is also taking place. Thus, control of temperature becomes more difficult.
3. The system is highly non-linear.
4. The disturbance during the batch especially the heat of the reaction increases to its highest at the end of the reaction causes many challenging control problems. When the rate of reaction is high, the removal of heat becomes very difficult task to be done due to the increases viscosity.
5. Being a batch process, there is no steady state operating point which makes tuning of the controller more difficult.

In many industrial batch polymerization processes, the design of a batch polymerization reactor control consists of two stages:

1) Off-line design of a control trajectory (recipe), and
2) Implementation and execution of the control trajectory.

There might some control objectives (e.g., polymer yield, molecular weight, composition, batch reaction time) that require special treatments. So we concentrate on the control of batch reactor using MATLAB to provide a system with optimization. During the time of work we faced problems with one strategy using for control of batch reactor, we make some in the system through changing manipulative variable and introduced second strategy for control. Now this Strategy is more reliable and trustable to work with, so we proceed with this strategy and design next controllers.

8.1 Conclusion

MMA emulsion polymerization was performed in order to measure the validity of mode1 proposed in the chapter 3 for conversion, MW, MWD and PSD of polymer. The data collected from the experiments were analyzed by the Malvern Mastersizer 2000 E, to evaluate the sizes of the polymer particles and monomer droplets, and by end group analysis to measure the molecular weight of the sample. The data were then incorporated into the respective models so an evaluation could be made and the objectives outlined in Chapter **1** could be addressed.

The thesis work that was performed led to the following conclusions:

(i) Satisfactory results for conversion were obtained under the different concentration conditions of monomer, initiator and emulsifier.

(ii) A dynamic model was developed for the reactor, particle size distribution and molecular weight distribution.

(iii) With reliable Malvern Mastersizer 200E Particle size distribution, monomer droplets and their characteristics were studied with effect of monomer, initiator and emulsifier concentration.

(iv) Molecular weight is characterized and explained the relation with PSD.

(v) Control of batch reactor is more difficult because of heterogeneous nucleation and reaction without steady state. We applied three controllers namely PID, MPC and NNPC for PSD and MW.

(vi) Performance indices were calculated for all the controllers.

(vii) We effectively obtained narrow distribution of particle size distribution using NNPC. Narrow distribution affects the rheology property and film formation characteristic of the polymer which is required in paint industries.

(viii) NNPC efficiently maintained the molecular weight at specific a value of 12500 gm/mol. High molecular weight strengthens the mechanical, tensile properties.

(ix) Entrapment of gas bubbles increases with increase in viscosity of the system.

The ultimate goal of the polymerization reactor temperature control is to obtain polymer product having desired properties. Therefore, the batch operation is carried out to control the molecular weight of the product through tracking the temperature trajectory. Molecular weight is very sensitive to the reaction temperature unlike the monomer conversion, so small changes in the reaction temperature may induce large deviation in molecular weight. The initial temperature was 343 K and the total reaction time is 200 min. The desired average molecular weight obtained is 12000 g/mol. PID shows the highest deviation from the experimental result. This implies that the polymer product having desire properties can be obtained by the controlling the reactor temperature with robust controller.

From this research study, the models for particle size distribution and molecular weight were better fitted with the experimental results. Higher concentration of emulsifier favours broader particle size distribution and high molecular weight. High concentration of initiator gives narrower distribution.

Rheological property value increases with narrow distribution of polymer. Narrow distribution of polymer is designed mainly for paint industries, especially methyl methacrylate and its co-polymers is used, smaller particles also favour the fast rate of film formation. A latex product with smaller particle size shows better colloidal stability because the colloidal stability of the particle is proportional to the particle size to the third power.

We use temperature for controlling end –use properties of the polymer. It is well known fact that rate of polymerization increases with increasing temperature.

Increase in temperature after a certain temperature, the size of the particle decreases. This inverse dependence between the particle size and the polymerization temperature is due to the increasing decomposition rate of the initiator with increasing monomer solubility in the aqueous phase, which increase the concentration of growing chains and, thus, reduce the latex size.

A mathematical model was developed and simulated the entrapment of gas bubbles (nitrogen gas) in the polymerization reactor.

8.2 Recommendations for Future Work

The results produced in this study validated with simulated results and gives valuable information. Results collected by the Malvern Mastersizer 2000E indicate that monomer droplets may be present in the system. More sophisticated apparatus for particle size distribution should be used like 200SM which works upon both static light scattering and dynamic light scattering technology.

NNPC is the best among three controllers, this should be applied practically to the batch reactors present in the industries so that high molecular weight with high rate of polymerization can be obtained and narrower particle size distribution can also be obtained, this is possible only with a batch reactor.

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Appendices

Appendix

1. Moments equation for molecular weight

P* represents the growing polymer chain

For Zero moment

$$\frac{d\lambda_0}{dt} = \frac{dP_1^*}{dt} + \frac{dP_2^*}{dt} + \frac{dP_3^*}{dt} + \cdots \qquad + \frac{dP_n^*}{dt} \tag{1}$$

$$\frac{d\lambda_0}{dt} = K_i \; R^* \; M - K_t\lambda_0^2 - \frac{\epsilon\lambda_0}{1+\epsilon x}\frac{dx}{dt} \tag{2}$$

$$\frac{d\lambda_0}{dt} = K_i \; R^* \; M - K_t\lambda_0^2 - \frac{\epsilon\lambda_0}{1+\epsilon x}\left(K_i R^* + K_p\lambda_0 + K_{tm}\lambda_0\right)(1-x) \tag{3}$$

For First moment

$$\frac{d\lambda_1}{dt} = \frac{dP_1^*}{dt} + \frac{2dP_2^*}{dt} + \frac{3dP_3^*}{dt} + \cdots \qquad + \frac{ndP_n^*}{dt} \tag{4}$$

$$\frac{d\lambda_1}{dt} = K_i \; R^* \; M - K_p M\lambda_0 - K_p\lambda_0\lambda_1 - \frac{\epsilon\lambda_1}{1+\epsilon x}\left(K_i R^* + K_p\lambda_0 + K_{tm}\lambda_0\right)(1 - x) - K_{tm}M(\lambda_1 - \lambda_0) \tag{5}$$

$$\lambda_k = \Sigma_{n=1}^{\infty} n^k P_n^* \tag{6}$$

Where k =0,1,2 …..n

$$\lambda_1 = \Sigma_{n=1}^{\infty} nP_n^* \tag{7}$$

$$\lambda_2 = \Sigma_{n=1}^{\infty} n^2 P_n^* \tag{8}$$

For dead polymer chain

$$\frac{du_0}{dt} = \frac{dD_1}{dt} + \frac{dD_2}{dt} + \frac{dD_3}{dt} + \cdots \qquad + \frac{dDn}{dt} \tag{9}$$

$$\frac{du_1}{dt} = \frac{dD_1}{dt} + \frac{2dD_2}{dt} + \frac{3dD_3}{dt} + \cdots \qquad + \frac{ndDn}{dt} \tag{10}$$

$$\frac{du_2}{dt} = \frac{dD_1}{dt} + \frac{4dD_2}{dt} + \cdots \qquad + \frac{n^2\,dDn}{dt} \tag{11}$$

2. Reproducibility

Particle Size Distribution

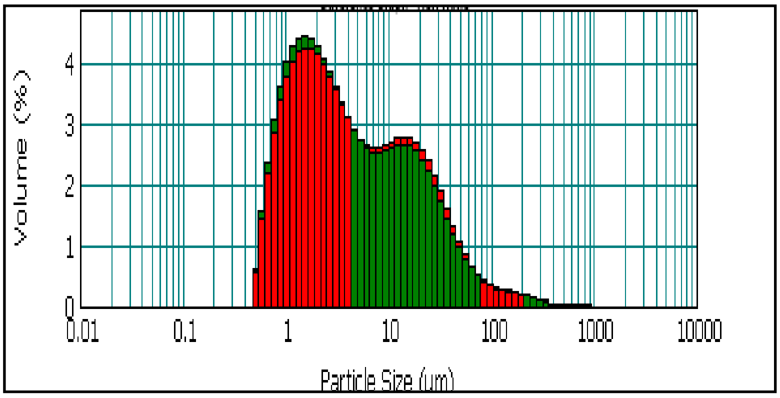


Fig a: Reproducibility of particle size distribution of PMMA latex at time=120 min using first formulation.

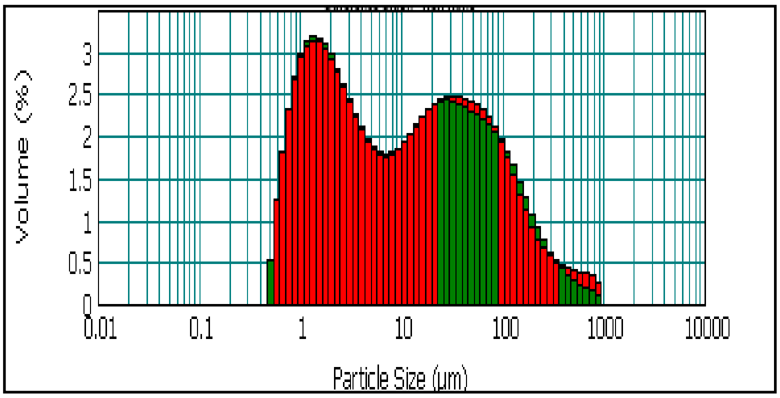


Fig b: Reproducibility of particle size distribution of PMMA latex at time 200 min using first formulation.

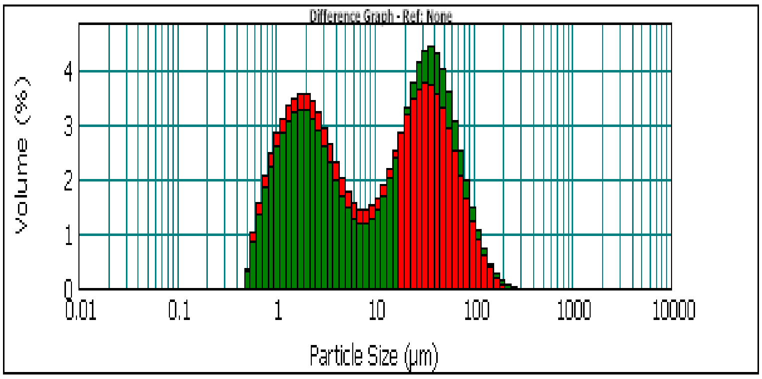


Fig : Reproduced results of PSD at 200 min using 2nd formulation.

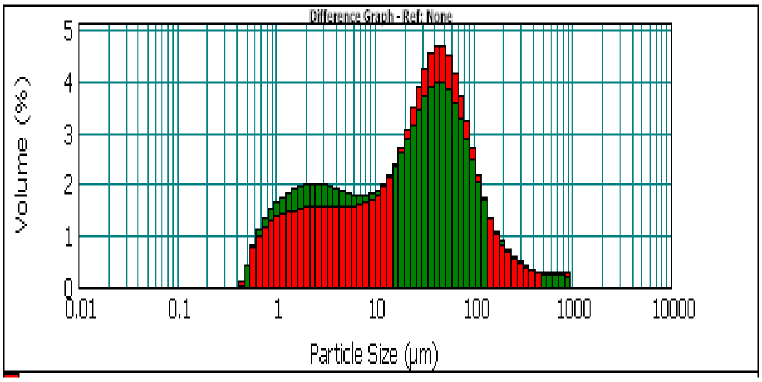


Fig: Reproduced results of PSD at 200 min using 2nd formulation.

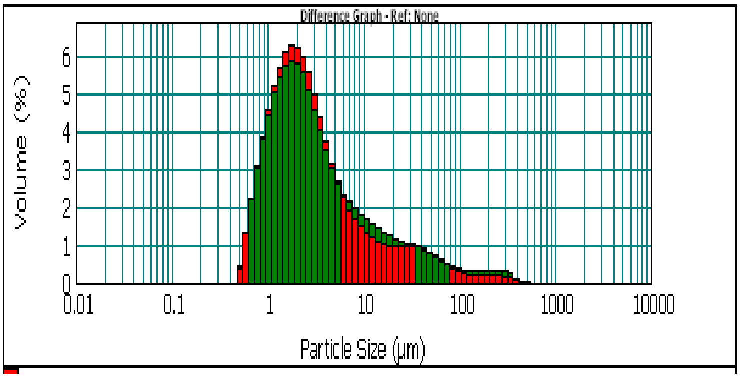


Fig : Reproduced results of PSD at 200 min using 3rd formulation.

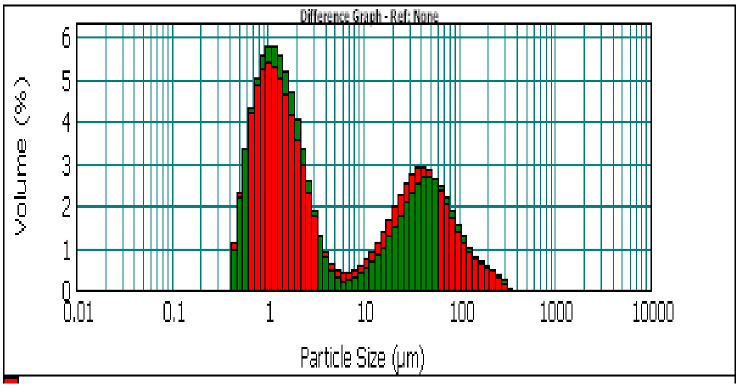


Fig: Reproduced results of PSD at 200 min 3rd formulation

Monomer Droplets

Reproducibility

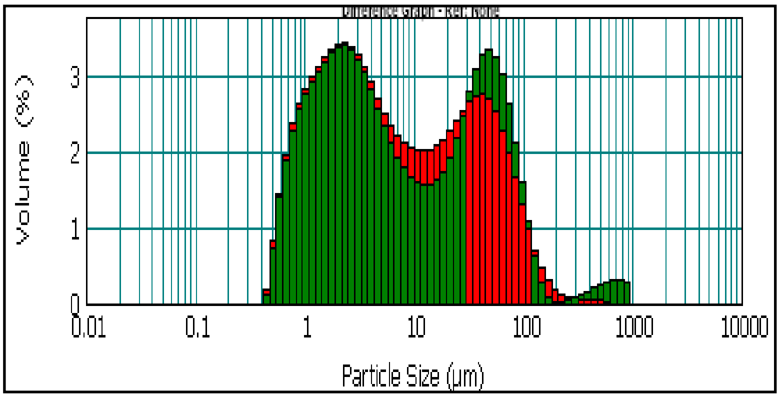


Fig a): Reproducibility of Particle size of monomer droplets (Surfactant conc-1gm).

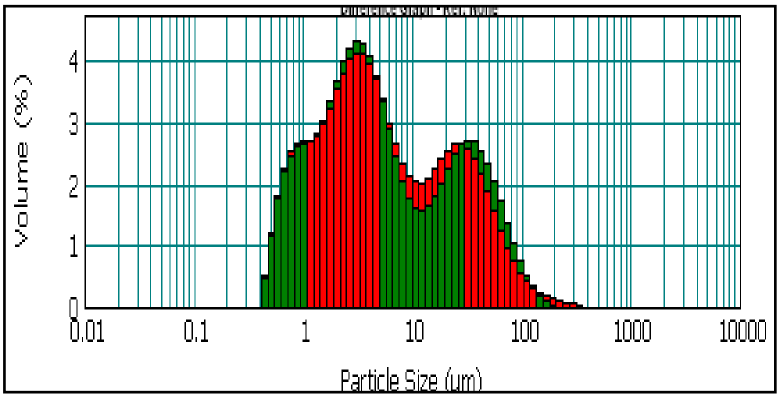


Fig b): Reproducibility of Particle size of monomer droplets (Surfactant conc-1.5gm).

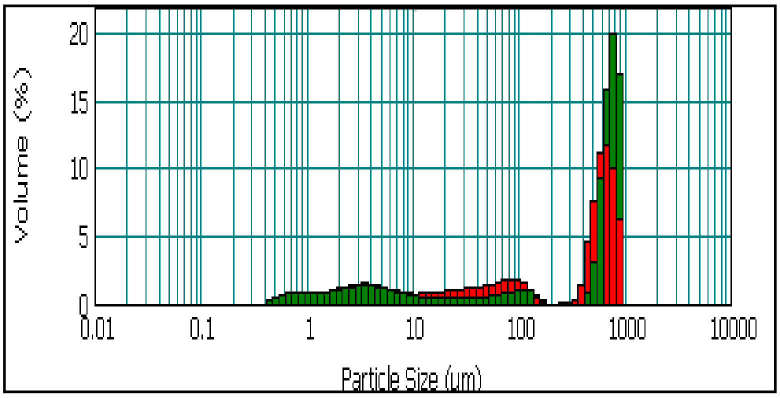


Fig c): Reproducibility of Particle size of monomer droplets (Surfactant conc-2gm).

Results as shown in fig (a) indicating that coagulation event is occurring which makes little disagreement between the timings and magnitude and complete agreement between the trends.

Good agreement between two runs indicating reproducibility as shown in fig (b). Concentration of the surfactant used is 2 gm which gives multimodal distribution in fig (c). Lower the concentration of emulsifier causes the distribution narrower but at the end due to coagulation particles appeared of larger size. Disagreement in Reproducibility appears at lager particle which is resulting by coagulation event

Matlab Programme for Particle Size Distribution

M file

```
function dy = batch_temp_mwd_new2 (t,y,Q)
% M0=3.56; %monomer concentration,mol/lit
% I0=.01485;%initiator concentration,mol/lit
% global f  kd kp ktrm kt  cp  x eps fcold fhot tcold  roe u vr  areahx vj fjout lambda cj roej thotfinal
global f  kd kp ktrm kt thotfinal cp  x eps fcold fhot tcold dr roe FcoldMax tji vr areaj areahx vj fjout lambda cj roej kem uc pi mw wm r nagg na k0 k1 k2 k3 k4 ei pii dw ket micelle rhoini
 count=0;
dy=zeros(13,1);
%if y(2)>=0
   count=count+1;
% cp=3137;
 dy(1)= -(2*f*kd*y(1));
%rate of initiation
dy(2)=-(kp*(2*f*kd/kt)^(1/2)*y(2)*(y(1))^(1/2));
%dx=kp*y(6)*(1-x);% monomer conversion
% y(4)=dy(4);
% dy(4) = (kp/kt^1/2)*((f*y(1)*kd)^1/2)*(exp(-kd));%conc. of polymer
% dy(3)=(fcold*tcold+fhot*thot)/vj-fjout*y(3)/vj* (cj*roej*vj)); +(q/(cj*roej*vj));
```

```
% dy(4)=-lambda*(.6*(kp*(f*kd/kt)^(1/2)*y(2)^1/2))/roe*(cp*roe*vr )/cp-
(q/(cp*roe*vr));
dy(3)=(FcoldMax*cj*(tji-y(3))+q)/(cj*roej*vj);
dy(4)=Q +(-lambda)*(.6*(kp*(f*kd/kt)^(1/2)*y(1)*y(2))-q)/(cp*roe*vr);
dy(5)=(2*f*kd*y(1))-(kt*y(5)^2)-(y(5)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)));%for
% Live polymer chain
%lamda0
dy(6)=(2*f*kd*y(1))-(kp*y(2)*((1-x)/(1+eps*x))*y(5))-(kt*y(6)*y(5))-
(y(6)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5))+ktrm*y(2)*((1-
x)/(1+eps*x))*(y(6)-y(5)));
% for lamda1
dy(7)=(2*f*kd*y(1))-(kp*y(2)*((1-x)/(1+eps*x))*(2*y(6)+y(5)))-(kt*y(5)*y(7))-
(y(7)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))-(ktrm*y(2)*((1-
x)/(1+eps*x))*(y(7)-y(5)/y(4)));
dy(8)=(kt*(y(5)^2))-y(8)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(5);
% dead polymer chain
dy(9)=(kt*y(5)*y(6))-(y(9)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(6)*y(4)*y(4);
dy(10)=(kt*y(5)*y(6))-kt*y(6)^2-(y(10)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))*ktrm*y(2)*((1-x)/(1+eps*x))*y(7);
% %dy(11)=(y(10)+y(7))/((y(9)+y(6))+y(3));%((kt*y(5)*y(6))+kt*y(6)^2-
(y(10)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))+ktrm*y(2)*((1-
x)/(1+eps*x))*y(7))/((kt*y(5)*y(6))+(y(9)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))+ktrm*y(2)*((1-x)/(1+eps*x))*y(6));
dy(11)=k4*(y(12)+y(13)-y(11))+k1*y(13);
dy(12)=rhoini*y(11)-(k4*y(12)-kt*10*y(12))+kem*micelle*(10e10)*2.6e-
8+kp*0.3*y(13);
%del(r-rnuc);polymer radicals,which would not diffuse out of the particle
%monomer radical formed from chain transfer rxn
```

```
dy(13)=(ket*ei*y(11)+ktrm*y(12))*0.3/(k4+kp*0.3+k1);%monomer radical formed from chain transfer rxn
```

S function file

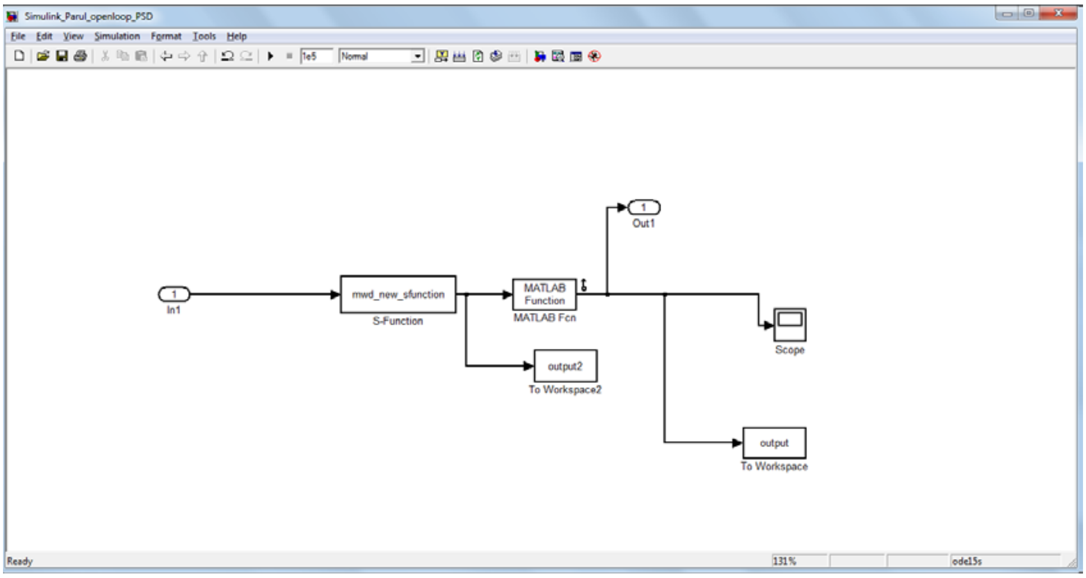
```
function [sys,y0,str,ts] = mwd_new_sfunction(t,y,u,flag)
% global f  kd kp ktrm kt  cp  x eps fcold fhot tcold dr roe  vr areaj areahx vj fjout lambda cj roej u thotfinal
global f  kd kp ktrm kt thotfinal cp  x eps fcold fhot  dr roe  vr areaj areahx vj fjout lambda cj roej FcoldMax tji kem uc pi mw wm rs rm nagg  Q na k0 k1 k2 k3 k4 ei pii dw ket micelle rhoini
 FcoldMax= 0.5;
FhotMax=  0.239; %0.0075;          %0.0009;
% if (manip>=0) && (manip<0.5)
kem=4*pii*rm*na*1.06*10e-7;
mw=0.15;
wm=100.12;
na=6.022*10e23;
k2=4*3.14*k0*na*1.06e-7;
k3=(4*pii*rs*k0*na*dw);
pii=3.14;
dw=1.5e-6;
k4=(k3*ei);
ei=35000;%j/mol

%------------------------
Qinit=90;
%------------------
pi=1e-5;
micelle= delmicelle;
rhoini=rho1;% rough value
 f=0.5;%factor efficiency
kd=1.4e-6; % Initiation rate coefficient (1/s)
%  kd=8.6e-5; % per min
```

```
 kp=0.83127; % m3/mol min
% ktrm=3.24e-2;% l/mol min
ktrm=5.4e-5;% m3/mol min
 kt=1.414e9;%l/mol min

cj=4.183; %J/kg-K
roej=rho2;%kg/m3

eps = 0.364;

tji =303.8; %K
dr = delr; %radius, m
roe=983;    %801; %kg/m3
thotfinal=400;   % Manipulating varible
uc=55; %W/m2-K
vr=3.14*(dr^2)* dr/2;%m3
areaj=2*(3.14*dr^2);
areahx=areaj*4;
vj=.00258*areahx/.4026;
fjout=fhot+fcold;
lambda=-23.85e6; %-69.71e6*1e-7;  %j/kmol
cp=1752; %J/kg-K
x=1;
y(:,:) = abs(y(:,:));


% if t>50000
%     FcoldMax=0.4;
% end
%
switch flag
case 0 %initializing
    str=[] ;
    ts = [0 0] ;
```

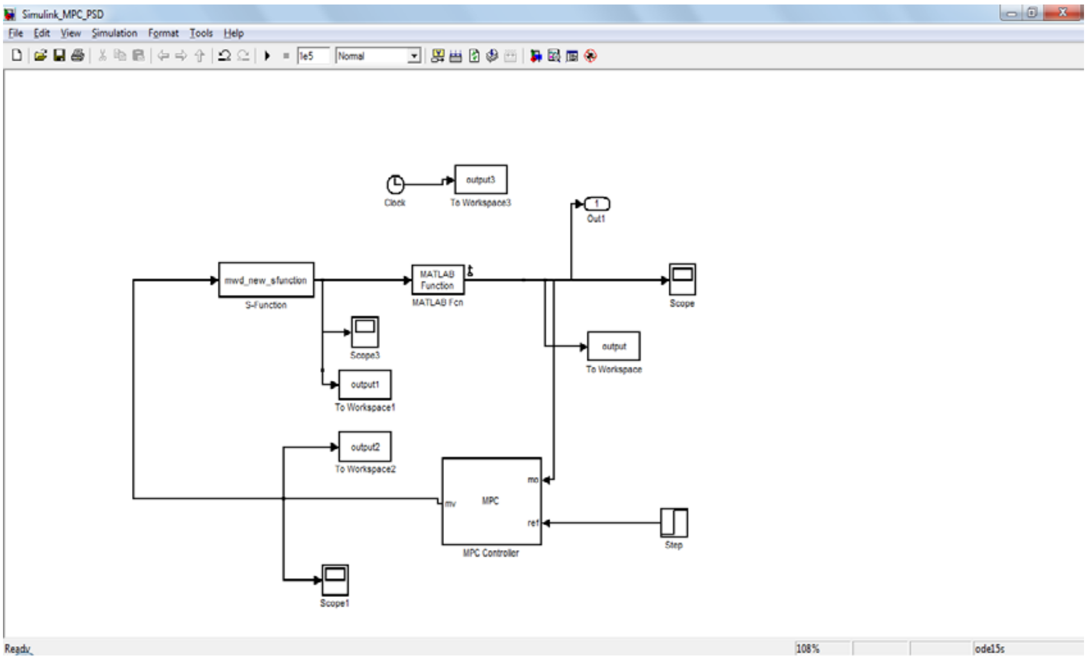
```
      s = simsizes ;
      s.NumContStates = 13;
      s.NumDiscStates = 0 ;
      s.NumOutputs = 16;
      s.NumInputs = 1 ;
      s.DirFeedthrough = 0 ;
      s.NumSampleTimes = 1 ;

    sys = simsizes(s) ;
%     y0=[0.142,8.58,290,320,0,0,0,0,0,0];
%  y0=[1.42,358,290,320,0,0,0,0,0,0];
% y0=[1.42,5.58,310,320,0,0,0,0,0,0,0.01,0.1,0];
%   y = y0;

    case 1 %derivatives
      %thotfinal=thot ;


Q = Qinit + u(1);
       sys = batch_temp_mwd_new2 (t,y,Q);
    case 3
        totp=y(11)+y(12)+y(13);
        if y(9)==0, molwt=0;
        else
            molwt=y(10)/y(9);
        end
        sys = [y; molwt;totp;Q];
        %dy= batch_temp_mwd_new2 (t,y,thotfinal);
     case {2 4 9}    % 2:discrete
                     % 4:calcTimeHit
                      % 9:termination


       sys =[];
    otherwise
```

```
    error (['unhandled flag =',num2str(flag)]) ;
end
```

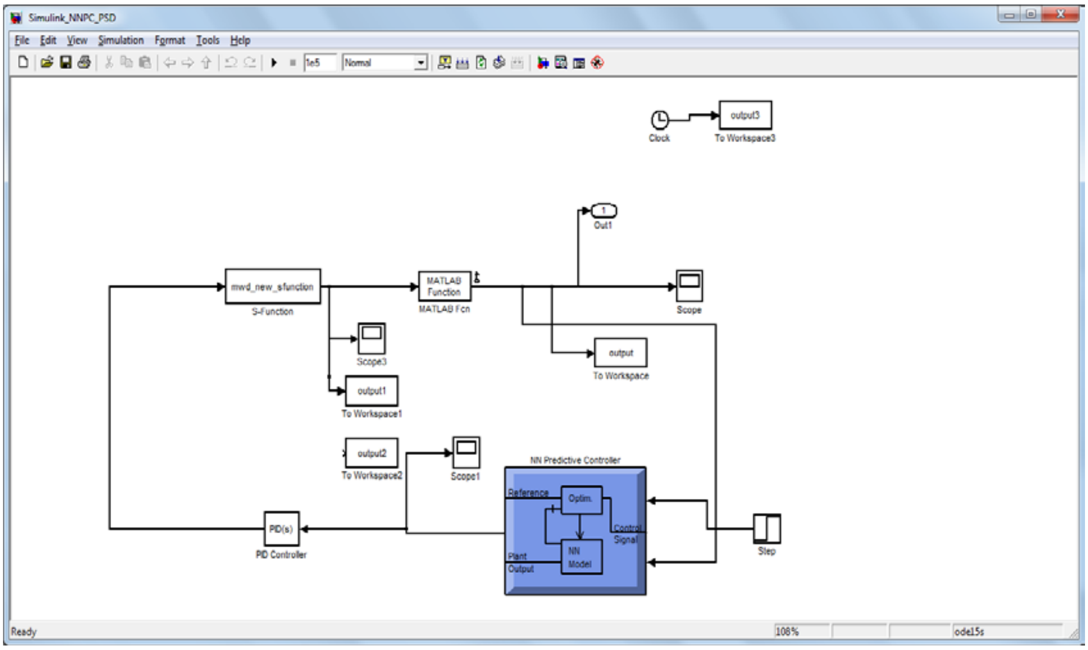
Simulink File for PID



Simulink for MPC



Simulink for NNPC



Matlab Programme for molecular weight distribution

M file

```
function dy = batch_temp_mwd1_new2 (t,y,Q)
% M0=3.56; %monomer concentration,mol/lit
% I0=.01485;%initiator concentration,mol/lit
global f  kd kp ktrm kt  cp  x eps fcold fhot tcold tji roe uc vr  areahx vj fjout lambda
cj roej thotfinal FcoldMax
count=0;
dy=zeros(10,1);
%if y(2)>=0
   count=count+1;
% cp=3137;
dy(1)= -(2*f*kd*y(1));
%rate of initiation
dy(2)=-(kp*(2*f*kd/kt)^(1/2)*y(2)*(y(1))^(1/2));
% dy(2)=-(kp*y(2)*(((2*f*kd*y(1))/kt)^1/2));
%dx=kp*y(6)*(1-x);% monomer conversion
% y(4)=dy(4);
```

```
% dy(4) = (kp/kt^1/2)*((f*y(1)*kd)^1/2)*(exp(-kd));%conc. of polymer
% dy(3)=(fcold*tcold+fhot*thot)/vj-fjout*y(3)/vj*/(cj*roej*vj +(q/(cj*roej*vj));
% dy(4)=-lambda*(.6*(kp*(f*kd/kt)^(1/2)*y(2)^1/2))/roe/cp*/(cp*roe*vr) -
(q/(cp*roe*vr));

% dy(3)=((ua*(y(3)-y(4)))+((fw*rhow*cw)*(tji-y(3))))/(mj*cw);
% dy(4)=((-delh*kp*(2*f*kd*y(1))^1/2)*y(2)^1/2+(ua*(y(3)-y(4))))/(m*cp);
dy(3)=(FcoldMax*cj*(tji-y(3))+q)/(cj*roej*vj);
dy(4)=Q +(-lambda)*(.6*(kp*(f*kd/kt)^(1/2)*y(1)*y(2))-q)/(cp*roe*vr);
% dy(3)=(fcold*tcold+fhot*thotfinal)/vj-fjout*y(3)/vj+q/(cj*roej*vj);
% dy(4)=-lambda*(.6*(kp*(f*kd/kt)^(1/2)*y(1)*y(2)))/(roe*cp)-q/(cp*roe*vr);
%[t,y]=ode45(@batch_temp,[0 8000],[0.142,8,0,0,320,343.15]);
% %------------------Molecular weight%distribution-------------------------
% dy(5)=(2*f*kd*y(1))-(kt*y(5))-(y(5)*eps*((1-x)/(1+eps*x))*(kp*y(5)-
ktrm*y(5)));%for lamda0
% dy(6)=(2*f*kd*y(1))-(kp*y(2)*((1-x)/(1+eps*x))*y(5))-(kt*y(6)*y(5))-
(y(6)*eps*((1-x)/(1+eps*x))*(kp*y(5))+((ktrm*y(5))-ktrm*y(2)*((1-
x)/(1+eps*x))*(y(6)-y(5))));
% % for lamda1
% % y(5)=dy(5);
% dy(7)=(2*f*kd*y(1))+(kp*y(2)*((1-x)/(1+eps*x))*(2*y(6)+y(5)))-(kt*y(5)*y(7))-
(y(7)*eps*((1-x)/(1+eps*x))*(kp*y(5)-ktrm*y(5)))-(ktrm*y(2)*((1-
x)/(1+eps*x))*(y(7)-y(5))); % for lamda 2
% % y(6)=dy(6);
% %%-------------------- Dead polymer-------------
%
% dy(8)=(kt*(y(5)^2))-y(8)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(5);
% dy(9)=(kt*y(5)*y(6))+(y(9)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(6)*y(4);
% dy(10)=(kt*y(5)*y(6))+kt*y(6)^2-(y(10)*eps*((1-x)/(1+eps*x))*(kp*y(5)-
ktrm*y(5)))-ktrm*y(2)*((1-x)/(1+eps*x))*y(7);
```

```
 %-------------------Molecular weight%distribution for live polymer---------------------
-----
dy(5)=(2*f*kd*y(1))-(kt*y(5)^2)-(y(5)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)));%for lamda0
dy(6)=(2*f*kd*y(1))-(kp*y(2)*((1-x)/(1+eps*x))*y(5))-(kt*y(6)*y(5))-
(y(6)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5))+ktrm*y(2)*((1-
x)/(1+eps*x))*(y(6)-y(5)));
% for lamda1
% y(5)=dy(5);
dy(7)=(2*f*kd*y(1))-(kp*y(2)*((1-x)/(1+eps*x))*(2*y(6)+y(5)))-(kt*y(5)*y(7))-
(y(7)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))-(ktrm*y(2)*((1-
x)/(1+eps*x))*(y(7)-y(5)/y(4))); % for lamda 2
% y(6)=dy(6);
%%--------------------- Dead polymer--------------

dy(8)=(kt*(y(5)^2))-y(8)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(5);
dy(9)=(kt*y(5)*y(6))-(y(9)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))-
ktrm*y(2)*((1-x)/(1+eps*x))*y(6)*y(4)*y(4);
dy(10)=(kt*y(5)*y(6))-kt*y(6)^2-(y(10)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))*ktrm*y(2)*((1-x)/(1+eps*x))*y(7);
% %dy(11)=(y(10)+y(7))/((y(9)+y(6))+y(3));%((kt*y(5)*y(6))+kt*y(6)^2-
(y(10)*eps*((1-x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))+ktrm*y(2)*((1-
x)/(1+eps*x))*y(7))/((kt*y(5)*y(6))+(y(9)*eps*((1-
x)/(1+eps*x))*(kp*y(5)+ktrm*y(5)))+ktrm*y(2)*((1-x)/(1+eps*x))*y(6));

   I(count)=y(1);
   M(count)=y(2);
   Tj(count)=y(3);
   Tr(count)=y(4);
   l0(count)=y(5);
   l1(count)=y(6);
```

```
   l2(count)=y(7);
   u0(count)=y(8);
   u1(count)=y(9);
   u2(count)=y(10);
   wt(count)=(y(10)/y(9));
 %end;
```

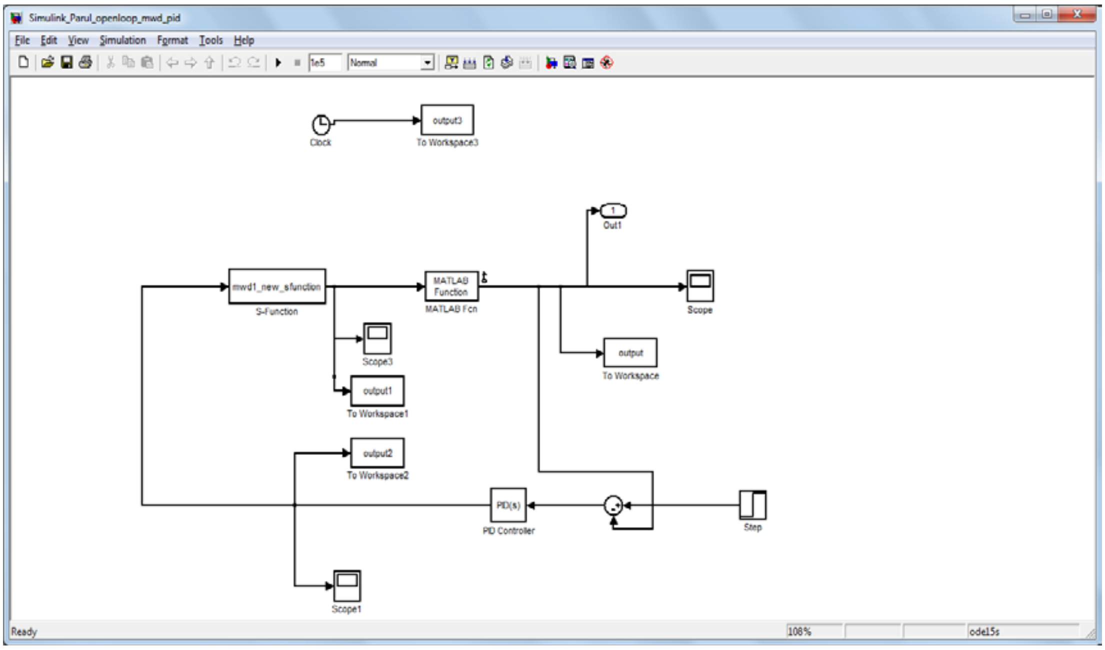
S Function file

```
function [sys,y0,str,ts] = mwd1_new_sfunction(t,y,u,flag)
global f  kd kp ktrm kt  cp tji  x eps fcold fhot tcold dr roe  vr areaj areahx vj fjout
lambda cj roej uc thotfinal Q FcoldMax

FcoldMax=0.5;
FhotMax=10e-3;
% if (manip>=0) && (manip<0.5)
%     fcold=(1-2*manip)*FcoldMax;
%     fhot=0;
% else
%     fcold=0;
%     fhot=(2*manip-1)*FhotMax;
% end
%fcold=5e-3;
%fhot=5e-3;
f=0.5;%factor efficientcy
kd=1.4e-6; % Initiation rate coeffiient (1/s)
%  kd=8.6e-5; % per min
kp=0.83127; % m3/mol min
% ktrm=3.24e-2;% l/mol min
ktrm=5.4e-5;% m3/mol min
 kt=1.414e9;%l/mol min
cj=4.29;    J/kg-K
roej= rho1;%kg/m3
eps=0.364;
```

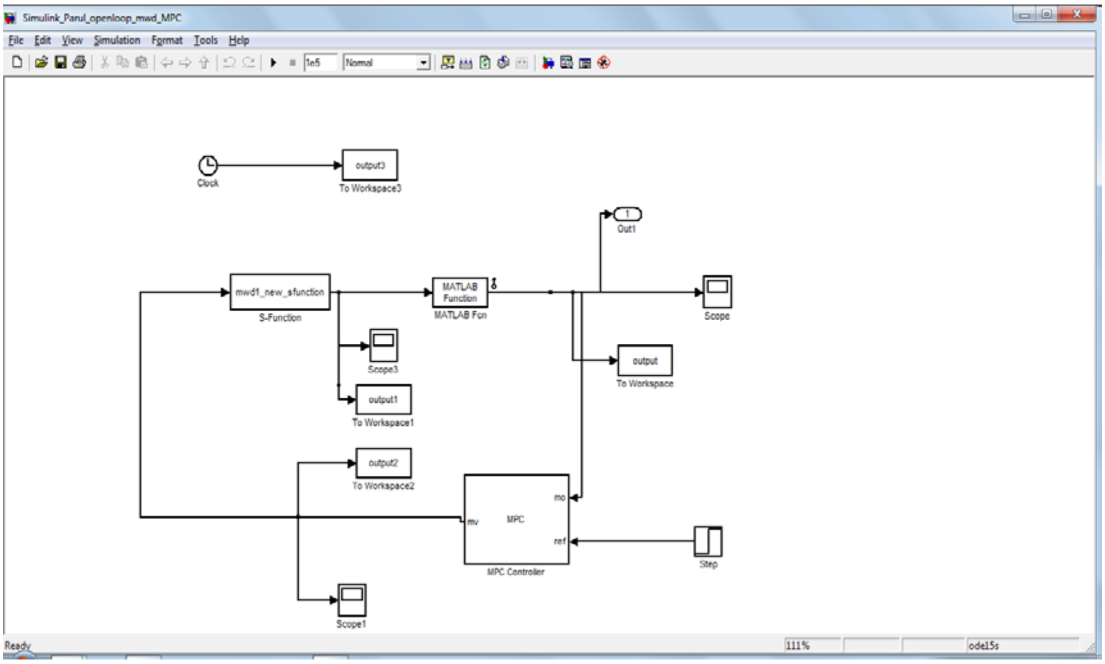
```
%---------------------------------------
Qinit=50;%140; %70;
%--------------------------------
tji=306.5 ;%303; %290; %K
dr=del2; %radius, m
roe= 983;%g/l%801; %kg/m3
thotfinal=360;   % Manipulating varible
vr=3.14*(dr^2)* dr/2;%m3
areaj=2*(3.14*dr^2);
areahx=areaj*4;
vj=.00258*areahx/.4026;
cp=1752; %J/kg-K
x=1;
y(:,:) = abs(y(:,:));
if t>50000
   FcoldMax=0.6;
end
switch flag
case 0 %initializing
     str=[] ;
     ts = [0 0] ;
      s = simsizes ;
      s.NumContStates = 10;
      s.NumDiscStates = 0 ;
      s.NumOutputs = 11;
      s.NumInputs = 1 ;
      s.DirFeedthrough = 0 ;
      s.NumSampleTimes = 1 ;

    sys = simsizes(s) ;
%     y0=[0.142,8.58,290,320,0,0,0,0,0,0];
% y0=[1.42,3.58,300,320,0.001,0.0001,0.001,0.001,0.001,0.1];
```

```
  y = y0;
    case 1 %derivatives
% if t<=1500
%     manip=0.609;
% else manip=0.4999;
% end
%          u=Q;
%       if (manip>=0 & manip<0.5)
%         fcold=(1-2*manip)*FcoldMax;
%         fhot=0;
%       else
%         fcold=0;
%         fhot=(2*manip-1)*FhotMax;
%       end
Q = Qinit + u(1);
     sys = batch_temp_mwd1_new2 (t,y,Q);
    case 3


        if y(9)==0, molwt=0;
        else
            molwt=y(10)/y(9);

        end
        sys = [y; molwt];
        %dy= batch_temp_mwd_new2 (t,y,thotfinal);
     case {2 4 9}    % 2:discrete
                     % 4:calcTimeHit
                      % 9:termination

       sys =[];
    otherwise
        error (['unhandled flag =',num2str(flag)]) ;
end
```

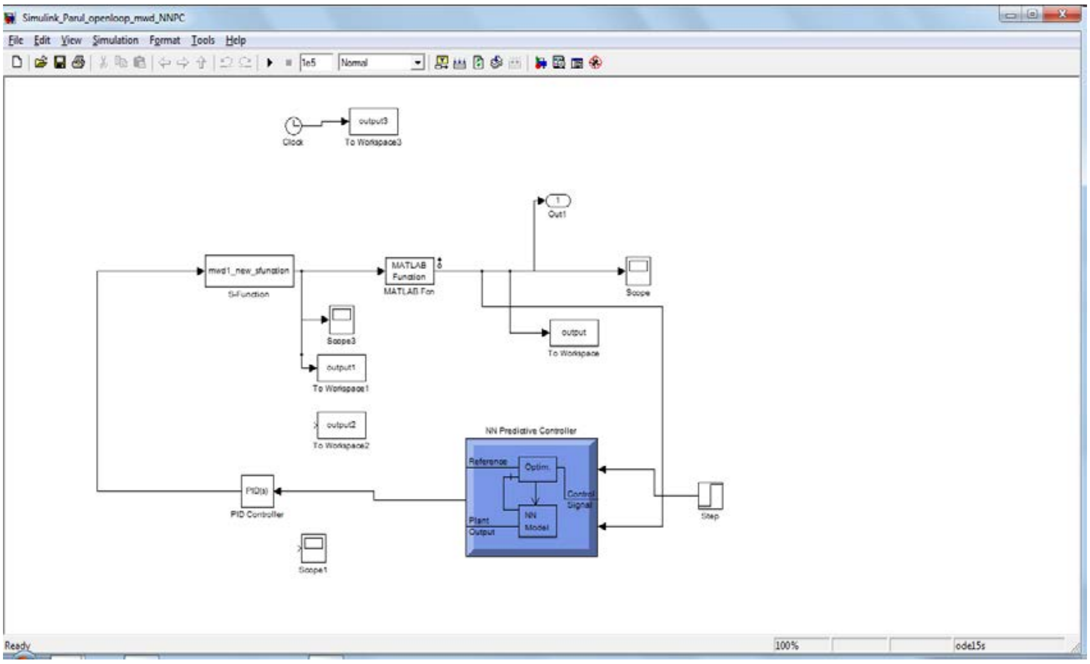
Simulink file of PID for molecular weight



Simulink file of MPC for molecular weight



Simulink file of NNPC for molecular weight


Simulink_Parul_openloop_mwd_NNPC
File
Edit
View
Simulation
Format
Tools
Help
1e5
Normal
Clock
output3
To Workspace3
1
Out1
mwd1_new_sfunction
S-Function
MATLAB Function
MATLAB Fcn
Scope
Scope3
output
To Workspace
output1
To Workspace1
output2
To Workspace2
NN Predictive Controller
Reference
Optim.
Control Signal
Plant Output
NN Model
PID(s)
PID Controller
Step
Scope1
Ready
100%
ode15s

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SYNTHESIS OF POLY (METHYL METHACRYLATE) BY BATCH EMULSION POLYMERIZATION

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ABSTRACT

Poly (methyl methacrylate) was synthesized by batch emulsion polymerization with Methyl Methacrylate as the monomer potassium peroxo-disulfate as the initiator, sodium stearate as the emulsifier and distilled water as a medium. The kinetics of free radical polymerization was studied . The kinetics have been modeled assuming homogeneous nucleation and the resulting equation were solved using runge-kutta method. Degree of conversion and rate of polymerization were studied.

Keywords:
PMMA, emulsion polymerization, free radical polymerization, homogeneous nucleation, emulsifier.

NOMENCLATURE

f : Initiator efficiency

P : Concentration of polymer

I : Initiator (mol/lit)

M : Monomer (mol/lit)

R : Primary Radical

K_d : Rate constant for Initiator Decomposition (min^{-1})

K_1 : Rate constant for Initiation (lit/mol min)

K_p : Rate constant for Propagation (lit/mol min)

K_{tc} : Rate constant for Termination by Combination (lit/mol min)

K_{td} : Rate constant for Termination by Disproportionation (lit/mol min)

K_{trTA} : Rate constant for transfer to Monomer/Initiator (lit/mol min)

K_t : Overall rate coefficient for termination (lit/mol min)

Introduction

PMMA is a versatile material and has been used in a wide range of fields and applications. The German chemist Fittig and Paul discovered in 1877 the polymerization process that turns Methyl Methacrylate into poly Methyl Methacrylate (Lovell 1997). PMMA is routinely produced by emulsion polymerization.

Water born polymerization such as emulsion polymerization are of great importance in industry application as they provide environmental friendly process, remove the reaction heat easily during polymerization and assume the feasible handling of the final product having a low viscosity. Research in controlled/free radical polymerization has been increased significantly during the past two decades (Yeonhwa Wi and 2008).

Emulsion polymerization involves the propagation reaction of free radicals with monomer within the monomer–swollen polymer particle dispersed in the aqueous phase. These discrete hydrophobic particles are stabilized by surfactant sodium stearate. Micelles are formed when the level of surfactant is greater than its critical micelles concentration (cmc). Particle nucleations are generated via the capture of radicals by micelles. These absorb monomer to achieve a critical chain length (.Guoquan Zhu and 2008).

PMMA is often used as a light or shatter-resistant alternative to glass. It is an economical alternative to polycarbonate (PC) when extreme strength is not necessary. It is often preferred because of its moderate properties, easy handling and processing, and low cost. PMMA is a versatile material and has been used in a wide range of fields and applications as a substituent of glass, medical technologies and implants and aesthetic use as well. This properties and uses of PMMA motivated us to work on.

The main objectives of this paper is synthesis of Poly Methyl Methacrylate by batch emulsion polymerization and develop a model to describe the emulsion polymerization of Methyl Methacrylate in a batch reactor at steady state and the comparison of model predictions with experimental observations and characterization of PMMA polymer by estimation of properties of polymer solution.We recently (Arora et all) presented this work in a preliminary form and the detailed results are given in this study.

Experimental Setup

The schematic diagram of the experimental setup as shown in Figure. I. A jacketed batch reactor provided with a high speed mixer is used for emulsion polymerization. Proper arrangements are provided for the control of reaction temperature and the RPM of the mixer. Proper arrangements are provided for administering the initiator under inert atmosphere. Inhibitor is removed by heating Methyl Methacrylate at a temperature of 60°C.recipe used is given in Table no.I.

Characterization

Viscosity of PMMA solutions varies from 1.07 cP to 1.42 cP with concentration of polymer solution. pH of PMMA solutions varies from 5.5 to 6.4 with concentration of polymer solution.,

An electrical conductivity meter (EC meter) measures the electrical conductivity in a solution. Commonly used in hydroponics, aquaculture and freshwater systems to monitor the amount of nutrients, salts or impurities in the water.

The common laboratory conductivity meters employ a potentiometric method and four electrodes. Often, the electrodes are cylindrical and arranged concentrically. The electrodes are usually made of platinum metal. An alternating current is applied to the outer pair of the electrodes. The potential between the inner pair is measured. Conductivity could in principle be determined using the distance between the electrodes and their surface area using the Ohm's law but generally, for accuracy, a calibration is employed using electrolytes of well-known conductivity. The results as shown in table no. V.

Conductivity of PMMA solutions varies from 0.027 to 0.092 with concentration of polymer solution from 4.8 gm/lt to 11.6 gm/lt (Jain 2008.).

Conductivity of polymer solution is measured by conductivity meter. Conductivity meter is firstly calibrated with 0.1 N Agcl solution.

Modeling of Batch Emulsion Polymerization for PMMA

The model is developed to describe the emulsion polymerization of Methyl Methacrylate in a batch reactor at steady state. Non-isothermal effects are considered by coupling the mass and energy balances through the Arrhenius dependence of the rate constants (Sangwai, Bhat et al. 2005). Conservation of energy accounts for the heat generated by the propagation reaction and heat removal through the wall of the reactor and by convective fluid flow. The density of the mixture is a function of the conversion, the amount of solvent introduced in the feed and the temperature. Heat capacities of the monomer, solvent and polymer are taken to be constant, independent of temperature. Monomer and polymer are assumed to have the same heat capacity on a unit mass basis (Min and Ray 1978) (Zeaiter, A. Romagnoli et al. 2002) (Tefera, Weickert et al. 1997). The set of coupled first order differential equations(Chern 2006) is listed in Table II. The Arrhenius expressions of the rate constants are listed in Table 3. The calculated results are the conversion, initiator and PMMA concentration profiles and rate of polymerization. Model predictions for different operating conditions have been compared with experimental observations. Reaction kinetics equations for batch emulsion polymerization are following in tableII.

Computation

Rate of change in Initiator I

$$R_i = fd[I^{\cdot}]/dt = 2\,fK_d\,[I] \tag{1}$$

Rate of change in Monomer M

$$R_p = -d[M]/dt = K_p\,(fK_d/K_t)^{1/2}[M][I]^{1/2} \tag{2}$$

Rate of change in Polymer P

$$d[p]/dt = (fK_d/K_t)K_{tc}[I] + (fK_d/K_t)K_{td}[I] + (fK_d/K_t)^{1/2}K_{trM}[M][I]^{1/2} + (fK_d/K_t)K_{trI}[I]^{3/2} \tag{3}$$

Initial Condition:-

At t = 0, I = Ii, M = Mi, P = 0,

Now, in order to solve the equations 1, 2 and 3 simultaneously we make use of the Runge-Kutta methods for the solution of ordinary differential equations(Sangwai, Bhat et al. 2005). We carry out the calculations for different values of I, M and P corresponding to time and using h=0.001 sec. Kinetics rate constant for free radical polymerization of PMMA is calculated at 70°C from literatures (Baillagou and Soong 1985) (Tefera 1997). Rate constant for free radical polymerization is shown in Table III.

We have the equations

$$R_i = fd[R^{\cdot}]/dt = 2fK_d[I] = \mathrm{f}\ (\mathrm{t, I, M, P})$$

$$R_p = d[M]/dt = K_p(fK_d/K_t)^{1/2}[M][I]^{1/2} = \mathrm{g}\ (\mathrm{t, I, M, P})$$

$$d[p]/dt = (fK_d/K_t)K_{tc}[I] + (fK_d/K_t)K_{td}[I] + (fK_d/K_t)^{1/2}K_{trM}[M][I]^{1/2}$$
$$+ (fK_d/K_t)K_{trI}[I]^{3/2}$$
$$= \mathrm{p}\ (\mathrm{t, I, M, P})$$

With the initial conditions:-

At t = 0, I = Ii, M = Mi, P = 0,

Now, using h =0.001 sec we calculate the values of I, M and P at different intervals using Turbo C^{++} version 3.0 and simulate the data. The corresponding results were plotted graphically.

Results & Discussion

pH of PMMA Solution is measured by pH meter at 25°C. Conductivity of PMMA solution is measured by conductivity meter. pH and conductivity of different concentrated PMMA solutions are tabulated in table VI. Dried polymer which is made in experiment runs is dissolved in 50 ml of benzene. Efflux time t_0 required for a specified volume of benzene solvent to flow through a capillary is measured by ostwald viscometer. Measured efflux time t_0 for benzene at 20°c is 3.81 seconds. Viscosity of benzene with respect to water is calculated by viscometer. η_0 = 1.005 cp, viscosity of samples are tabulated in Table no. V.

Results of batch emulsion polymerization has been done by simulation. Degree of conversion X increase with time t initially and then equilibrates between

0.04 and 0.06 as shown in Figure III, a sharp increased has been observed because of Trommsdorff effect , this was due to the localized increase in viscosity of the polymerizing system which caused the motion of the radical hindered to approach each other for the termination, hence it decrease the termination rate. Figure IV shows linear increase at conversion 0.03 and suddenly shoot up at value of 3.5 of rate of polymerization R_p in very short time, data's are given in table IV. This could be because of exothermic nature of reaction, and also autoacceleration must be caused by the raised viscosity of the polymerization region when the concentration of formed polymer molecules was increased and termination decreased from concentration 0.035 to0.045. Initiator concentration profile in figure V shows that the concentration of initiator decrease with time from concentration 0.185 mol/lit to 0.168 mol/lit, because the initiator radical combines with monomer particle and leads to chain propagation, which finally leads to formation of polymer. The faster the initiation rate the narrower should be the particle size distribution. Monomer concentration profile in figure VI shows that the concentrations of Methyl methacrylate monomer exponentially decrease with time from concentration 5.0 mol/lit to 0.164 mol/lit. This could be because the monomer is the raw material for the polymerization reaction, the concentration of monomer decreases as the reaction proceeds forward with time.

Polymer concentration in figure VII shows that the concentration of polymethyl methacrylate increases with time from concentration 0 to 0.000213 mol/lit. As the reaction proceeds in the forward direction, the product concentration increases with respect to time.

We got the degree of conversion from 0 to 0.04553, pH of the polymer solution varies from 5.5 to 6 and conductivity varies from 0.027 to 0.092 (mhos). Number average degree of polymerization for disproportion was 334.29 and its number average molecular weight was 33429.21 gm/gmol.The kinetic chain length obtained was 334.29. Kinetic chain length is inversely proportional to the radical concentration. Increasing the radical concentration in radical polymerization leads to small sized polymer molecule.

Encountered Difficulties in Batch Emulsion Polymerization of PMMA

The following difficulties are encountered during batch emulsion polymerization of PMMA

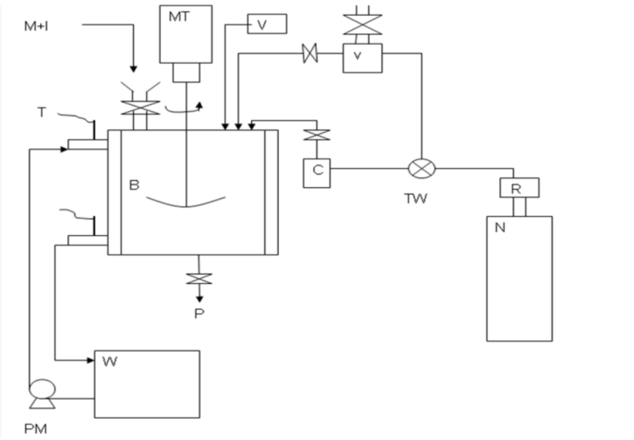
1. In batch reactor, the outlet of the reactor is clogged during the polymerization process. It could be because of emulsifier particles.
2. In batch emulsion polymerization process, it is difficult to maintain constant temperature during the process. Emulsion polymerization is exothermic reaction so temperature of reaction goes higher than the desired temperature. For maintaining the constant temperature hot water is circulated through the jacket of the batch reactor.

Conclusion

PMMA Polymer was successfully prepared by batch emulsion polymerization as shown in figure II and characterized. The simulation of the process was carried out using Runge-Kutta algorithm on C++ computer language. Corresponding graphs were obtained for concentration of initiator, monomer, PMMA with respect to time hence the complete analysis of batch polymerization process was done.

Degree of conversion and rate of polymerization is calculated at particular time which shows the trommsdorff effect. The graphs were plotted from results and discussed. With the successful synthesis of PMMA from emulsion polymerization,it is suggested that this technique can be extended for the preparation of other polymers as well.

Figure I



B = batch reactor; N = N_2 gas cylinder; R = gas regulator; C = gas supply controller; TW = three way valve; v = initiator vessel; V= vacuum pump; MT = motor; T = thermometer; PM = pump; W = water tank; M = monomer; I = Initiator, P = Polymer.

Figure II

Figure III

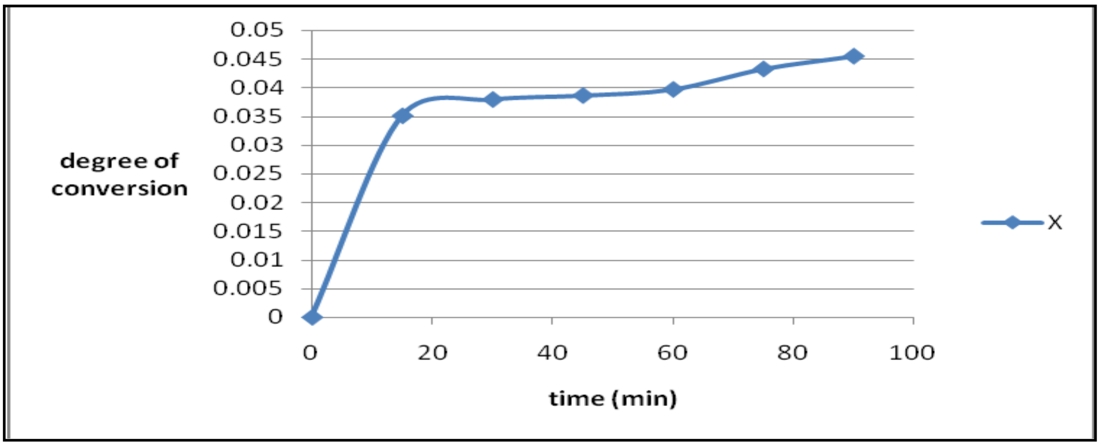


Figure IV

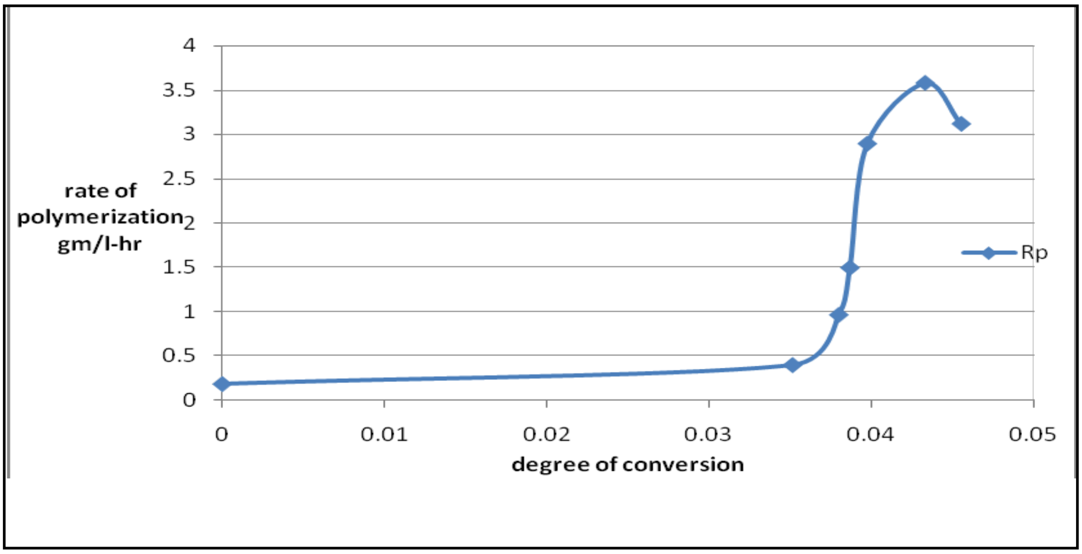


Figure V

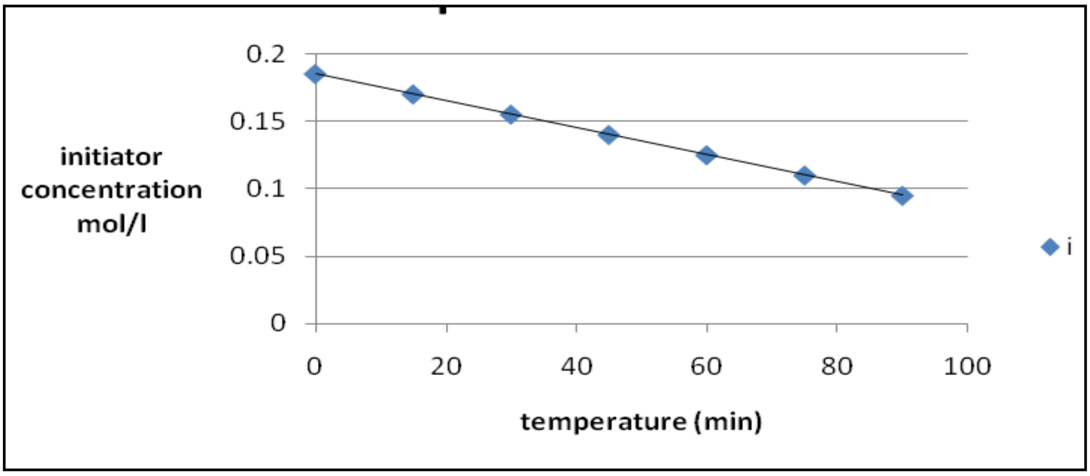


Figure VI

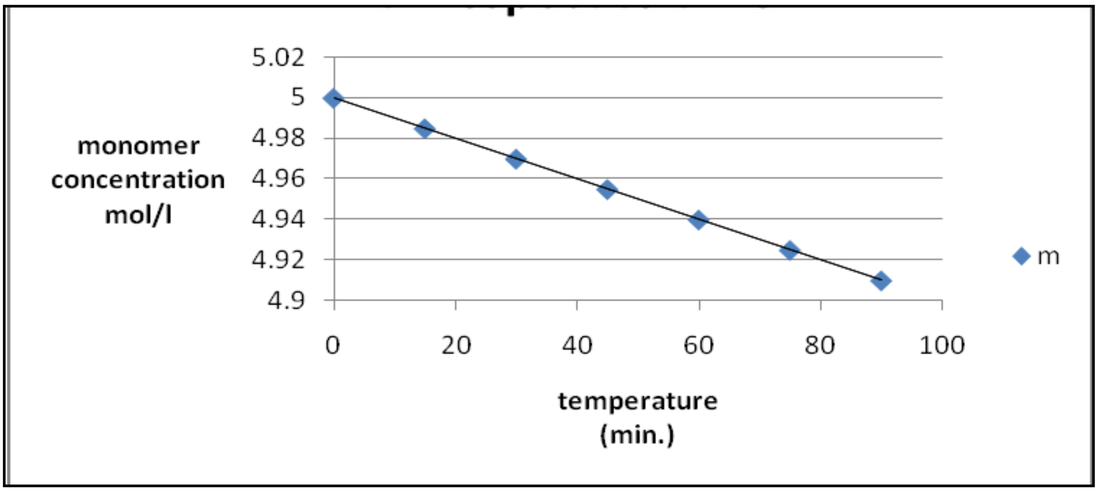


Figure VII

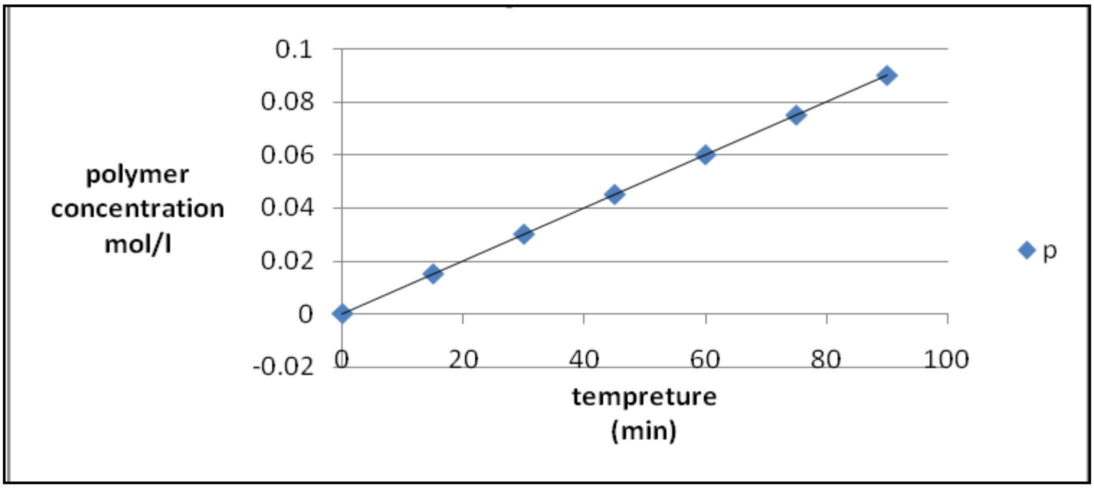


Table I

Contents	
Ion-exchanged double distilled water	180 ml
Methyl Methacrylate	106 ml
Sodium stearate	2 gm
Potassium persulfate	1 gm
N_2 gas	supply at rate of 3 LPM
Hydroquinone	Present in Monomer
Temperature of Reaction	70 ^{0}C ± 1 ^{0}C
Stirring speed N	700 rpm to 750 rpm

Table II

Species	Mass balance equations for batch emulsion polymerization reactor
For initiator	$R_i = fd[I^{\cdot}]/dt = 2fK_d[I]$
For monomer	$R_p = -d[M]/dt = K_p(fK_d/K_t)^{1/2}[M][I]^{1/2}$
For polymer	$d[p]/dt = (fK_d/K_t)K_{tc}[I] + (fK_d/K_t)K_{td}[I] + (fK_d/K_t)^{1/2}K_{trM}[M][I$ $+(fK_d/K_t)K_{trI}[I]^{3/2}$

Table III

Constants	**Value of constants**
F	0.58
K_d	0.001834 min^{-1}
K_p	49876.54 l/mol min
K_{trM}	1.40813 l/mol min
K_1	K_p
K_{td}	K_t
K_{tc}	0.0
K_t	1.414 * 10^9 l/mol min

Table IV

Time (min)	**Initiator concentration (mol / lt)**	**Monomer concentration (mol / lt)**	**PMMA concentration (Mol / lt)**
0	0.185	5.0	0.0
15	0.182078	2.652442	0.000037
30	0.179202	1.6993186	0.000074
45	0.176372	0.965976	0.000110
60	0.173586	0.360244	0.000146
75	0.170844	0.267043	0.000181
90	0.168146	0.163858	0.000213

Table V

Beaker no.	**Weight of polymer**	**Concentration in 50 ml benzene (gm/lit)**	**Efflux time t for polymer solution**	$\eta_{rel}=\eta/\eta_0 = t / t_0$	**η in cp**
1	0.24	4.8	4.08	1.07	1.075
2	0.32	6.4	4.12	1.08	1.085
3	0.42	8.4	4.51	1.18	1.186
4	0.48	9.6	5.03	1.32	1.326
5	0.58	11.6	5.43	1.42	1.427

TableVI:

Beaker no.	Concentration of PMMA solution gm/lt	pH	Conductivity (mhos)
1	4.8	5.5	0.027
2	6.4	5.8	0.051
3	8.4	6.0	0.055
4	9.6	6.1	0.075
5	11.6	6.4	0.092

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LIST OF FIGURES AND TABLES

Figures

Tables

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List of Publications

Research paper published in international journal

- Arora,P., Jain,R., Mathur,K., Sharma,A., Gupta,A.(2010), " Synthesis of poly (methyl methacrylate) by batch emulsion polymerization". African Journal of Pure and Applied Chemistry. 4(8), p. 151-157.
- Arora, P., Gupta, A.(2013)" Control of Molecular weight distribution in batch emulsion polymerization using PID controller : Case Studies".*International Journal of Engineering Research*. 2(7), p 462-466.
- Arora, P., Gupta,A. (2013)." Comparison of two different strategies to control particle size distribution in batch emulsion polymerization using PID controller." *International Journal of Scientific Engineering and Technology*.2 (11), p (1138-1148).
- Arora, P. and Gupta, A.(2014)" Non-linear Model predictive control of particle size distribution in batch emulsion polymerization." International Journal of scientific Engineering and Research. 5(9),p 984-1003.

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