

**MULTIWAY PARTIAL LEAST SQUARE FOR
MODELING AND MONITORING OF
POLY METHYL METHACRYLATE REACTOR**

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UNIVERSITI SAINS MALAYSIA

2014

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MODELING AND MONITORING OF
POLY METHYL METHACRYLATE REACTOR**

by

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**Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science**

February 2014

ACKNOWLEDGMENTS

In the name of Allah, the Most Gracious and the Most Merciful

Alhamdulillah, all praises to Allah for giving me guidance, strength and blessing in completing this thesis. Foremost, I would like to express my sincere gratitude to my supervisor Dr Suhairi Bin Abdul Sata for the continuous support for my master study and research, for his patience, motivation, enthusiasm and immense knowledge. His guidance helped me in during the time of research and writing this thesis. A thousand thanks also to his family for their warm support.

I would like to express my appreciation to the Dean School of Chemical Engineering, Profesor Dr. Azlina Harun@Kamaruddin for her support and help towards my postgraduate affairs. My acknowledgement also goes to all technicians and office staffs of School of Chemical Engineering for their co-operations.

I wish to extend my warmest thanks to my fellow friends in this area group: Norhana Taib, Nor Hafizah, Shahida Azman, Nur Azura Rosli, Nor Fazliani, Saad Rahem and Mohd Fariz. They really helped me a lot in this research. Without them I was unable to finish this study.

I owe my loving thanks to my husband Zulkifeli Bin Dohadi for his encouragement and understanding. In addition, I would like to thank my family: my parents, Osman bin Ahmad and Badariah Binti Bakar for the endless support since I was born until now. Dedication a special thanks to my brother, sisters and also my in law family for the continuous support throughout my study. To those who indirectly contributed in this research, your help are meant to me. Thank you so much.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
LIST OF ABBREVIATION	xiv
LIST OF SYMBOLS	xv
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER ONE: INTRODUCTION	
1.1 Introduction	1
1.2 Problem statement	3
1.3 Objectives	5
1.4 Scope of study	5
1.5 Thesis organization	6
CHAPTER TWO: LITERATURE REVIEW	
2.1 A general introduction of polymerization process	8
2.1.1 Radical polymerization methods	9
2.1.2 Modelling of polymerization process	10
2.2 Multiway Partial Least Squares (MPLS)	14
2.2.1 Overview of MPLS method	15

2.2.2	Determination of batches of data for Multiway scheme of MPLS method	19
2.3	Application modelling to predict output properties	20

CHAPTER THREE: METHODOLOGY

3.1	Batch polymerization process model	26
3.2	Development of MPLS model	32
3.2.1	Determine the suitable range of MPLS model	33
3.2.2	Data arrangement	35
3.2.2 (a)	Data arrangement of M1 model	36
3.2.2 (b)	Data arrangement of M2 model	40
3.2.3	Pre-treatment data of M1 and M2	43
3.2.4	Projection to latent structure	46
3.2.4 (a)	Projecting data to latent structure of M1 model	46
3.2.4 (b)	Projecting data to latent structure of M2 model	47
3.2.5	Determine the number of Principal Component (PC)	49
3.3	New batch output predictions	49
3.3.1	The new batch process prediction	51
3.3.2	The effect of deviated input variables on M1 model	52
3.3.2 (a)	The deviated jacket temperature data towards output prediction	52
3.3.2 (b)	The deviated reactor temperature data towards output prediction	53
3.3.2 (c)	The deviated coolant flowrate towards output prediction	54
3.3.2 (d)	Initiator loading changes and their prediction	55

3.3.3	Prediction of M2 model	55
3.3.3 (a)	Prediction of output properties produced at time 150 minutes	56
3.3.3 (b)	Predicting the end output properties by a current input properties	56
3.3.4	Model evaluation	56

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1	Polymerization process model	60
4.2	MPLS model development	63
4.2.1	Determine a suitable range of data for MPLS model	64
4.2.2	Input data profile of MPLS model	70
4.2.3	Determine the number of Principle Component (PC)	76
4.3	Output prediction	78
4.3.1	New batch output predictions	79
4.3.2	Study on the effect of deviated input variables on MPLS model	85
4.3.2 (a)	Effect of jacket temperature changes towards output prediction	86
4.3.2 (b)	The effect of reactor temperature changes on output prediction	88
4.3.2 (c)	Effect of coolant flowrate change on output prediction	90
4.3.2 (d)	The effect of initiator loadings changes	92
4.3.3	Prediction of M2 model	95
4.3.3 (a)	Prediction of output properties produced at time 150 minutes	95

4.3.3 (b)	Predicting the end output properties by a current input properties	95
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CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1	Conclusions	97
5.2	Recommendations	98

REFERENCES	100
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APPENDIX	107
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PUBLICATION	114
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LIST OF TABLES

No. Table	Title	Page
Table 2.1	Mechanism of general polymerization	9
Table 2.2	Literature reviews on polymerization process.	14
Table 2.3	MPCA/MPLS approaches in polymer	23
Table 3.1	Parameters used in polymerization model	28
Table 3.2	The range of data to build MPLS model	35
Table 3.3	Input X matrix of M1 model	39
Table 3.4	Output Y matrix of M1 model	39
Table 3.5	Input X matrix of M2 model	42
Table 3.6	Output Y matrix of M2 model	42
Table 3.7	Calculation of mean and standard deviation of X data	44
Table 3.8	The new X data after being centered and scaled	45
Table 3.9	Calculation of mean and standard deviation of Y data	45
Table 3.10	The new Y data after being centered and scaled	46
Table 4.1	Average percentage error of Mw, Mn and conversion of PC=1 to PC=3 number	78
Table 4.2	Average percentage error of 8 new batches predictions.	85
Table 4.3	The average percentage error on the study of jacket temperature changes towards prediction	88
Table 4.4	The average percentage error on the study of reactor temperature changes towards prediction	90
Table 4.5	The average percentage error on the study of coolant flowrate changes towards prediction	92
Table 4.6	The average percentage error on the study of other changes towards prediction	94

Table 4.7	The average percentage error of Mw, Mn and monomer conversion to the predicted values at 150 minutes	95
Table 4.8	The average percentage error of Mw, Mn and monomer conversion to the predicted values at 320 minutes	96

LIST OF FIGURES

No. Figure	Title	Page
Figure 3.1	Methodology flowchart	25
Figure 3.2	Schematic diagram of MMA polymerization reactor	30
Figure 3.3	Control loop diagram.	30
Figure 3.4	The illustration of compress and uncompress step.	34
Figure 3.5	Three dimensional of X and Y data for M1 model.	36
Figure 3.6	Three dimensional of X data and two dimensional of Y data for M2 model	36
Figure 3.7	Three way array data of X and Y for M1 model. (Remarks: RT=Reactor temperature, CF=Coolant flowrate, MC=Monomer conversion)	37
Figure 3.8	A transformation of three way array to two dimensional data of M1 model. (Remarks: RT=Reactor temperature, JT=Jacket temperature, CF=Coolant flowrate, MC=Monomer conversion)	38
Figure 3.9	Three way array data of X and Y for M2 model. (Remarks: RT=Reactor temperature, JT=Jacket temperature, CF=Coolant flowrate, MC=Monomer conversion)	41
Figure 3.10	The X and Y data after being unfolded of M2 model. (Remarks: RT=Reactor temperature, JT=Jacket temperature, CF=Coolant flowrate, MC= Monomer conversion)	41
Figure 3.11	Projection of X and Y data to the latent structure at their corresponding time for M1 model	47
Figure 3.12	Projection of X and Y data to the latent structure at their corresponding time for M2 model	48
Figure 3.13	Score T matrix	48
Figure 3.14	P matrix	49

Figure 3.15	Prediction on output properties of new batch using created MPLS model	50
Figure 3.16	Jacket temperature profile of new batch (above: 1°C increased, below: 3°C increased)	53
Figure 3.17	Reactor temperature profile of new batch (above: 1°C increased, below: 3°C increased)	54
Figure 3.18	Coolant flowrate profile of new batch(above: 0.3 g/min increased, below: 0.8 g/min increased)	55
Figure 3.19	Schematic diagram of MPLS prediction	58
Figure 4.1	Conversion profile at 50°C	61
Figure 4.2	Conversion profile at 70°C	61
Figure 4.3	Conversion profile at 90°C	62
Figure 4.4	Average molecular weight as function of conversion for process at 70°C	62
Figure 4.5	Average molecular weight as function of conversion for process at 90°C	63
Figure 4.6	Mw of FPM and predicted results at 62°C.	64
Figure 4.7	Mn of FPM and predicted results at 62°C.	65
Figure 4.8	Conversion of FPM and predicted results at 62°C.	65
Figure 4.9	Mw of FPM and predicted results at 62°C.	66
Figure 4.10	Mn of FPM and predicted results at 62°C	67
Figure 4.11	Conversion of FPM and predicted results at 62°C	67
Figure 4.12	Mw of FPM and predicted results at 62°C.	68
Figure 4.13	Mn of FPM and predicted results at 62°C.	69
Figure 4.14	Conversion of FPM and predicted results at 62°C.	69

Figure 4.15	Input data (Jacket temperature, reactor temperature, outlet coolant flowrate) of 20 batches of reaction	71
Figure 4.16	Predicted by PC=1 in NIPALS algorithm.	76
Figure 4.17	Predicted by PC=2 in NIPALS algorithm.	77
Figure 4.18	Predicted by PC=3 in NIPALS algorithm	77
Figure 4.19	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 59°C	80
Figure 4.20	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 60°C	80
Figure 4.21	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 61°C	81
Figure 4.22	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 62°C	82
Figure 4.23	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 63°C	82
Figure 4.24	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 64°C	83
Figure 4.25	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 65°C	84
Figure 4.26	Prediction of Mw, Mn and conversion with the new batch reactor temperature was simulated at 66°C	84
Figure 4.27	Predicted results of Mw, Mn and conversion which the jacket temperature increased 1 degree Celsius	86
Figure 4.28	Predicted results of Mw, Mn and conversion which the jacket temperature increased 3 degree Celsius	87
Figure 4.29	Predicted results of Mw, Mn and conversion which the reactor temperature increased 1 degree Celsius	88
Figure 4.30	Predicted results of Mw, Mn and conversion which the reactor temperature increased 3 degree Celsius	89

Figure 4.31	Predicted value of output properties with the coolant flowrate changed from 100 to 101 g/min	90
Figure 4.32	Predicted value of output properties with the coolant flowrate changed from 100 to 103 g/min	91
Figure 4.33	Prediction of new batch at reactor temperature 63°C and initiator loading 0.0248 mol/l. ('-' is for actual result, '.' is predicted value)	93
Figure 4.34	Prediction of output properties of new batch with initiator loading 0.0208 mol/l. ('-' is for actual result, '.' is prediction value)	94

LIST OF ABBREVIATIONS

AIBN	2, 2'-azobisisobutyronitrile
BPO	Benzoyl Peroxide
CF	Coolant flowrate
CSTR	Continuous stirred tank reactor
E	X residual
F	Y residual
FPM	First Principle Model
GLC	Globally linearizing control
GPC	Generalized predictive control
I	Batches
J	Input variables
JT	Jacket temperature
K	Times in MPLS model
LDPE	Low-density polyethylene
M	Output variables
MC	Monomer conversion
MLR	Multiple linear regressions
MMA	Methyl Methacrylate
MPLS	Multiway Partial Least Squares
MSE	Mean square error of prediction
Mw	The weight average molecular weight
Mn	The number average molecular weight
N	Number of measurement

NIPALS	Nonlinear iterated partial least square
NLPCA	Nonlinear Partial Least Squares
P	Loading X
PID	Proportional Integral Derivative
PC	Principal Component
PCA	Principal Component Analysis
PLS	Partial Least Squares
PVC	Polyvinyl chloride
Q	Loading Y
RMSE	Root Mean Squared error
RT	Reactor temperature
SBR	Styrene-butadiene rubber
Std	Standard deviation
T	Score X
U	Score Y
X	Input data
X_{mean}	Mean of X data
X_{std}	Standard deviation of X data
Y	Output data
Y_{mean}	Mean of Y data
Y_{std}	Standard deviation of Y data

LIST OF SYMBOLS

Symbol	Description	Unit
A (T)	Temperature dependant parameter in gel effect model	-
At	Heat transfer area	m ²
B	Constant parameter in gel effect model	-
C _p , C _{pc}	Specific heats for mixture and coolant, respectively	kJ/ (kg K)
D	Intermediate variable in the gel and glass effect models	-
f	Intermediate variable in the gel and glass effect models	-
I, I ₀	Initiator and initial initiator concentration, respectively	mol / l
k _d	Dissociation rate	L/min
k _{po} , k _{t0}	Overall propagation and termination rate constants at zero monomer conversion	L/min-mol
k _{td} , k _{tc}	Termination by combination and disproportionation reaction rate constant	L/min
M _c	Coolant flow rate	g/min
M, M ₀	Monomer and initial monomer concentration	mol/l
q	Heat from the electrical heater	W
R _h	The overall heat transfer coefficient	J
R _m	Rate of monomer consumption	mol/L
t	Time	min

T	Temperature	K
T_c, T_{ci}, T_{co}	Average, inlet and outlet coolant temperature, respectively	K
T_{gp}	Glass transition temperature	K
U	Overall heat transfer coefficient	W/ (m ² K)
V, V _c	Reactor and coolant volume, respectively	m ³
x	Monomer histories for the reaction at 70 ⁰ C.	-

Greek letters

θ_p	temperature-dependant parameter in gel effect model
θ_t	temperature and initiator loading concentration dependant parameter in gel effect model
ρ, ρ_c	density of mixture and coolant, respectively
τ_d, τ_i	derivative and integral time constant
$-\Delta H_p$	heat of polymerization process
$\lambda_{n=0,1,2}$	zeroth, first and second moment of the growing radicals
$\mu_{n=0,1,2}$	zeroth, first and second moment of the dead polymers

MULTIWAY PARTIAL LEAST SQUARE UNTUK PERMODELAN DAN PENGAWALAN REAKTOR POLY METHYL METHACRYLATE

ABSTRAK

Pempolimeran merupakan proses di mana unit-unit monomer bergabung melalui tindak balas kimia untuk membentuk rangkaian monomer yang panjang dipanggil polimer. Proses yang tidaklelurus ini mengeluarkan haba dan pembolehubah keluar seperti berat molekul yang tidak boleh didapati ketika proses sedang beroperasi. Dengan itu ianya perlu diukur melalui analisis makmal dan hanya sampel yang terhad sahaja boleh didapati semasa proses sedang dijalankan.

Ketidakhadiran pembolehubah keluaran seperti berat molekul dan penukaran monomer membawa pada pembangunan model inferensi. Dalam kajian ini model pelbagai cara kuasa dua terkecil separa telah digunakan. Model ini adalah salah satu kaedah Chemometric yang terkenal dimana ianya mampu memantau dan meramalkan pembolehubah keluaran. Model ramalan ini menyediakan tempat dimana pembolehubah keluaran boleh diramalkan berdasarkan data operasi seperti suhu reaktor, suhu jaket dan kadar aliran penyejuk. Model ramalan ini memerlukan sejumlah besar data yang dikumpulkan hasil daripada proses sebelumnya. Proses ini merupakan proses yang dapat menghasilkan keluaran seperti yang dikehendaki.

Dalam kajian ini, ianaya memberi tumpuan kepada ramalan keluar proses pempolimeran seperti penukaran monomer, berat molekul purata dan jumlah berat molekul purata. Ini adalah kerana sifat semulajadi pembolehubah ini yang tidak boleh didapati semasa proses sedang beroperasi. Kajian ini juga membantu untuk memantau pembolehubah di samping mengesan produk di luar spesifikasi. Idea di sebalik model tambahan pula adalah memberikan nilai ramalan pada masa tertentu.

Di samping itu, data-data untuk kajian ini diperolehi melalui simulasi selain daripada loji sebenar ataupun eksperimen. Suhu reaktor, suhu jaket dan kadar aliran penyejuk telah dikenal pasti sebagai pembolehubah masukan manakala berat dan jumlah berat molekul purata serta penukaran monomer digunakan sebagai pembolehubah keluaran. Data simulasi ini telah dianggap sebagai proses yang sebenar.

Model ramalan yang dicadangkan ini telah berjaya meramalkan pembolehubah keluaran dari data pembolehubah masuk yang baru apabila reaktor beroperasi pada suhu 61-64°C. Ramalannya menghasilkan peratusan purata kesilapan yang rendah berbanding suhu di luar julat data pembangunan. Data pembangunan merupakan data yang digunakan untuk membentuk model ramalan. Jika ramalan baru di lakukan ke atas data baru di mana ianya berada di dalam julat data pembangunan, ia juga menghasilkan peratusan kesilapan yang rendah. Model tambahan juga menunjukkan bahawa ianya berjaya meramalkan hasilan pembolehubah keluaran pada masa 150 minit dan 320 minit. Ramalan menghasilkan peratusan yang rendah.

MULTIWAY PARTIAL LEAST SQUARE FOR MODELING AND MONITORING OF POLY METHYL METHACRYLATE REACTOR

ABSTRACT

Polymerization is the process in which monomer units are combined by chemical reaction to form long chains monomer called polymer. The output variables such as molecular weight and conversion are unavailable online thus they need to be measured through laboratory analysis and moreover only a limited sample are made during the process.

The unavailability output variables leads to the development of inferential model which in this study used Multiway Partial least squares (MPLS). MPLS model is one of the famous Chemometric method which able to monitor and predict the process output properties. This inferential model prepared a place where output properties such as molecular weight can be predicted based on operating data such as reactor and jacket temperature and coolant flowrate. This inferential model requires a large amount of data which accumulated during previous processes. These data are considered as normal process which produced desired output properties.

The present study focuses on the prediction the output properties of Methyl Methacrylate (MMA) polymerization such as monomer conversion, the weight average molecular weight (M_w) and the number average molecular weight (M_n). This is due to the nature of these properties since these output properties are not available online. This work helps to monitor the properties and it can be used to detect off specification product. The idea behind the additional model is that this model gives a prediction value at specific time during the process.

Moreover in this study, the properties data were obtained via simulation instead of real plant data or experimental. However, this simulated data were assumed as a real process. Simulated reactor temperature, jacket temperature and coolant flowrate were identified as input variables meanwhile molecular weight (Mw and Mn) and monomer conversion as output variables that been used in MPLS model.

The proposed inferential model was successfully predicts the output properties of new input data at reactor temperature 61-64°C. The predictions gave low average percentage error result compared to the temperatures out of the range of development data. Development data are the data used to build MPLS model. Whenever inputs data was in the range in development data, the percentage error was obviously minimum. The additional model was also successfully predicted the output properties at time 150 minutes and 320 minutes. The errors of predicted output properties were low.

CHAPTER ONE

INTRODUCTION

This chapter firstly covers the introduction of polymerization process and the method of MPLS in predicting and process monitoring. This chapter also provides the objectives, the scope of this research study and lastly thesis organization.

1.1 Introduction

A polymer is a large molecule that is built up by the repetition of small molecules called monomer. This repetition is called polymerization process. Polymer industry is one of the important industries in the world producing the most essential things in our daily lives. Mankind has used polymers since a long times ago such as tyre for vehicle, gloves for protecting hands, footwear for foot protection, rubber-based components and material for transport and construction industries. This industry evolves drastically in chemical industry instead of pharmaceutical, petroleum, food, textile and etc.

Polymer reactor either continuous or batch is designed to produce polymer in wide range of molecular weight. Molecular property is an importance output property to be controlled in order to produce the good and high quality product. This property cannot be measured directly or online thus its need to be measured in the laboratory so that this process needs a delay time to discover its results. The operating conditions in polymer reactor influence the molecular properties of the polymer being produced. Furthermore these properties are difficult to measure frequently because of limited sample.

Polymer producers faced many challenges and the obvious challenge is the heat release by the process reaction. In fact the rapid growth of polymer manufacturer gives an increased demand satisfaction of customer to the end product produce. This creates a dynamic environment where the polymer industries undergo continuous improvement to keep existing in the markets. Thus manufacturers need to concern several aspects such as improve the behaviour of the process, their effect on output properties and efficient process technology. The need to maintain the efficiency of producing the consistent high quality product leads to the development of inferential model.

A big achievement in polymerization reaction engineering is the Chiu et al (1983) model, which this model successfully described the polymerization over entire conversion range based on free volume theory. This model proposed a Methyl methacrylate process model which diffusional limitations affected the rate constants. This model compared to others described the effects of composition, temperature and molecular weight continuously in their model. The other models involved break points to characterize the onset of diffusional limitations.

In chemical process industries, process monitoring and controlling are extremely important in terms of the contribution towards producing a high quality product. Process monitoring plays an important role in current technology as the output of the model is monitor via the prediction based on operational data. Statistical process control (SPC) is effective in monitoring chemical processes and it is applied to monitor and control a process via a prediction chart. In addition it can detect any deviation process via monitoring scheme and the occurrence of off-specification product can also be detected. SPC is a method which uses statistical method in quality control. It is believed that the deviation can be detected and removed more

quickly by observing the output properties prediction. In some approach this monitoring process provides acceptable limits where the prediction of the model should lie within this limits. Beside, this process can lead to the identification of unwanted output properties. On top of that this process is able to gives timely information on the process performance and also it helps to reveal the progress of their properties.

This SPC method is a soft sensing tool that has been developed to gives an online measurement of polymer properties. Partial least squares (PLS) and Neural Network (NN) are the famous methods offer that approach. These methods can be modelled by using the historical data of previous processes. NN is similar as MPLS which can make predictions of future data. NN is a software simulation of a biological brain. Its can predict an output pattern when it recognizes a given input pattern. This is different to MPLS, which MPLS consisted equation that can help to predict output data and this method is easy to implement.

Multiway PLS (MPLS) is an extension method of PLS which MPLS generally applied to batch process. Batch process data exist in three dimensional which contains a few batches, variables and time points. In addition, this method is able to handle large volume of data. This method compresses a large volume of data into low dimensional data. MPLS model indirectly describe the process by its low dimensional data of latent structure.

1.2 Problem statement

Producing a consistent high quality product is an objective of all chemical processes especially polymerization process. Producing an intended polymer product is not an easy task as their reactions are nonlinear and highly exothermic. This highly