Model-based optimization of the production of polyvinyl acetate

Fernando Aller

Institute Jožef Stefan, Department of Systems and Control,
Jamova 39, SI-1000 Ljubljana, Slovenia; Email:
Fernando.aller@ijs.si;

Abstract: A detailed dynamic model of the polymerization reaction of vinyl acetate in a real-life industrial reactor has been developed. The purpose of this model is to allow for different optimization and control studies. With the recipe and the operating procedures observed in the factory as inputs, the model predicts with reasonable accuracy the quality variables, namely: the final conversion, the average particle diameter, the solids content and the viscosity. The model provides further insight into the reaction kinetics and allows us to make knowledge-based decisions. The model is intended to run a model-based optimization of the policy of adding monomer in order to reduce the batch time. This variable has to be modified together with the initiator flow rate to keep the quality variables constant.

Keywords: Vinyl Acetate, polymerization, optimization, gPROMS® .

1 INTRODUCTION

In an environment of increasing demands and competitiveness, polymer manufacturers need to improve their production capabilities with the minimum of expenditure. The first option to be considered, before deciding whether to invest in additional equipment, is to optimise existing resources.

Mitol d.d., a medium-sized factory in Sežana, Slovenia, is currently working at over ninety per cent of its capacity. The company now wants to increase its production capacity. Current research efforts are focused on reducing the batch time. The large quantities of raw materials and equipment resources involved in a batch prevent us from performing experiments directly in the plant. For this reason, developing a reliable model of the polymerization reaction as carried out in the factory is considered to be the best option.

No model to date has dealt with the behaviour of the reaction in a commercial manufacturing process. Although the fundamental steps and mechanisms in the reaction remain the same, other considerations regarding the operating procedures and the mechanisms of control need to be included. The influence of human operators also introduces a degree of uncertainty; a completely different situation to the accuracy and extensive documentation of the experiments performed in laboratories.

2 THE PROCESS

The reaction modelled is the polymerization of vinyl acetate, using poly(vinyl alcohol) as the protective colloid and potassium persulphate as an initiator. The 7-m^3 reactor is continuously stirred. The use of a polymeric emulsifier affects the kinetics of the reaction and the mechanism of stabilization of the particles [1-2]. It also increases the rate of thermal decomposition [3][4].

The process followed in Mitol can be divided into three main steps:

- Initial amounts of monomer (around 10%) initiator, as well as the whole amount of poly(vinyl alcohol) are introduced into the reactor and heated. The thermal decomposition of the initiator starts the reaction.
- Upon reaching 72ºC the heating is stopped. The remaining monomer is then fed in a separate stream at a constant flow rate of 370 kg/h. The temperature in the reactor during this step should be kept within the range 75–80ºC. This control is performed manually by adding small amounts of initiator when the temperature decreases.
- When all the monomer has been added a larger amount of initiator is added in order to finish the reaction. The temperature is then allowed to increase to 90ºC. The reaction is finished when the temperature starts to decrease again.

Regarding the procedures followed during the production, some special features need to be highlighted:

- The control of the temperature during step 2 is done manually. A condenser operating in an open loop provides the cooling. When the temperature is reducing, more initiator is added in order to accelerate the exothermic polymerization reaction and increase the temperature.
- The flow rate of the monomer is constant.
- The operator, who bases his decisions on the temperature profile, decides the number of additions of initiator.

The main variables affecting the duration of the reaction and consequently the productivity are as follows: the temperature in the reactor, the initial amount of monomer, the subsequent feed rate of monomer and the addition of the initiator [5]. The model has to estimate correctly the influence of each of the variables, as these will be the variables modified during the optimization process. The main quality variables are as follows: the particles size, the final conversion, the solids content and the viscosity. These variables need to be accurately calculated by the model, as they will define the final characteristics of the product and also the duration of the reaction.

3 THE MODEL

The model of the polyvinyl acetate production was developed using the gPROMS® modelling tool. The four quality variables (conversion, particles size, solids content and viscosity) are the outputs of the model. The initial amount of monomer, the temperature, the flow rate of the monomer, and the manual addition of initiator are the model inputs. The parameters involved are mostly taken from the existing literature. However, some of them have needed further adjustment due to the existing uncertainties in the polymerization theories. The complete set of equations is not included here due to its complexity. However, it will soon be available in the journal 'Mathematical and Computer Modelling of Dynamical Systems'.

The aim of the model is to optimize the policy of adding the monomer and the initiator in order to reduce the batch time, while at the same time maintaining the quality. The variables defining the quality are the final conversion, the particle diameter, the solids content and the viscosity. So the model has to predict, with a reasonable accuracy, the values of these variables under different operating conditions.

The inputs to this model, i.e., the temperature and the flow rates of the monomer and the initiator, are presented in figures 1, 2 and 3 respectively. The temperature and monomer flow-rate profiles are real data from the process. The addition-of-initiator data comes from simulating the decisions made by the operators. When the temperature is reducing they add a certain amount of initiator in order to increase the temperature. Hence, the addition of initiator occurs in the valleys of the temperature profile.

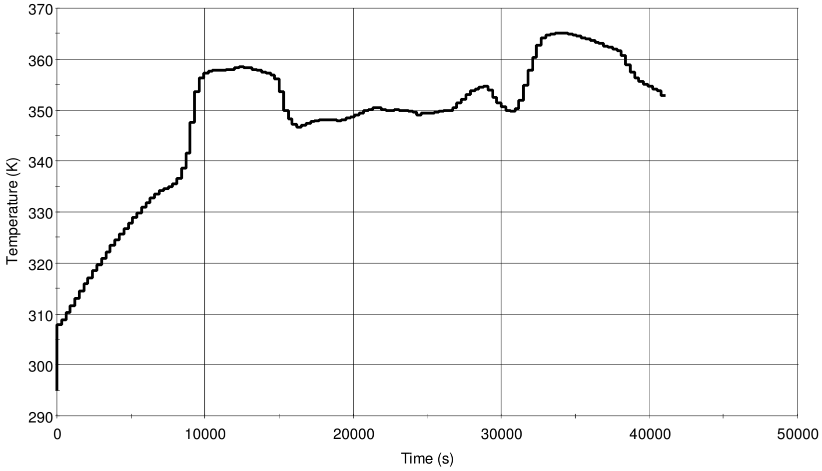

Fig. 1: Temperature profile of batch 110

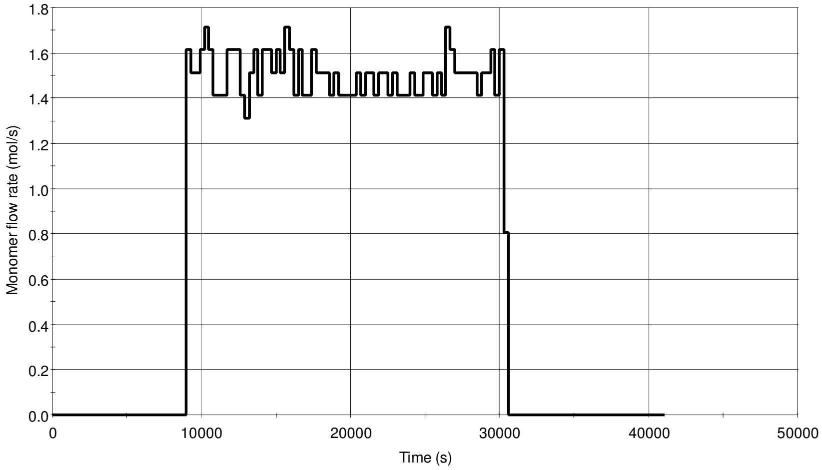

Fig. 2: Monomer flow rate of batch 110

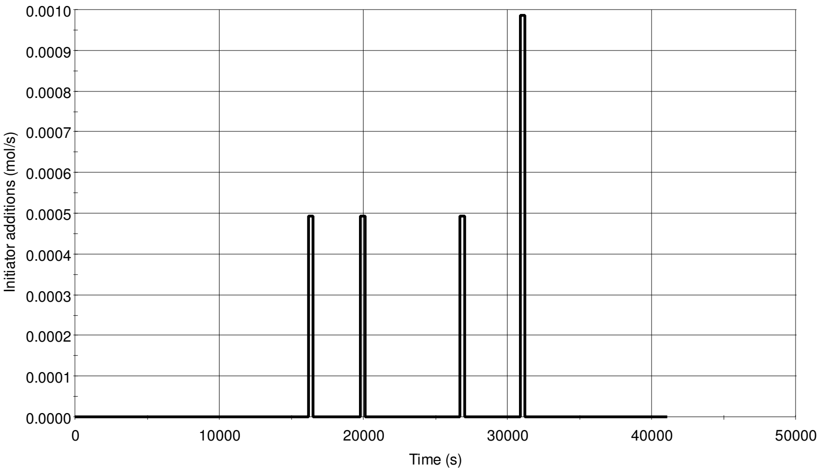

Fig. 3: Initiator additions during Batch 110

The model was validated against real data from six batches of different durations and temperature profiles. The figures correspond to batch 110. The other batches show similar graphs, consistent with the different times and input variables that were used. The profile of each output variable is depicted in the accompanying figures and explained below.

The conversion was measured only at the end of the process, after most of the remaining monomer was extracted by a vacuum pump. The conversion estimated using the model was made prior to the use of this pump, and as a result it is lower than that measured in the factory. There are two features about the conversion profile that we can extract from the observation of the reaction. The operator starts the monomer pump when the reflux through the condenser has almost ceased. At this point the conversion is high. With the continuous addition of monomer the global conversion is decreased. When all the monomer has been added the addition of a double dose of initiator, together with the halt to the flow rate of monomer, causes the conversion to increase to its final value. Although the exact value at the end of the reaction is not accurately known, due to the improvement introduced by the vacuum pump, the R&D personnel working in the factory estimate it at over 99%. In figure 4 we can see that the profile estimated by the model follows the expected behaviour.

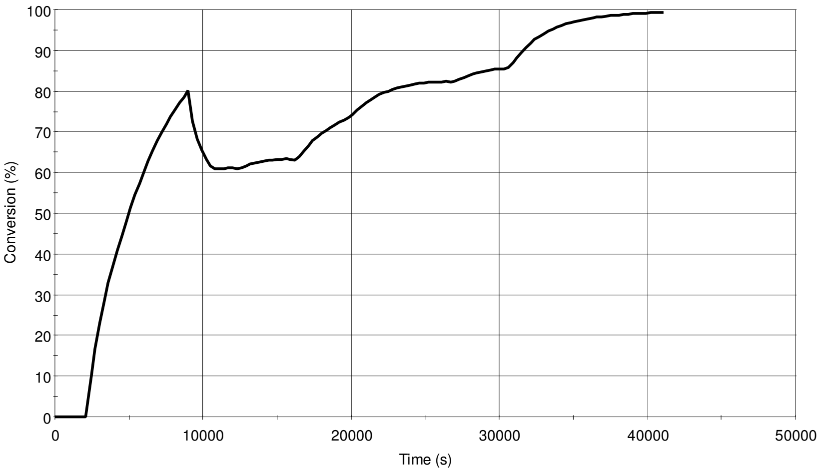

Fig. 4: Conversion against time (Batch 110)

According to the quality specifications of the final product, the average diameter of the particles has to be in the range 1.0–1.5 microns. In figure 5 we can see the evolution of the swollen and unswollen average diameters throughout the reaction. The points where they approach correspond to the peaks in the conversion, just before the addition of monomer is started and at the end of the reaction.

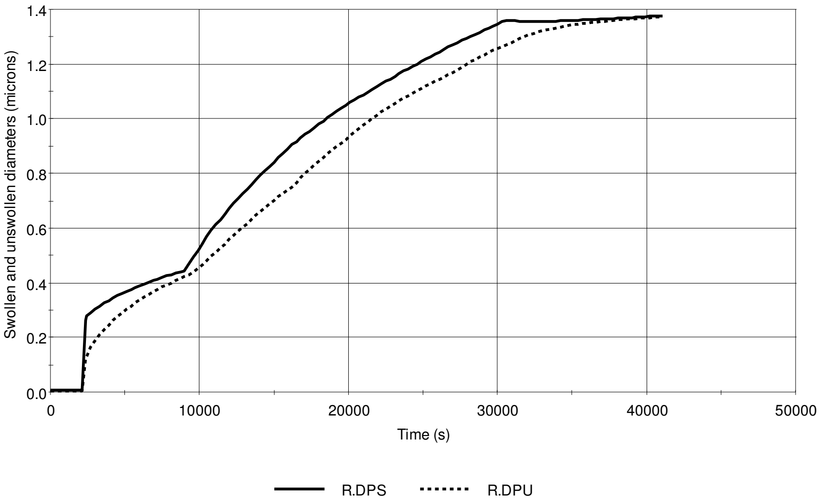

Fig. 5: Swollen (Dps) and unswollen (Dpu) diameters of the particles (Batch 110)

The results calculated by the model are summarized in table III. The final conversion is over 99% in all cases. The diameter of the particle, around 1.4 microns, is also in the quality range of the product (from 1.0 to 1.5 microns). The solids content seems to be slightly overestimated, since the range for this variable is 0.44–0.46. The viscosity is below its upper quality limit of 34000 in most cases. However, this is not a determinant variable, since too high values can be corrected simply by adding more water.

Batch No.	Duration	Model values			
		X (%)	D_{pu} (μm)	Sc	ν (P)
110	40800	99.29	1.37	0.470	33967
114	39000	99.12	1.33	0.467	33500
116	38100	99.38	1.37	0.465	33446
117	411000	99.72	1.36	0.47	34179
175	41100	99.18	1.34	0.467	32626
266	52500	99.69	1.38	0.472	34532

Table III: Values predicted by the model

4 OPTIMIZATION AND CONTROL

Based upon the described model, the optimization and control strategies will be developed. No results about this topic are available yet, but an outline of the main ideas to be developed is given below.

Two variables can be modified during the semi-batch reaction of polymerization of polyvinyl acetate: the flow rate of monomer and the flow rate of initiator. These flow rates are the controlled variables. The only measured variable is the temperature, which is not a reliable indicator of the state of the reaction. The semi-batch reaction has different stages, and even within each stage the concentrations of the different species inside the reactor differ. The effect that an addition of a certain amount of one of the reactants is going to have on the temperature is strongly dependant on the state of the reactor. The state of the reactor at a certain time is defined by the temperature in the reactor, which can be measured, but also by the concentrations of reactants in the reactors and in the different phases. These concentrations cannot be measured on-line. Thus, to predict the effect that a certain amount of the reactants will have on the reaction, we need an accurate estimation of the state of the reaction.

The model developed will be used for the on-line estimation of the state of the reaction. The model will also predict the possible evolution of the reaction, determining the corrective actions to be taken. We have to take into account that the model is not the reaction, and its estimations are only approximate. To avoid the accumulative deviation of the model from the real behaviour of the reactor, on-line corrections have to be introduced. The heat produced by the reaction is a good indicator of its state. As the heat released by the reaction cannot be directly measured, a rough estimation is introduced in the model, based upon the heat exchanged in the heating coat and the condenser.

The control algorithm will try to keep the highest concentration of monomer in the water without going beyond the limit of solubility. This ensures a maximum concentration of monomer on the particles that ensures a high rate of polymerization. The addition of initiator will be used for the control of temperature. It has to keep the reaction at its highest speed but taking care that the heat released can be evacuated by the cooling system.

5 CONCLUSIONS

The control and optimization of a polyvinyl acetate reaction requires the knowledge of its current state and its future evolution. The available measurements are not enough to accurately predict it, so a dynamical model of the reaction has been developed. The results of the model are encouraging and so an outline of its application in control and optimization of the reaction is given.

6 ACKNOWLEDGMENTS

Financial support from the PRISM Marie Curie Research Training Network is gratefully acknowledged (Contract No: MRTN-CT-2004-512233).

References

[1] C.M Gilmore, G.W. Poehlein and F.J. Schork, 1993, Modelling Polyvinyl Alcohol Stabilized Vinyl Acetate Emulsion Polymerization I. Theory, *Journal of Applied Polymer Science*, 48, 1449-1460.

[2] C.M Gilmore, G.W. Poehlein and F.J. Schork, 1993, Modelling Polyvinyl Alcohol Stabilized Vinyl Acetate Emulsion Polymerization II. Comparison With Experiment, *Journal of Applied Polymer Science*, 48, 1461-1473.

[3] Polyvinyl Alcohol: Properties and Applications, edited by A. Finch, 1973, John Wiley and Sons Ltd.

[4] Vinyl acetate emulsion polymerization and copolymerization with acrylic monomers, 2000, H. Yildirim Erbil, CRC Press LLC.

[5] Stephane M. Lepizzera, Archie E. Hamielec, 1994, Nucleation of particles in seeded emulsion polymerization of vinyl acetate with poly(vinyl alcohol) as emulsifier, *Macromol. Chem. Phys.,* 195, 3103-3115.

[6] Maurice Morton, Samuel Kaizerman and Mary W. Altier, 1952, Swelling of latex particles, paper presented at the 122nd National Meeting of the American Chemical Society, Division of Polymer Chemistry.

[7] Process Systems Enterprise Ltd., 2004, gPROMS® Introductory User Guide.

[8] Process Systems Enterprise Ltd. ,2004, gPROMS® Advanced User Guide.