Dynamic Modelling and Experimental Validation of the Methylmethacrylate Cell Cast-Process for Plastic Sheet Production

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Abstract

In this work the development of a dynamic 2-dimensional Methyl-Methacrylate polymerization mathematical model able to predict conversion rates, polymer temperature and molecular weight distributions is addressed. The polymerization process is carried out in a sheet reactor that is heated by forced circulating air. The conduction heat transfer part of the model is casted in terms of a 2-dimensional partial differential equation which is discretized using the numerical method of lines. The resulting set of ordinary differential equations, representing heat, mass and polymerization kinetic, are then solved by standard ODE solvers. A comparison of the model prediction capabilities against experimental data is also presented.

Keywords: cell-cast, methyl-methacrylate, method of lines, sheet reactor.

1 Introduction

The main goal of this work is to develop a representative dynamic mathematical model gathering and integrating previous works on radical chain polymerization modelling of Methyl-Methacrylate (MMA) and heat transfer theory as to achieve the essential task of understanding the industrial MMA cell-cast system as well as setting the base for future optimization and control works. A desirable first step in the analysis and optimization of a polymer reactor is the development of an accurate mathematical model which describes the changes in the state variables in terms of the control variables[1].

The cell-cast process is widely used in the chemical industry to produce PolyMethyl-Methacrylate (PMMA). In this process (see Fig. 1) MMA monomer is poured into a sealed mold formed by two glass sheets. Once assembled, the mold containing the MMA monomer, mixed with initiators, is introduced into a heat exchange medium (commonly an air convective oven). At this stage of the process, the polymerization system inside the mold can be considered as a non-isothermal batch reactor. There are two main process stages in the system. The first one, where the air transfers heat to the sheet reactor in

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order to initiate the polymerization reaction (thermal initiators are commonly used in the polymerization of PMMA), followed by the change of heat flow direction once the exothermic polymerization reaction reaches the onset of the auto acceleration or gel effect. One of the most serious problems related with the free radical polymerization scheme is due to this auto acceleration phenomenon. This effect is associated with the high viscosity increase of the system due to the rising of polymer concentration as the reaction takes place and the consequently low rate of diffusion controlled reaction termination. The onset of the gel effect frequently causes uncontrollable reactions, resulting in excessive temperature rise, fast conversion and plugging of continuous equipment[2]. Even though total processing time decreases with the onset of the gel effect, the industrial processing of PMMA tries to avoid it or at least to predict it because commonly leads to non-controlled polymerization reactions where the amount of instantaneous heat generation cannot be dissipated by the system.

In this paper, we assume that conduction is the dominant heat transfer mechanism; therefore the dynamic 2-dimensional heat conduction equation[3] was used for modelling the heat transfer phenomena along both the length and width of the polymer sheet and the glass sheet in contact with the polymer. Mass balances, that incorporate the MMA bulk free radical kinetic polymerization mechanism, were also modelled. For the numerical solution of the system of partial differential equations (PDEs), representing the heat transfer behavior and mass balances, the method of lines was used[4].

The outline of this paper is as follows. In section 2 the mathematical model of the PMMA cell-cast system and its numerical solution are described; in section 3, some results and comparison of the prediction capabilities of the model are shown; the dynamic model response is compared against real industrial data. Conclusions are mentioned in section 4.

2   Modelling and Numerical Solution

For optimization and control purposes of the PMMA plastic sheet production, a dynamic mathematical model able to compute monomer conversion, molecular weights distribution and polymer temperature is required. The mathematical model derived in this section assumes that the polymerization really starts at the convective oven (a pre-polymerization batch stage is sometimes used but because conversion rates are relatively low we neglect modelling this stage; besides, modern PMMA cell-cast technology is aimed to remove the pre-polymerization stage. So, one of the objectives of this work consists in analyzing the advantage of carrying out the complete PMMA cell-cast process in the oven. Accordingly, only one plastic sheet was taken for deriving the model (Fig. 2); the same heat transfer and polymerization phenomena was assumed to occur in the rest of the plastic sheets. Of course, this assumption holds as long as all the plastic sheets have similar heating patterns. Because of symmetry considerations, only half of the sheet width (from the center to the external surface) was taken into account.

From a reaction engineering point of view, the PMMA plastic sheet process can be considered as taking place in a constant volume batch reactor. Polymerization kinetics, coupled to mass balance equations, describe conversion and molecular weights dynamic time evolution. Because of large thermal effects are involved, through polymerization heat of reaction and the so-called gel effect, the model should incorporate the polymer energy balance equation. Air is forced circulated through the oven to provide the required energy to rise up the plastic sheet temperature until a point where significant polymerization rates take place. Inside the monomer, the dominant heat transfer mechanism is conduction. Therefore, heat is transferred along the x and y axis giving rise to the following two-dimensional dynamic heat transfer equation (the model takes into account polymer volume contraction effects only along the y-direction):

$$\frac{\partial T}{\partial t} = \alpha_M \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] + \frac{\alpha}{V} \frac{\partial T}{\partial y} \frac{\partial V}{\partial y} - \frac{V_o}{V} T \epsilon k_p (1-x) \lambda_o + \frac{Q}{\rho C p} \qquad (1)$$

whose derivation is straightforward[10]. T is the polymer temperature, V is the volume occupied by the reaction mixture, V_o is the initial monomer volume load, ϵ is the contraction factor, k_p is the propagation step rate constant, α_M is the monomer thermal diffusitivity, x is the monomer conversion, λ_o is the zero moment, Q is the released heat of reaction, ρ is the polymer density and c_p is the heat capacity. The

two-dimensional heat transfer equation is subject to the following initial and boundary conditions:

$$T = T_o \text{ @ } t = 0 \tag{2}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=0} = 0 \tag{3}$$

$$\left.\frac{\partial T}{\partial x}\right|_{x=L} = 0 \tag{4}$$

$$\left.\frac{\partial T}{\partial y}\right|_{y=0} = 0, \quad \left.\frac{\partial V}{\partial y}\right|_{y=0} = 0 \tag{5}$$

$$\left.\frac{\partial T}{\partial y}\right|_{y=W} = \frac{k_M}{k_\nu}\frac{\partial T}{\partial y}, \quad \left.\frac{\partial V}{\partial y}\right|_{y=W} = 0 \tag{6}$$

where T_o is the initial monomer temperature, L is the sheet length, W is the sheet width, k_M is the monomer thermal conductivity and k_ν is the glass thermal conductivity.

The energy balance for the glass sheet is given as follows:

$$\frac{\partial T_\nu}{\partial t} = \alpha_\nu \left[\frac{\partial^2 T_\nu}{\partial x^2} + \frac{\partial^2 T_\nu}{\partial y^2} \right] \tag{7}$$

where T_ν is the glass temperature and α_ν is the glass thermal diffusitivity. The balance is subject to the following initial and boundary conditions.

$$T_\nu = T_o \text{ @ } t = 0 \tag{8}$$

$$\left.\frac{\partial T_\nu}{\partial x}\right|_{x=0} = 0 \tag{9}$$

$$\left.\frac{\partial T_\nu}{\partial x}\right|_{x=L} = 0 \tag{10}$$

$$\left.\frac{\partial T_\nu}{\partial y}\right|_{y=W} = \frac{k_M}{k_\nu}\frac{\partial T_\nu}{\partial y} \tag{11}$$

$$\left.\frac{\partial T_\nu}{\partial y}\right|_{y=W+\delta} = \frac{h}{k_\nu}(T_a - T_\nu) \tag{12}$$

where h is the heat transfer coefficient, T_a is the surrounding temperature and δ is the glass width.

The corresponding initiator and monomer mass balances are given next.

$$\frac{\partial I}{\partial t} = D_{Ir}\left[\frac{\partial^2 I}{\partial x^2} + \frac{\partial^2 I}{\partial y^2} \right] + r_I \tag{13}$$

$$\frac{\partial M}{\partial t} = D_{Mr}\left[\frac{\partial^2 M}{\partial x^2} + \frac{\partial^2 M}{\partial y^2} \right] + r_M \tag{14}$$

where I is the initiator concentration, M is the monomer concentration, D_{Ir} is the initiator diffusitivity, D_{Mr} is the monomer diffusitivity, r_I is the initiator rate expression and r_M is the monomer rate expression.

The balances are subject to the following initial and boundary conditions.

$$I = I_o, \ M = M_o \text{ @ } t = 0 \tag{15}$$

$$\left.\frac{\partial I}{\partial x}\right|_{x=0} = 0, \quad \left.\frac{\partial M}{\partial x}\right|_{x=0} = 0 \tag{16}$$

$$\left.\frac{\partial I}{\partial x}\right|_{x=L} = 0, \quad \left.\frac{\partial M}{\partial x}\right|_{x=L} = 0 \tag{17}$$

$$\left.\frac{\partial I}{\partial y}\right|_{y=0} = 0, \quad \left.\frac{\partial M}{\partial y}\right|_{y=0} = 0 \tag{18}$$

$$\left.\frac{\partial I}{\partial y}\right|_{y=W} = 0, \quad \left.\frac{\partial M}{\partial y}\right|_{y=W} = 0 \tag{19}$$

where I_o is the initiator initial concentration and M_o is the monomer initial concentration. The bulk MMA polymerization kinetics was taken as described in Chiu et al [2].

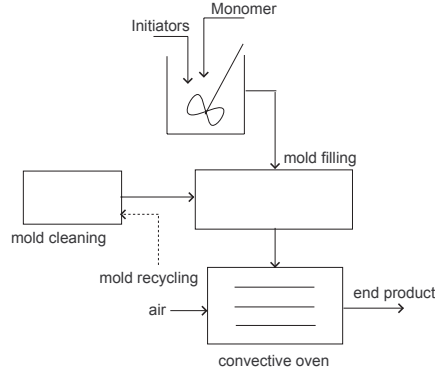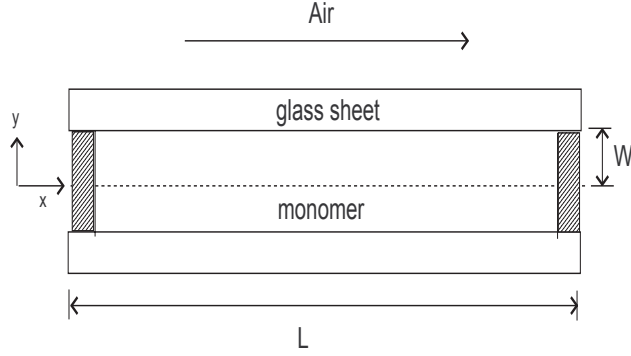Figure 1: Industrial Cell-Cast process for PMMA plastic sheet production.

Figure 2: Glass sheet mold containing the prepolymerized monomer.

3 Results and discussion

In this part we discuss some representative results obtained from performing simulation runs.

- **Base case**. Figure 3 shows the polymer conversion degree, temperature and molecular weights (M_n and M_w) evolution behavior through out time. After some trials, we found that, in most of the analyzed cases, 6 internal x points were enough to represent the system response along the sheet longitude. The amount of discrete points along the y direction strongly depended upon the sort of analyzed case. Therefore, for each x point only the system behavior at the extremes of the sheet is displayed, meaning that behavior at intermediate y points is located between those points and, for this reason, it is not displayed. The plots should be read from left to right (ie. the leftmost x point is the one where heating air reaches first the sheet). Nominal design and simulation conditions are shown in table 1.

  The gel effect suddenly appears around 7 hrs. This auto acceleration effect causes a conversion rate increment driving the system from 0.4 to 0.8 conversion degree. The point with the highest temperature, due to the dynamic heat transfer evolution, reaches gel effect first and consequently starts the polymerization process before the adjacent points. This is why at around 9 hrs the highest temperature point, corresponding to the one closest to the convective heat transfer source (air, in this case), reaches 0.8 conversion degree while the farthest point is just about 0.5 conversion degree.

Table 1: Nominal design information.

Monomer initial concentration	=	9.98	mol/lt
Initiator initial concentration	=	0.0129	mol/lt
Initiator efficiency	=	0.58	
Glass transition temperature	=	387	^{o}K
Heat of reaction	=	-58.19	kJ/mol
Polymer thermal conductivity	=	0.09	W/(m-^{o}K)
Polymer density	=	996	kg/m^3
Polymer heat capacity	=	1674	J/(kg-^{o}K)
Glass thermal conductivity	=	0.78	W/(m-^{o}K)
Glass density	=	2700	kg/m^3
Glass heat capacity	=	840	J/kg-^{o}K
Air heat transfer coefficient	=	55	W/(m^2-^{o}K)
Initiator diffusion coefficient	=	8.86×10^{-11}	m^2/s
Monomer diffusion coefficient	=	4.5×10^{-12}	m^2/s
Air temperature	=	318	^{o}K
Sheet length	=	1.8	m
Monomer width	=	0.006	m

- **Experimental validation**. In order to test the validity of the proposed dynamic model a set of experiments were run, data were collected for two different experimental operating conditions; these data represents real industrial information. Temperature data were measured at the beginning of the polymer sheet ($x = 0$) and at the end of the sheet ($x = L$), see figure 2 . A comparison between model predictions and experimental data is shown in figure 4. The dynamic model is able to track the polymer temperature profile during the first two hours. The results look reasonably good, although the model anticipates the onset of the gel effect and was unable to predict the 70 ^{o}C temperature peak. One way to improve the temperature peak prediction would be to correct the kinetic parameters related to the gel effect.

4   Conclusions

A first principles dynamic 2-dimensional model able to predict conversion rates, temperature and molecular weight distributions in a sheet reactor has been developed. Our aim in developing this model is to test the advantages of using heating ovens for the sheet polymerization against the traditional industrial process which consists in carrying out the polymerization process in hot water baths, where nonuniform conversion rates and molecular weights distribution are normally obtained. Therefore, by proper operation, heating ovens should lead to polymerization products with uniform polymerization properties. A major conclusion from this work lies in the fact that the pre-polymerization stage is unnecessary as far as the process is properly designed and operated. The model prediction capabilities seem to be acceptable, however some improvements need to be done. We expect to use the derived first principles model for dynamic optimization studies and for real time control.

References

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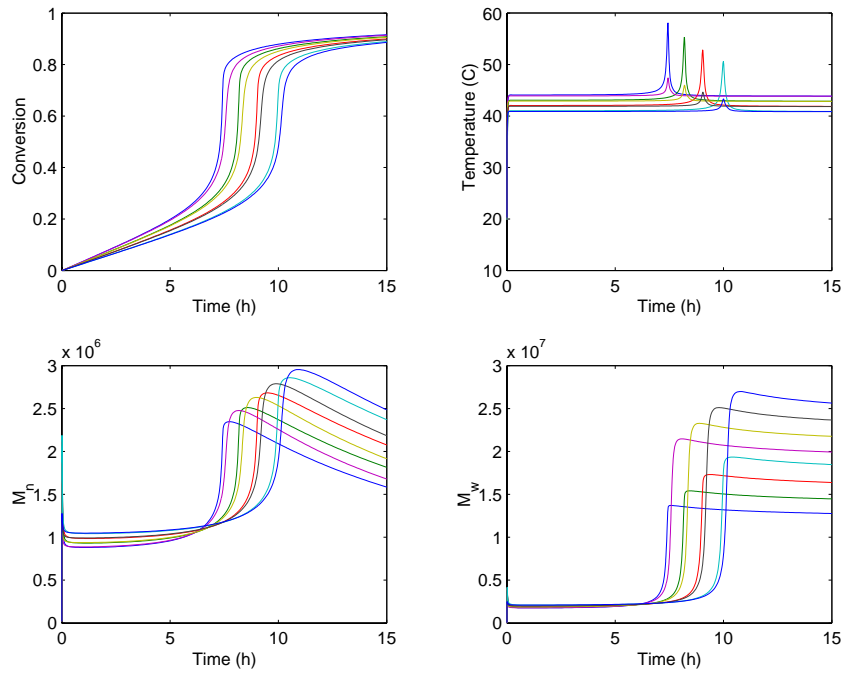
Figure 3: System response for nominal design conditions.

Figure 4: Comparison of the dynamic model response against experimental data. `Exp1` and `Exp2` stand for polymer temperatures measured at $x = 0$ and $x = L$ (see figure 2), respectively; while `Mod1` and `Mod2` represent model predictions at these points.