APPLICATION OF THE MARKOV CHAIN THEORY FOR MODELLING RESIDENCE TIME DISTRIBUTION IN A SINGLE SCREW EXTRUDER

Dennis PONOMAREV, Martial SAUCEAU*, Clémence NIKITINE,
Elisabeth RODIER and Jacques FAGES

Ecole des Mines Albi, RAPSODEE centre, UMR CNRS 2392, Albi, France, F81013
* martial.sauceau@enstimac.fr

Abstract

A Markov chain model is proposed for modelling residence time distribution of a tracer flowing together with a polymer through a single screw extruder, which has been designed for polymer extrusion with injection of supercritical CO_2. The model has two dimensions and takes into consideration different velocity profiles of the flowing polymer between the screw and the barrel wall. In addition, the model allows obtaining the system response on any testing signal as unit step, Dirac or sinusoidal functions.

In this work, the influence of the barrel temperature is considered. Experimental results of residence time distribution are given at different temperatures. A procedure of the model parameter identification from experiments was proposed. Within the range of working temperatures tested, a linear dependence of the velocity profile parameters was used to fit the experimental and model data.

Introduction

Extrusion is a process for converting a raw material into a product of uniform shape and density by forcing it through a die under controlled conditions [1]. Material transport is achieved by a single or twin-screw inside a barrel and the pressure produced by the screw force the material through the die. Industrial applications of the extrusion process dates back to the 1930's; it is extensively applied in the plastic, food and rubber industries, where it is one of the most important manufacturing processes [1]. However, it implies high temperatures and mechanical constraints, prohibiting the use of fragile molecules. A particular application is polymer foaming. Foams are generally obtained by the addition of chemical blowing agents (CBA) which are mixed with the polymer matrix and it is their thermal decomposition which produces a gas. In that way, porosity cannot be well controlled and is thus often heterogeneous. This also implies the presence of residues in the final product and the need for an additional step to eliminate them. Hence, the use of pressurised fluids, such as the chlorofluorocarbons (CFC) or volatiles organic compound (VOC), in place of CBA has been considered. Porosity could then be controlled and no residue left in the foam. The polymer foams could then be produced by a green process provided the fluid used is environmentally friendly.

A supercritical fluid (SCF) is defined as a substance whose both pressure and temperature are above the critical values. It has intermediate properties between those of gases and those of liquids [2]. Supercritical carbon dioxide (SC CO_2) is most often used because it is non-toxic, non-flammable, chemically inert, and its supercritical conditions are easily reached (T_c=31°C, Pc=7.38 MPa).

Due to its high polymer solubility, SC CO_2 has often been used in polymer processing [33]. The special combination of gas-like viscosity and liquid-like density makes it an excellent solvent or plasticizer in these applications, e.g. polymer composites, microcellular foaming or particle production. Thus, mechanical and physical properties of material can be modified.

Our laboratory has developed a supercritical carbon dioxide-assisted extrusion process, which leads to the manufacturing of micro-structured polymeric foams [4, 5]. Presence of SC CO2 in extrusion process modifies rheological and thermo-physical properties of the polymer in the barrel of the extruder and acts as a blowing agent during the relaxation at the passage through the die. Thus, its rather high solubilisation in the polymer results in extensive expansion at the die. The reduction of viscosity decreases the mechanical constraints and the operating temperature within the extruder. Thus, coupling extrusion and SC CO2 would allow the use of fragile or thermolabile molecules, like pharmaceutical molecules. The absence of residues in the final material is also an advantage for a pharmaceutical application.

This process has been applied to a pharmaceutical polymer, Eudragit E100 [6]. A first study has been performed to understand the different phenomena implied in extrusion process and to determine correlations between the operating conditions and the expansion, the cell size and the cell density in macro or microcellular foaming [7].

In another work, residence time distribution (RTD) has been determined in different operating conditions to better understand flow mixing in the single screw extruder [8]. A model based on the combination of a continuous stirred tank reactor (CSTR) and a plug flow reactor in series was used to model the RTD data obtained [8]. The authors also added some volumes representing the stagnant zones where convection is reduced. Such an approach allowed a better description of the experimental RTD curves, which usually had a rapid increase at the beginning (like a plug flow) and a long decline at the end (like a mixing effect). This method fits quite well the experimental results though it has some drawbacks. Equations for each reactor were based on the material mass balance for a Dirac function, and thus must be adapted if the test signal changes. Moreover, the approach did not allow adding other phenomena to the model without being completely changed.

In this work, a model based on the theory of Markov chains is proposed for modelling these RTD. The model has two dimensions and it takes into consideration different velocity profiles occurring between the screw and the barrel wall. Therefore, it is possible to take into account the effect of the difference in pressure and drag flow. The model allows obtaining the system response on any testing signal as unit step, Dirac or sinusoidal functions. The model is applied to RTD experimental results at different temperatures.

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Figure 1. Experimental extruder

Cell model of the extruder

Figure 1 presents the geometry of the extruder [7]. This equipment has an input from a small hopper and an output from the die. The free volume is not constant inside and diminishes towards the outlet. The polymer enters as granules, melts inside, is mixed with supercritical CO_2 and is pumped by the screw towards the outlet.

To build a model based on the theory of Markov chains, the whole free volume of the extruder is divided into several cells according to the radial and the axial directions. To choose a number of cells, it is assumed that the length of one cell is equal to two screw flights. According to the length of the screw, 16 working cells are defined in the axial direction, plus one cell representing the die that has approximate length of one screw flank (Figure 2).

The number of cells in radial direction has been arbitrarily fixed to 10. This number can be modified depending on how many layers are necessary. These cells represent the finite volumes between the screw and barrel walls. The last column corresponds to the accumulating cells, in which the matter goes into at the outside of the die. Therefore, each cell has a given volume and consequently a given mass when the extruder is filled. As far as the free volume par length unit is a variable function along the screw, it would be necessary to use cells of variable volume. However, it is assumed that each cells has the same mass to bring more transparency to the model.
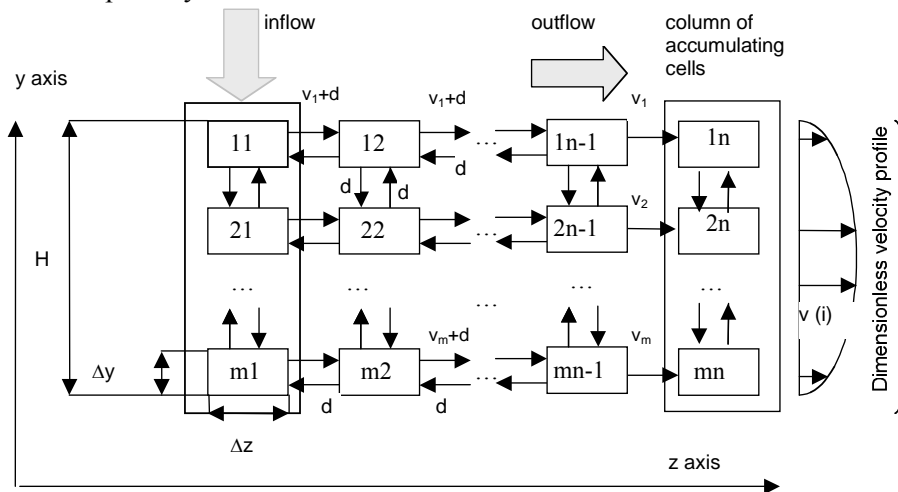

Figure 2. Scheme of the Markov chain model

Finally, the free volume of the extruder is divided into a finite number of discrete intervals n,m according to two directions. These intervals are called system states. In this case, continuous probability density distribution function is replaced by the probabilities of the state S_i. Some additional information is published in [9, 10, 11, 12]. The set of probabilities S_i forms a state vector whose elements can be tracer concentration or mass in a cell:

$$S = \begin{vmatrix} S_1 \\ S_2 \\ ... \\ S_{nm} \end{vmatrix} \qquad (1)$$

The mass of the tracer is initially distributed in the first column of cells which represents the volume under the hopper. If the mass of the injected tracer is M_{tr}, then each element of the state vector (1) corresponding to the cells of the first column will have the mass (M_{tr}/m). The other elements of the state vector are equal to zero because there is no tracer in the other cells at the beginning of the process.

The relationships between the cells are determined by the transition probabilities. Probability means the part of the mass in a cell which may transit to another cell. Hence, the value P_{ij} is the probability for a part of particles in the cell j to transit to the cell i. If i=j, then P_{ij} is the probability for the mass to remain in the cell during the time interval of one transition (Figure 3). However, we will use another presentation in which a backward probability equals to d and a forward probability equals to d+v (Figure 3).
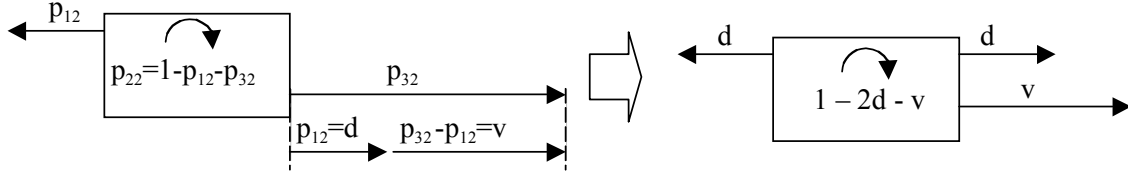

Figure 3. Representation of transition probabilities

ΔM is the mass, which is passing through the cell during Δt due to the convection part of transition (due to velocity v) and goes to the next cell. If Q is the mass flow rate in the cell, the mass passed is $Q\Delta t$, and the forward transition probability v is:

$$v = \frac{\Delta M}{M_{cell}} = \frac{Q\Delta t}{M_{cell}} \tag{2}$$

According to the Fick's first law, the mass transported by diffusion from one cell to another can be written as:

$$d = \frac{D}{\Delta z^2}\Delta t \tag{3}$$

D is the dispersion coefficient, Δz is a spatial length characterising the cell through which the mass transfers. The parameter d can be thus interpreted as the inverse of the adimensional Peclet number, which allows the comparison between transport by convection and transport by diffusion. To determine all the relationships between cells, the transition probabilities are placed in the matrix of transition probabilities, which contains blocks of matrices on its diagonals, therefore:

$$P = \begin{bmatrix} P_{11} & P_{12} & Z & ... & Z & Z \\ P_{21} & P_{22} & P_{23} & ... & Z & Z \\ Z & P_{32} & P_{33} & ... & Z & Z \\ ... & ... & ... & ... & ... & ... \\ Z & Z & Z & ... & P_{mn-1,mn-1} & P_{mn-1,nn} \\ Z & Z & Z & ... & P_{mn,mn-1} & P_{mn,mn} \end{bmatrix} \tag{4}$$

Z are zero matrices of the size mxm, P_{ii} are the transition matrices inside i^{th} column, P_{ij} are the matrices of transition probabilities from j^{th} to i^{th} columns.

According to Figure 2, it can be written:

$$P_{11} = \begin{vmatrix} 1-2d-v_1 & d & 0 & ... & 0 & 0 \\ d+v_1 & 1-3d-v_2 & d & ... & 0 & 0 \\ 0 & d+v_2 & 1-3d-v_3 & ... & 0 & 0 \\ ... & ... & ... & ... & ... & ... \\ 0 & 0 & 0 & ... & 1-3d-v_{m-1} & d \\ 0 & 0 & 0 & ... & d+v_{m-1} & 1-2d-v_m \end{vmatrix} \qquad (5)$$

The same principle is implied for building other matrices P_{ii} in accordance with the scheme. The matrix of transition probability P_{12} is:

$$P_{12} = \begin{vmatrix} d & 0 & 0 & ... & 0 & 0 \\ 0 & d & 0 & ... & 0 & 0 \\ 0 & 0 & d & ... & 0 & 0 \\ ... & ... & ... & ... & ... & ... \\ 0 & 0 & 0 & ... & d & 0 \\ 0 & 0 & 0 & ... & 0 & d \end{vmatrix} \qquad (6)$$

The other matrices are built using this method. It is necessary to note that the elements on the main diagonal of matrices P_{ii} are calculated to keep the condition of normalization requiring that the sum of all probabilities staying on each column of the matrix P has to be equal to 1. Thus, we place all the matrices in the matrix P and then calculate the elements of the main diagonal from the condition of normalization. This approach is quite convenient but it is necessary to check that negative elements do not appear.

After building the final matrix, there are different values of probabilities v and d which must be defined in order to calculate the RTD. To solve this problem, a normalized parabolic function has been chosen for v with an argument i (which is the number of cell rows or layers m):

$$v_i = v_0\left(1 - \beta\left(\frac{i-m_0}{m_0}\right)^2\right) \quad \text{with} \quad m_0 = \frac{m-1}{2} + \lambda \qquad (7)$$

β, λ and v_0 are three parameters: "parabola bend", parabolic peak shift from the row m/2 and "amplitude" coefficient respectively. In this study, we kept λ constant equal to 2, when the peak is centred. The function v_i can take values in the range [0,1].
Therefore, giving some values to v_0 and β, we obtained the probability or dimensionless velocity profile distribution. On the other hand, such combination of these parameters must verify that the equation of throughput balance is checked.

Afterwards, the general process to calculate RTD is defined by:

$$S^{j+1} = P.S^j \qquad (8)$$

S^i is the current state vector and S^{i+1} is the state vector characterising the system after one transition. Thus, the process evolution is calculated after each transition. By assuming that

the duration of one transition is Δt, we obtain a discrete outflow for discrete time steps in seconds. The model has 4 parameters: Δt, β, d and M_{cell}. The effective mass of material inside the extruder is lower than the total mass of material because of the zones where the polymer does not circulate. Moreover, this effective mass for the same material is a function of process characteristics as temperature and screw rotation speed. Therefore this mass is difficult to determine and the cell mass is considered as an additional parameter in our model.

The tracer outflow E(i) can be calculated using the following equation:

$$E(i) = \sum_{(mn-m)+1}^{mn} \left(S_j^{i+1} - S_j^i \right)$$

(9)

Having found the RTD, other characteristics like the mean residence time and centred variance were also calculated. Therefore, such approach integrates different velocity profiles and calculates characteristics of the flowing of material.

Model results

The first step of experimental work was to measure RTD for different temperatures at a constant screw speed of 40 rpm: 130°C (Figure 4), 140°C (Figure 5) and 150°C (Figure 6).

The parameters of the model were found by using a numerical method of four parameter optimisation for the least square error between experimental and modelled cumulative RTD. The values of calculated parameters are given in table 1. The values of model parameters for the temperature 140°C were taken as the mean between the experiments at 130°C and 150°C. Both differential and cumulative experimental RTD are well represented by the model. This was confirmed by the coherent values of calculated mean times and centred variances, excepted centred variance at 130°C which was three times higher. This result shows the linear dependence of the velocity profile parameters with temperature.

Table 1. Results obtained with the model

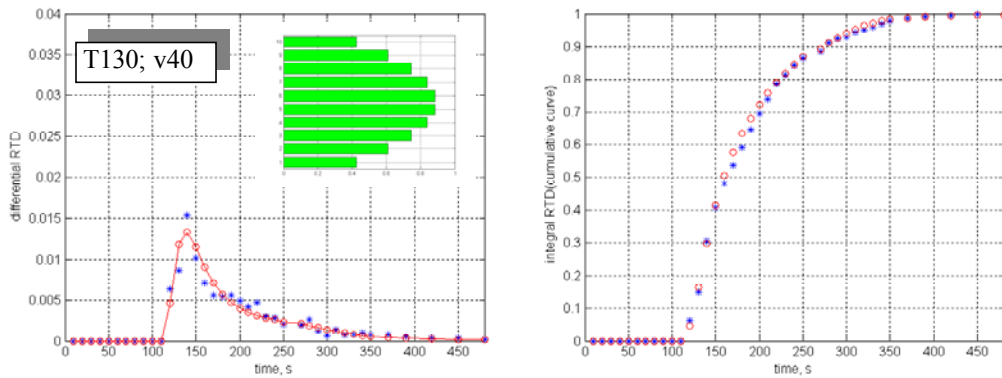| Temperature	130°C	140°C	150°C
M_{cell} (kg)	0.126	0.121	0.115
β (-)	0.85	0.77	0.70
Δt (s)	6.9	5.5	4.2
d (-)	0.027	0.013	0.008
mean time (s)	184.1	132.3	96.0
mean time difference with experiment (%)	11	1	8
centred variance (for normalized curve)	0.33	0.13	0.14
variance difference with experiment (%)	319	10	24

Figure 4. RTD at 130°C (a – differential, b – cumulative)
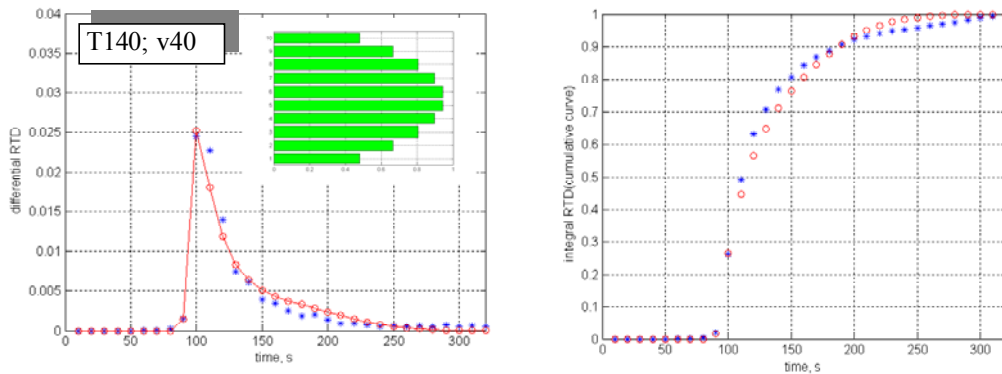

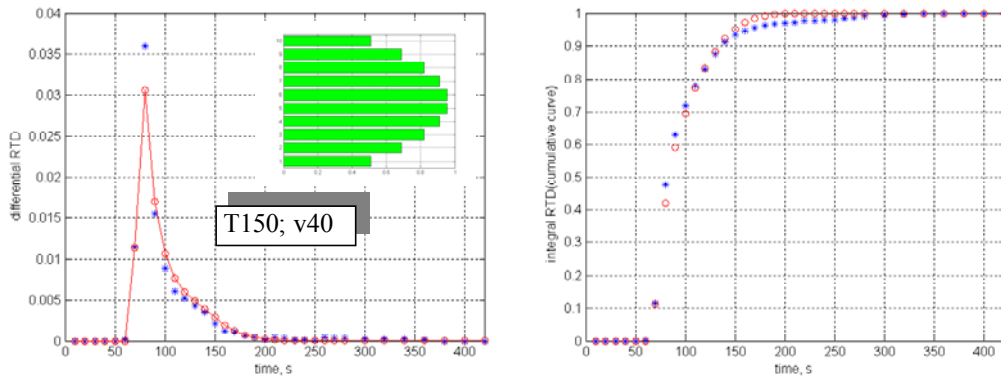Figure 5. RTD at 140°C (a – differential, b – cumulative)

Figure 6. RTD at 150°C (a – differential, b – cumulative)

The parameter M_{cell} depends on the temperature: the higher the temperature, the lower the cell mass. The determination of the experimental filling ratio according to the different operating conditions allows knowing that it increases with temperature. Hence, these considerations suggest that the opportunity for stagnant zones increases with temperature.

The coefficient β diminishes as the temperature increases, what means that the velocity profile is less curved as far as polymer viscosity decreases. This suggests an enhanced plug flow and this is consistent with analysis of the same experimental curves with a combined continuous stirred tank reactor exchanging with stagnant zones and plug flow reactor in series previously performed [6].

Lastly, d decreases with temperature suggesting an increase of convective flow compared to the dispersive one, which is consistent with the decrease of β and the flattening of the velocity profile.

Conclusion

A two-dimensional model of the RTD in a single screw extruder is proposed. It is based on the theory of Markov chains and it takes into consideration different velocity profiles occurring between the screw and the barrel wall. It allows calculating response for any test signal.

It has been applied to the XFSC process, in which supercritical CO_2 was injected in the melting zone of a single screw extruder. Finally, the response for three different temperatures is presented. Within the range of working temperatures, a linear behaviour of the velocity profile parameters was observed. The model can thus be used to predict RTD characteristics on this temperature interval without performing any additional experiments.

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