

# Modelling the continuous foaming in the die during supercritical CO<sub>2</sub> assisted extrusion.

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## ABSTRACT

Extrusion assisted by supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) is an emerging process used for foaming polymers with a good control of the porosity formation [1]. Sc-CO<sub>2</sub> is injected in the heating barrel of an extruder and it acts both as a plasticizer inside the extruder and as an expansion agent during the return to atmospheric pressure through the die. In this work, the continuous foaming taking place in the die extruder has been modelled by implementing a method based on the study of Shimoda et al. [2]. In a first step, the model has been validated by comparing our results with those previously obtained in the literature. Then, the pressure profile has been modified to study its effect on the pore size distribution. This profile can be optimized to control the final porous structure.

## INTRODUCTION

Expanded thermoplastics from petrochemical origin are used in a large range of applications due to excellent mechanical properties, in addition to low density and cost. However, to solve issues linked to environmental impact and waste management, the use of biobased and biodegradable polymers to make foams with a green technology is highly recommended. Extrusion assisted by supercritical CO<sub>2</sub> (sc-CO<sub>2</sub>) is considered as a green process for the manufacturing of foam [1]. In this process, sc-CO<sub>2</sub> is injected in the heating barrel of an extruder and it dissolves in the polymer under pressure. It results in the modification of the melt properties inside the extruder and also in the polymer foaming through the die. This process has shown great interest and is frequently investigated with biopolymers as recently reviewed by Chauvet et al. [2].

Several models have been implemented for polymer foaming in batch processes, but only few studies are dealing with modelling in a continuous process mainly because flow induces many changes in the nucleation mechanism and physical properties.

Shafi et al. [3–6] have developed a model for the nucleation and the growth of the bubbles in batch mode. Only few publications study the modelling of extrusion foaming [7]. This is due to the great complexity of the phenomena involved: flow induces many changes in the nucleation mechanism and the physical properties. In this work, the method of Shimoda et al. [7] will be applied.

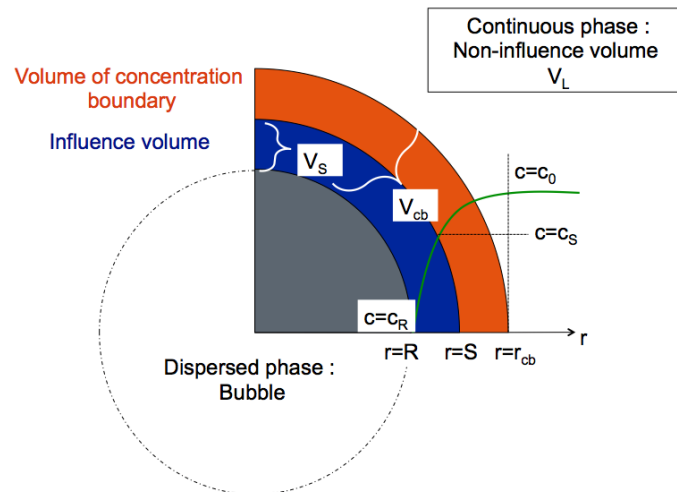
The goal of this study is to describe the cell nucleation and growth in the die and to be able to predict the size distribution of the pores in the final product [3]. We have chosen to model the continuous foaming, taking place in the die extruder, by discretizing the space to bring back to

a succession of batch models on the basis of the study of Shimoda et al. [2]. These authors enriched a model previously developed by Shafi et al. [4,5,6], which implements simultaneously both cell nucleation and growth in the die by defining an influence volume around the cell.

## MODELLING

The cell nucleation and growth are represented by classical equations [7], leading to a system of differential equations (ODE system). Then, the notion of influence volume is introduced [4-6]. This influence volume is a region around the cell where no nucleation of another cell can occur (figure 1). It means that, once a cell appears, a volume is reserved around this cell for a later growth and the future new cells will be able to appear only in the non influence volume  $V_L$ . The non-influence volume is thus equal to the polymer volume at the beginning. It will decrease with the nucleation and, when it reaches zero, the nucleation stops and cells can continue to grow by consuming the gas of their influence volume.

Moreover, in this influence volume, the gas concentration profile is approximated by a polynomial function what allows to reformulate and solve the ODE system.



**Figure 1.** Representation of the different volumes near the bubble (adapted from [8])

The approach for solving the problem is described on figure 2. The time is discretized along the die by using a time interval  $\Delta t$  defined by the user. For each time interval, nucleation of a new population (if it exists) and growth of previous ones are taking place (1<sup>st</sup> step). Each time interval also permits to calculate new values of the influence volume, non-influence volume, gas concentration and nucleation rate. The cell populations are calculated as long as non-influence volume  $V_L$  is higher than 1 % of its initial value. Once the 1<sup>st</sup> step is finished, a final 2<sup>nd</sup> step allows to calculate the final size and number of cells inside their influence volume, and thus the final porosity of the sample.

## RESULTS

### Comparison with the literature

To validate the model, a comparison has been made with previous results by using the same operating conditions and at  $\Delta t=0.01$  s [9]. In this example, the pressure of the polymer is

considered equal to atmospheric pressure during the whole process, what is equivalent to a batch process. The results are presented on the figure 3. The results are the same as in the previous work. However, it must be noticed that the nucleation factor was not provided and has been multiplied by  $10^7$ . At the beginning, we can observe an induction time of about 0.1 s during which nothing happens. Then, a rapid decrease of the mean concentration of the dissolved  $\text{CO}_2$  occurs due to the nucleation and growth of cells. Finally, the different phenomena last until about 2.4 s.

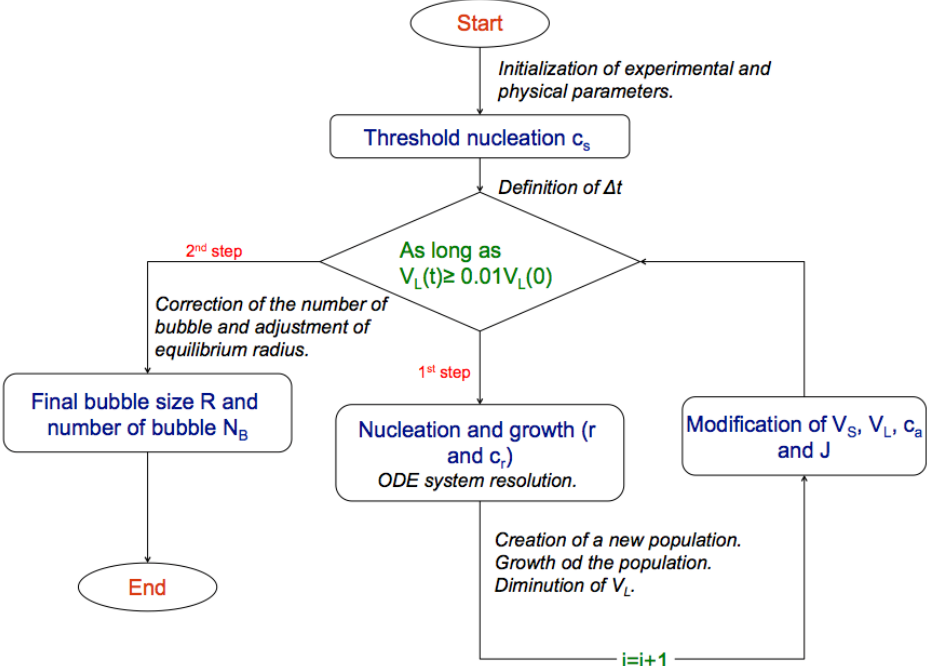


Figure 2. Functional algorithm

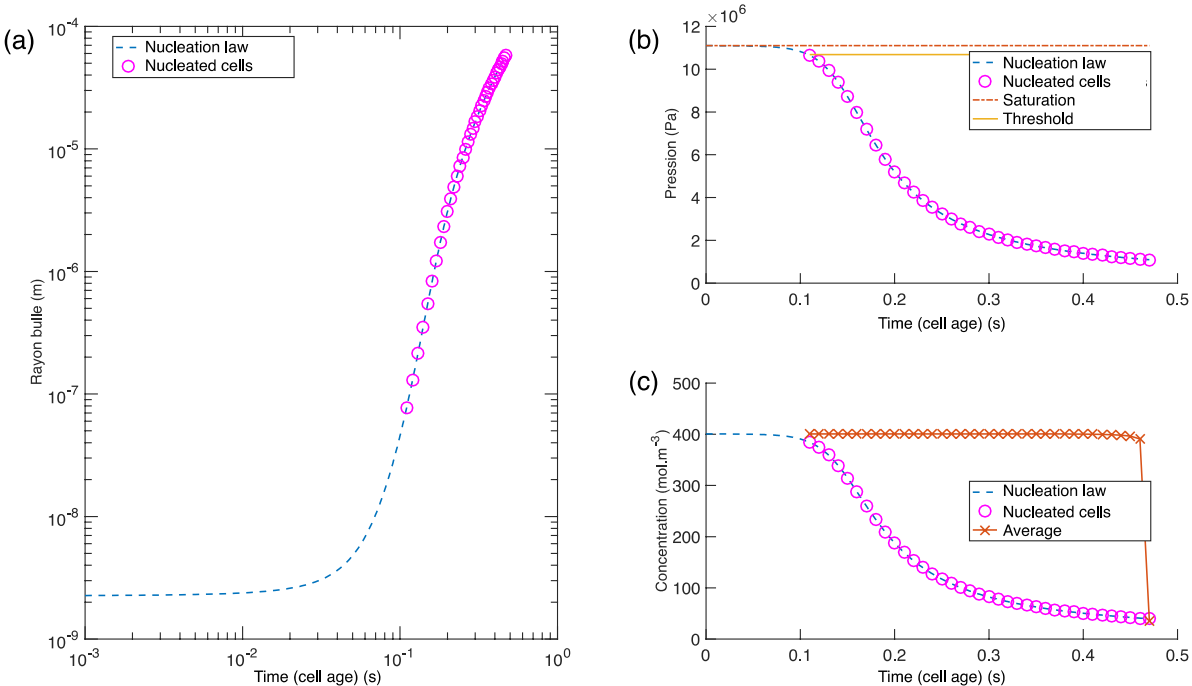


Figure 3. Evolution vs. time: (a) cell radius, (b) pressure inside cell at its appearance, (c) gas concentration (average and at the surface of the nucleated cells)

### Influence of the time interval $\Delta t$

The table 1 presents the influence of the time interval  $\Delta t$  on nucleation start time and finish time, population and cell numbers and the characteristics of the cells at equilibrium. The line in red is the reference, which corresponds to the results of the figure 3. Population number increases obviously, but the cell number remains constant at  $1.68 \times 10^{13}$ . Finally, until  $\Delta t = 0.01$  s, the effect of  $\Delta t$  on the characteristics of the cells is rather limited. For higher  $\Delta t$ , the bad quality of the discretization results in an overestimation of these characteristics. In conclusion, the time interval  $\Delta t$  has to be lower than 0.01 s, but not too low as it would result in a large calculation time.

$\Delta t$ (s)	t start of nucleation (s)	t end of nucleation (s)	Population number	Cell number	$R_{\min}$ ( $\mu\text{m}$ )	$R_{\max}$ ( $\mu\text{m}$ )	$R_{\text{mean}}$ ( $\mu\text{m}$ )
0,001	0,109	0,469	361	$1,6768 \times 10^{13}$	0,3	185	83,3
0,005	0,110	0,470	73	$1,6770 \times 10^{13}$	0,4	186	85
<b>0,01</b>	<b>0,110</b>	<b>0,470</b>	<b>37</b>	<b><math>1,6774 \times 10^{13}</math></b>	<b>0,4</b>	<b>186</b>	<b>80</b>
0,05	0,150	0,450	7	$1,6983 \times 10^{13}$	5	171	85
0,1	0,200	0,500	4	$1,6877 \times 10^{13}$	18	208	132

**Table 1.** Influence of time interval  $\Delta t$

### Modification of the pressure profile

Firstly, the final pressure has been kept constant during the process but at higher values than previously (table 2). The induction time is still present and more or less constant. On the contrary, the higher the pressure, the longer the nucleation due to the lower supersaturation. It results in a longer duration of the growth and thus an increase of the cell sizes.

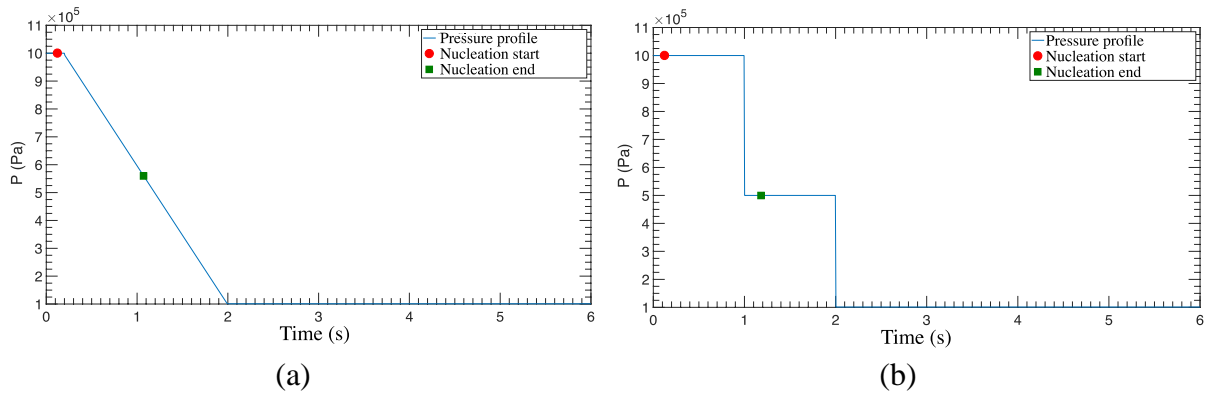
$P_{\text{polymer}}$ (Pa)	t start of nucleation (s)	t end of nucleation (s)	Population number	Cell number	$R_{\min}$ ( $\mu\text{m}$ )	$R_{\max}$ ( $\mu\text{m}$ )	$R_{\text{mean}}$ ( $\mu\text{m}$ )
$1 \times 10^6$	0,12	1,59	148	$7,2811 \times 10^{10}$	0,3	519	342
$5 \times 10^5$	0,11	0,45	35	$2,2274 \times 10^{13}$	0,4	174	79

**Table 2.** Influence of the pressure  $P_{\text{polymer}}$

An interest of the modelling is that several pressure profile can be rapidly tested. In this work we have tested 2 different profiles for a same duration: a linear and a two-step decrease (figure 4). The modification of the pressure profile does not change the induction time but increases the nucleation duration. In consequence, the cell characteristics are modified with in particular a higher cell size. It seems thus possible to control the final porosity by implementing an optimization of the pressure profile.

Pressure profile	t start of nucleation (s)	t end of nucleation (s)	Population number	Cell number	$R_{\min}$ ( $\mu\text{m}$ )	$R_{\max}$ ( $\mu\text{m}$ )	$R_{\text{mean}}$ ( $\mu\text{m}$ )
Profile 1	0,12	1,07	371	$9,1597 \times 10^{10}$	0,3	672	233
Profile 2	0,12	1,53	276	$7,0160 \times 10^{10}$	0,3	837	246

**Table 2.** Influence of the  $P_{\text{polymer}}$  profile



**Figure 4.** Pressure decrease profile (a) linear profile 1, (b) two steps profile 2

## CONCLUSION

Modelling pore number and size is fundamental for a better understanding and mastering of the continuous polymer foaming by CO<sub>2</sub>-assisted extrusion process. This paper presents a modelling strategy in two stages: (i) a discontinuous model to represent the nucleation and bubble growth in a batch, (ii) implementation of this model to a continuous extrusion process by discretizing the flow in the die.

Firstly, the model has been validated by comparing our results with those previously obtained in the literature. Then, the pressure profile has been modified to study the effect of this profile on the pore size distribution. It seems possible to control the final porosity by implementing an optimization of the pressure profile.

The perspective of this work will be to compare theoretical porous structure with experimental foamy samples. The model will be adjusted using fitting parameters of the studied system. The sensitivity of the model to the variation of the operating parameters will also be studied.

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