

# Modeling of Bulk Polymerization of $\epsilon$ -Caprolactone in Shear Flow

Linjie Zhu<sup>(a)</sup> Kun S. Hyun<sup>(b)</sup> and K. A. Narh<sup>(a)</sup>

(a) Department of Mechanical Engineering

(b) Polymer Processing Institute and Department of Chemical Engineering  
New Jersey Institute of Technology, Newark, NJ 07102-1982

## Abstract

Continuous polymerization of monomers and chemical modification of polymers have historically been done in diluted systems. Recent development in extrusion technology makes it possible to carry out the reaction in extruders. The use of extruder as reactors not only provides good micro mixing in high viscous systems, but also gives the opportunity for solvent free processing as well. In the present study, the process of bulk polymerization of  $\epsilon$ -caprolactone in an unwrapped channel flow was simulated with a proposed 2-D channel model by Finite Element Method (FEM), with consideration for different conversion ratios and heat transfer conditions at walls. The calculation shows that the reactive procession relies greatly on boundary conditions for conversion ratio and temperature at walls. The 2-D model does not give reasonable results because the mixing of fluids in the channel is not considered. A modified 2-D model, incorporating the mixing of fluid in the channel and the magnitude of the conversion ratio at the fixed walls, was proposed. The effect of mixing mechanisms of fluid in channel on reaction was investigated.

## 1 Introduction

Reactive extrusion is an efficient and environment-friendly technique for both continuous polymerizing monomers and chemical modification of polymers. The simulation of reactive extrusion is challenging since the coupling of kinetic laws of reaction, rheological behavior, and polymer flow in extruders is very complex. Because reactive process is sensitive to temperature and residence time, and the extruder has excellent mixing capability, the simulation model may have great effect on the calculation results.

The twin screw extruder is a commonly used processing device in reactive extrusion because of its flexible structure and excellent mixing capability. However, the flow in twin screw extruders is difficult to predict because of the complex nature of the geometry of the screw elements and the boundary conditions of the flow. In the recent works of the modeling of reactive extrusions [1-5], average temperature and average residence time are generally used in the cross section of the extruder, i.e. the temperature at different positions in the channel cross section is assumed to be equal, so is the residence time. Such a simplification makes the simulation easy, but this does not represent the real situation in extrusions. It is known that the flow in the screw channel is a laminar flow, not a plug flow. Furthermore, the twin screw extruder provides strong axial and circular mixing to the fluid in the channel.

In our recent studies [6], the simplified model described above was named as 1-D model. Accordingly, a new model, to be referred to 2-D channel model, was proposed based on the assumptions that the temperature and residence time are locally different in the cross section of the channel. With the 2-D model, the effects of heat transfer conditions and conversion ratios at the walls on the reactive process were discussed. It was found that the high conversion layers always stayed in the regions near the fixed wall, and the residence time near the fixed wall was several thousand times that near the moving wall. It indicated that even the 2-D channel model was not realistic enough if compared with the reactive progression in extruders, since the effect of the mixing of fluid in the channel on the reaction was not considered. A modified 2-D channel model incorporating the mixing of fluid in the channel and the boundary condition for the conversion ratio at fixed walls was proposed. The effect of mixing of fluid in channel on reaction kinetic was investigated.

## 2 Theories

### 2.1 Model System

In the present study, polymerization of  $\epsilon$ -caprolactone was selected as a model system, referred to the works of Dubois [7] and Gimenez [8]. To make the simulation tractable, the minimum viscosity of the system was assumed to be 0.5 Pa s. That is, in the simulation, if the calculated viscosity is smaller than 0.5 Pa s, 0.5 P·s is used. The heat of polymerization of  $\epsilon$ -caprolactone is 250 kJ/kg.

### 2.2 Simulation Models

#### 2.2.1 1-D Channel Model

In 1-D channel model, the processing properties (residence time and temperature, respectively) are assumed to be equal at different locations of the channel cross section. Consequently, the conversion ratio at different positions in the channel cross section is equal to each other, so is the viscosity. Under a drag flow condition, the velocity in the channel has a linear distribution (Fig. 1). The average residence time in the channel,  $\Delta t_R$  is calculated by:

$$\Delta t_R = \frac{L}{\bar{V}} \quad (1)$$

$$\bar{V} = \int_0^W V_x dy / W = V_0 / 2 \quad (2)$$

where  $L$  and  $W$  are the channel length and width, respectively;  $\bar{V}$  is averaged velocity, and  $V_x$  the velocity distribution in the channel;  $V_0$  is the velocity of the moving plate. Clearly, the residence time  $\Delta t_R$  is a function of the channel length only since the velocity of the moving plate,  $V_0$ , is constant.

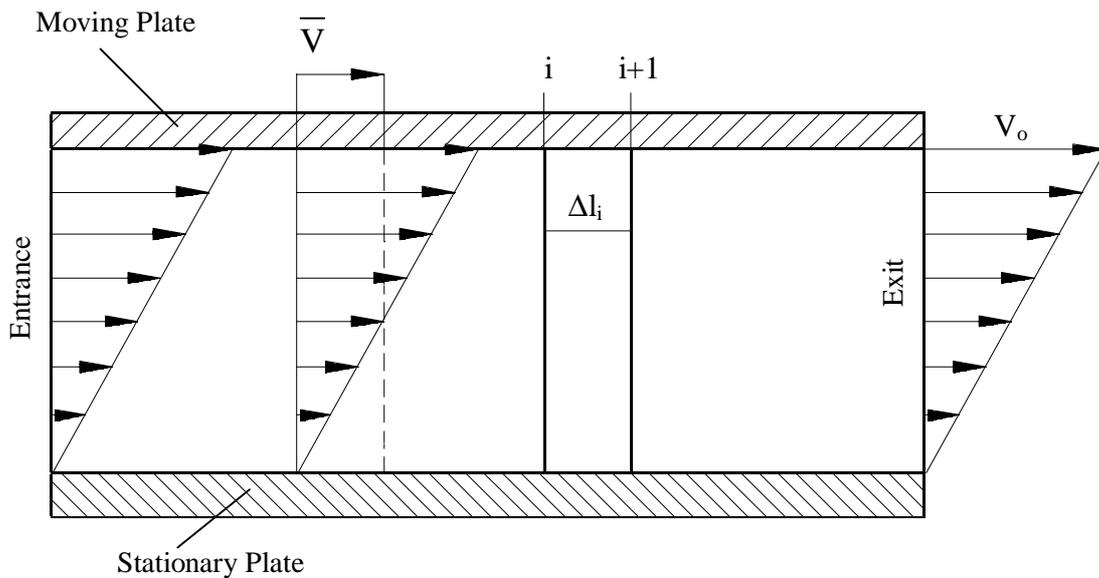


Fig. 1 1-D channel model

#### 2.2.2 2-D Channel Model

In 2-D channel model, both the residence time and temperature in the cross section of the channel vary from position to position. The temperature and velocity in the channel were calculated with Finite Element Method (6), and the conversion ratio was obtained by particle tracing in the flow.

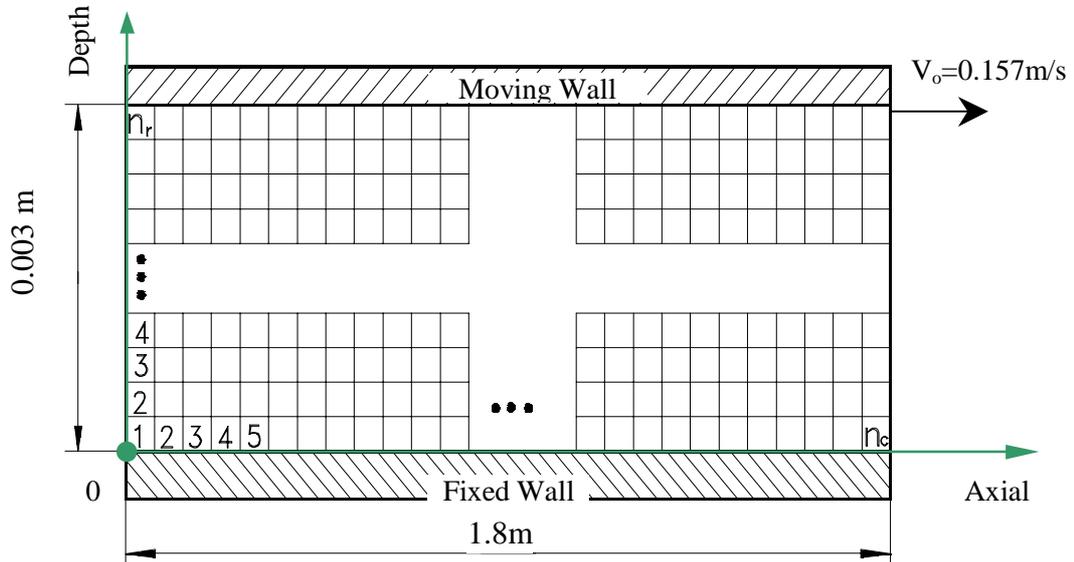


Fig. 2 Simulation domain and boundary conditions  
( $n_r=20$ ,  $n_c=12,000$ )

### 3. Simulation Results

In the present study, polymerization of  $\epsilon$ -caprolactone in a rectangular channel was investigated. The concentration ratio of monomer to initiator was 400. It was assumed that the fluid in the channel was under a drag flow only.

Fig. 2 shows that the upper plate moves at a velocity of 0.157 m/s, while the bottom plate is stationary. The channel length and width is 1.8 m and 0.003 m, respectively. The temperature at the channel entrance was 100°C. 4-node bilateral element was used in generating the finite element mesh. The total element number is 240,000. Two heat transfer conditions at walls were used in the simulation, i.e. adiabatic condition and constant temperature at walls.

#### 3.1 Effects of conversion ratio at fixed walls on reaction

In fluid mechanics, it is usually assumed that there is no slip between fluid and walls. However, in the modeling of reactive extrusion, such a non-slip condition at the fixed wall may result in various reactive situations. For an example, if the monomer is mixed ideally uniform with the initiator, the conversion ratio is 1.0 at the fixed wall since the residence time is infinite there, i.e. the reaction is fully complete at fixed walls. On the other hand, when the monomer is not well mixed with the initiator (there is just a layer of monomer with insufficient initiator adhering to the walls), because the residence time is infinite and the mixing between monomer and initiator is weak at the surface of the fixed walls, the conversion ratio is very low there. The extreme situation is that the conversion ratio at the fixed wall equals zero. In this part, the reactive process with these two extreme conditions at the fixed walls, i.e. zero conversion and complete conversion, were compared and discussed.

### 3.1.1 Reaction with adiabatic conditions at walls

Figs. 3 a and b show that the conversion ratio is higher in the regions near the fixed wall (the bottom wall) than near the moving wall; the reactive process based on zero conversion at fixed walls has a slower increase in conversion ratio than that based on complete conversion at fixed walls. Figs. 4a and 4b show that the velocity is large near the moving wall, while it is very small near the fixed wall, which might produce a stagnant area in the channel. Furthermore, in the reaction based on complete conversion at the fixed walls, the stagnant area is much closer to the entrance and the velocity near the fixed wall is lower than those based on zero conversion at fixed walls. Figs. 5a and 5b show that the temperature based on complete conversion at fixed walls is lower than that based on zero conversion at fixed walls. In the former, the temperature at the exit is about 115°C, while it is about 140°C in the latter.

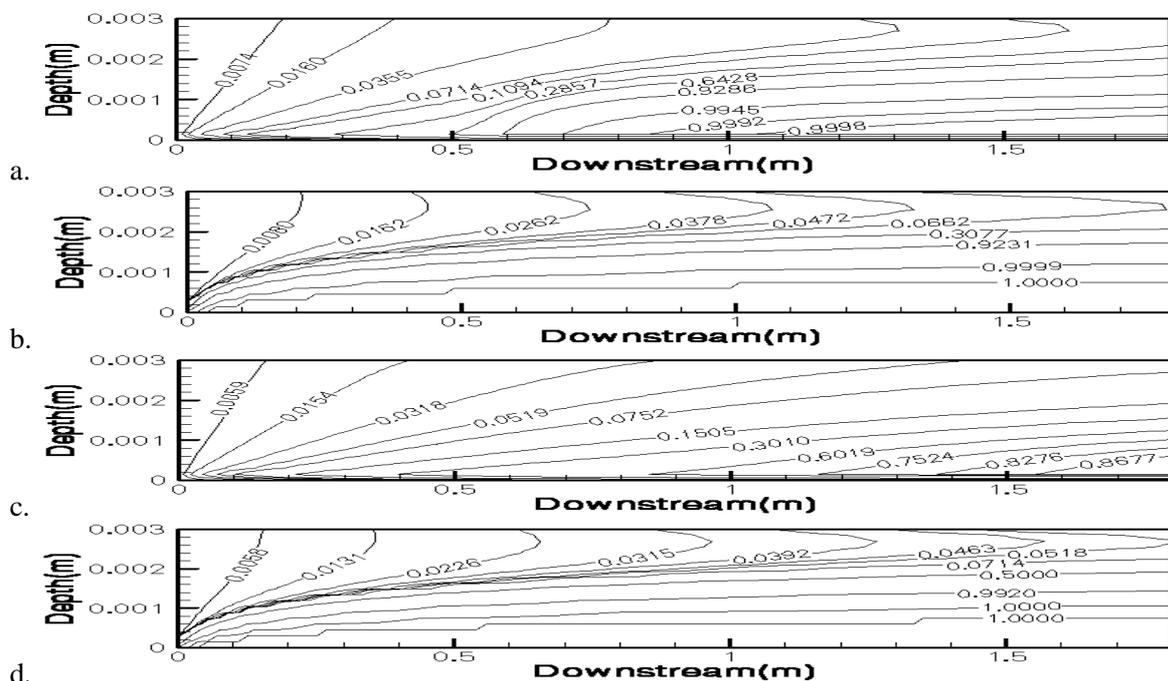


Fig. 3 Conversion ratio profiles based on 2-D channel model

a. zero conversion at fixed walls and adiabatic conditions at walls; b. complete conversion at fixed walls and adiabatic conditions at walls; c. zero conversion at fixed walls and constant temperature at walls; d. complete conversion at fixed walls and constant temperature at walls;

The above differences can be explained as following. It is known that high conversion ratio means high molecular weight and high viscosity. In our studies, the conversion ratio at the channel entrance (Fig. 2) is assumed to be zero. When the conversion ratio at the fixed wall is assumed to be 1 (i.e. complete conversion), it is easy to image that at the channel entrance, the viscosity near the fixed wall is much higher than that near the moving wall. Because the low viscosity layers (near the moving wall) can hardly drag the high viscosity layers (near the fixed wall) forward, the velocity of fluid near the fixed wall becomes very small. Low velocity means long residence time, which causes a big conversion ratio increase. A large increase in conversion ratio results in a rapid increase in molecular weight and viscosity. Consequently, the width of the regions with high conversion ratio (very close to 1) increases along the downstream (Fig. 3 b).

On the other hand, when the conversion ratio at the fixed wall is zero (i.e. zero conversion), at the channel entrance, the difference in the viscosities near the fixed wall and the moving wall is small. When compared with the reaction based on complete conversion at fixed walls, the velocity near the fixed wall is larger and the residence time is shorter; accordingly, the increase in conversion ratio is

smaller, but the temperature increase is larger, because the temperature increase depends on the ratio of the conversion ratio increase to the residence time increase.

### 3.1.2 Reaction with constant temperature at walls

In this part, the temperature at the walls is assumed to be 100°C. The differences in conversion ratios, temperatures, and velocities based on complete conversion and zero conversion at fixed walls (Figs. 3c - d, Figs. 4c - d and Figs. 5c - d) are very similar to the previous case (adiabatic conditions). That is, the reaction based on complete conversion assumption has a faster increase in conversion ratio, a larger stagnant region and a slower temperature increase than that based on a zero conversion at fixed walls. Furthermore, Figs. 5c and d show that the highest temperature is in the middle of the channel and the temperature increase during reaction is very small. This is because the channel width is very small, and the reaction heat is easily conducted to the walls.

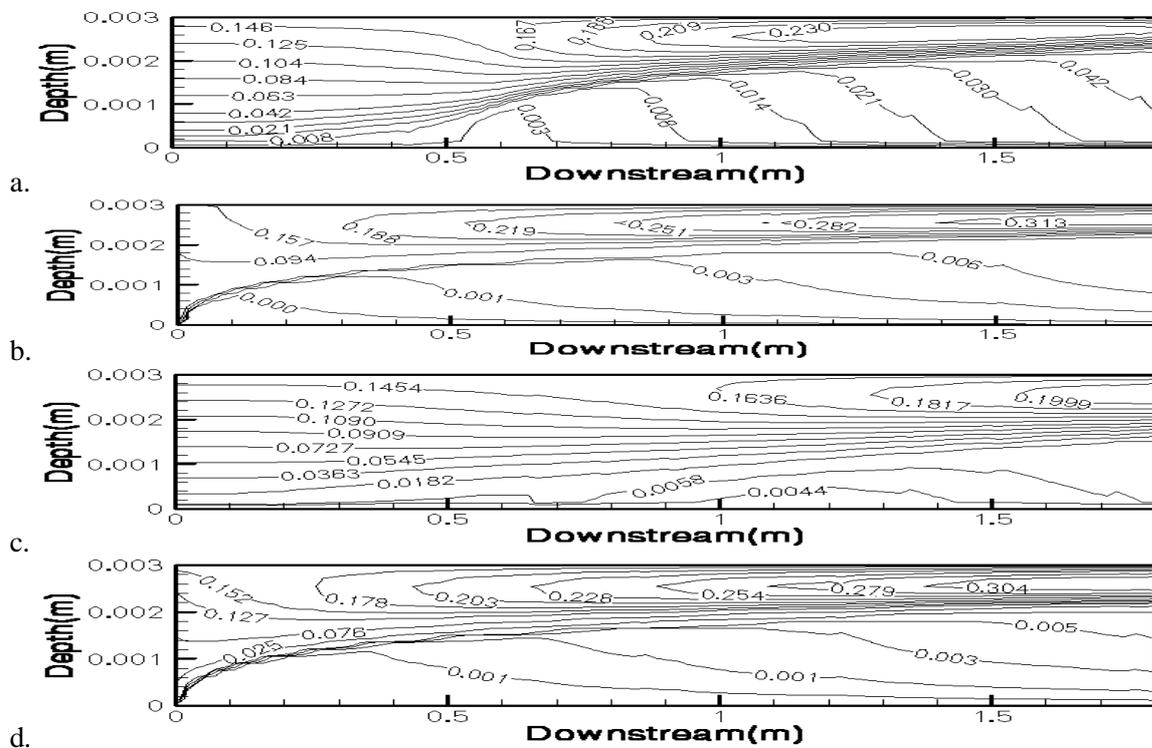


Fig. 4 Velocity profiles based on 2-D channel model

a. zero conversion at fixed walls and adiabatic conditions at walls; b. complete conversion at fixed walls and adiabatic conditions at walls; c. zero conversion at fixed walls and constant temperature at walls; d. complete conversion at fixed walls and constant temperature at walls;

### 3.1.3 Comparison of reaction with different heat conditions at walls

In order to investigate the effects of heat transfer conditions on walls upon reaction, average conversion ratio and average temperature in the channel cross section were calculated. Fig. 6a shows that the average conversion ratio based a constant temperature of 100°C at the walls is much lower than that based on an adiabatic condition when the conversion at the fixed wall is zero, whereas the difference in the average conversion ratios based on 100°C at walls and adiabatic conditions is very small when the conversion at fixed walls is 1. This can be explained by the relationship between the

two parameters, temperature and residence time. As shown in Fig. 6c, when the conversion ratio at the fixed wall is 1, the maximum residence time in the channel is about 15,000 s based on an adiabatic condition at walls, which is shorter than that based on 100°C at walls, about 18,500 s. The residence time is so long that the differences in temperature may have no significant effect on the reaction. That is, in the reaction based on complete conversion at walls, the residence time is a dominant factor. The difference in conversion ratios based on adiabatic conditions and 100°C at walls is not significant, due to the small divergence in the residence time.

However, when the conversion ratio at fixed walls is zero, the residence time based on adiabatic conditions and constant temperature conditions are small (Fig. 6c). Consequently, the temperature becomes a dominant factor for the reaction. Because the temperature in the reaction based on the adiabatic conditions is much higher than that based on a temperature of 100°C at walls (Fig. 6b), the conversion ratio increase becomes much larger in the former.

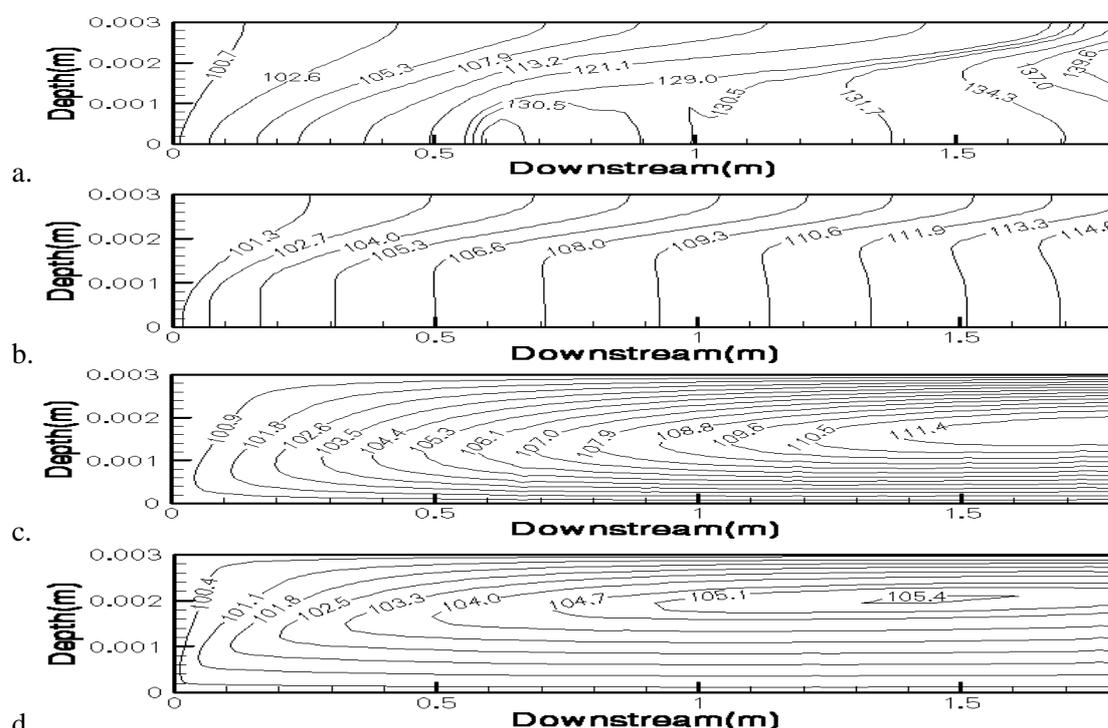


Fig. 5 Temperature profiles based on 2-D channel model

- a. zero conversion at fixed walls and adiabatic conditions at walls; b. complete conversion at fixed walls and adiabatic conditions at walls; c. zero conversion at fixed walls and constant temperature at walls; d. complete conversion at fixed walls and constant temperature at walls;

## 3.2 Modified 2-D channel model

### 3.2.1 Proposed model for conversion ratio at fixed walls

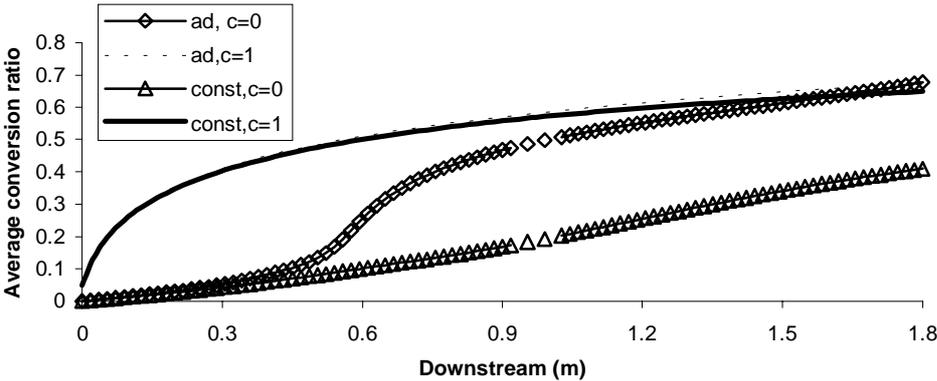
Zero conversion and complete conversion at fixed walls are two extreme situations in the reactive progression. Figs. 3 – 6 show that the profiles of conversion ratio, temperature, velocity and residence time based on these two assumptions are quite different from each other, in the cases of both adiabatic conditions and constant temperature at walls. It indicates that these two extreme conditions cannot be

used as boundary conditions in the simulation. The most realistic assumption appears that the conversion ratio at the fixed wall should be somewhere between these two extreme situations.

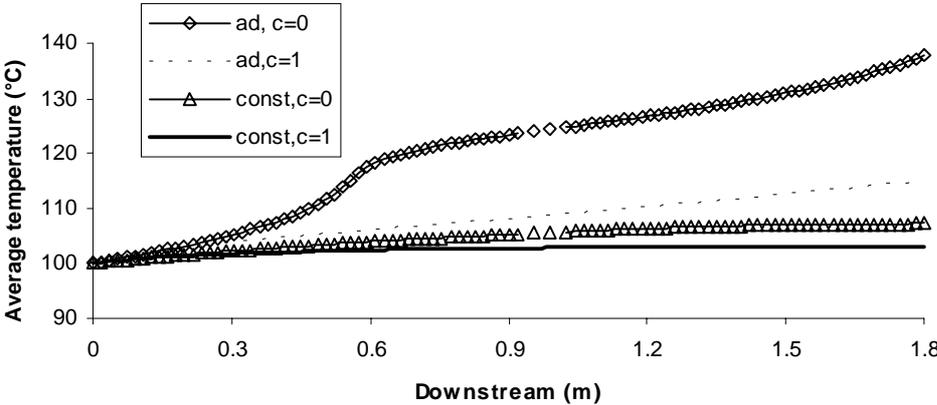
### 3.2.2 Effect of mixing on reaction

Fig. 6c shows that the maximum residence time at the channel exit is in a range of 15,000– 19,000 s when the conversion at the fixed wall is 1, and it is in a range of 250 – 360 s when the conversion at the fixed wall is zero. In Fig. 6c, the symbol *Linear* represents the residence time at the channel exit, when the velocity distribution in the channel is linear (i.e. simple shear flow, as in Fig. 1), in which the maximum residence time is about 230 s. It shows that the residence time near the fixed wall obtained from the 2-D channel model is quite different from that of the simple shear flow, especially in the cases based on complete conversion at the fixed wall. This is due to the fact that near the fixed wall, the materials are conveyed at very low velocities (Fig. 4), where some stagnant areas may be formed. This scenario does not reflect the real situation in the extruder. Generally, the rotation of the screw flight moves the high conversion layers away from the barrel surfaces (i.e. stationary walls), and the in-channel circular flow provides mixing in the cross section of the channel. This implies that it is necessary to incorporate such a mixing in the 2-D channel model.

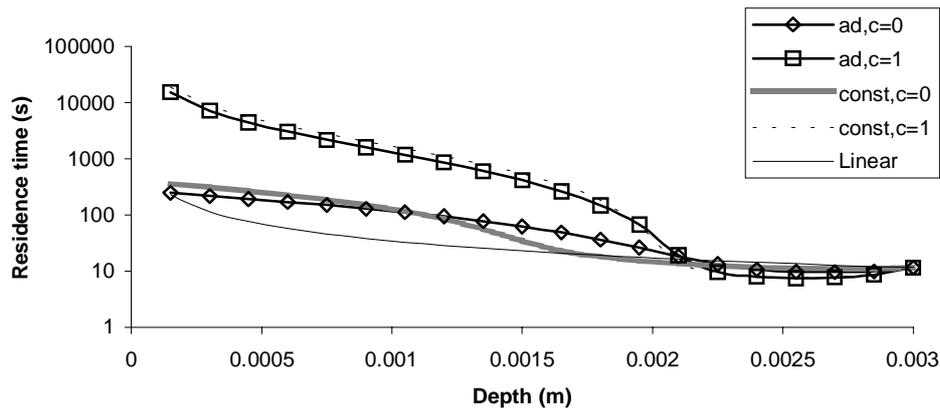
In our study, a modified 2-D channel model was proposed, with incorporating the boundary condition of conversion ratio at fixed walls and the mixing of fluid in the channel. The effects of mixing mechanisms on reaction were investigated. This part will be presented in the meeting.



a.



b.



c.

Fig. 6 Comparison of simulation results with adiabatic conditions and with a constant temperature of 100°C at walls  
a, average conversion ratio; b, average temperature; c, residence time at the exit of the channel;  
(ad, adiabatic conditions; const, constant temperature at walls; Linear, simple shear flow with linear velocity distribution in the channel, as in Fig. 1)  
(c=0, zero conversion ratio at fixed walls; c=1, complete conversion at fixed walls)

## 4. Conclusions

In the present study, the polymerization of  $\epsilon$ -caprolactone in a channel flow was simulated with a 2-D channel model by Finite Element Method. In the simulation, two extreme conditions for the conversion ratio at the fixed walls, i.e. zero conversion and complete conversion, and two heat transfer conditions at walls, i.e. adiabatic and constant temperature, were used. It showed that the reactive process relied largely on these boundary conditions. The simulation results indicated that the conversion ratio at the fixed walls should be somewhere between these two ideal conditions. Furthermore, near the fixed wall, the residence time was extremely high and the velocity was very low. This indicated that the initial assumptions in the 2-D channel model were not realistic.

A modified 2-D channel model was proposed, which incorporates the mixing of fluid in the channel and the magnitude of the conversion ratio at the fixed walls. To investigate the effect of mixing of fluid elements upon the reactive progression, three cross channel mixing models were proposed. The simulation shows that different mixing models cause different reactive progressions. This not only indicates that the 1-D channel model is not good in simulating the reactive extrusion, but also suggests that the reactive progression can be optimized by introducing different mixing mechanisms in the twin screw extrusion.

## 5. References

1. F. Berzin, B. Vergnes, and L. Delamare, *Modeling of Peroxide Initiated Controlled Degradation of Polypropylene in a Twin Screw Extruder*, Poly. Eng. Sci. 40, 344-356, 2000
2. T. Fukuoka, *Numerical Analysis of A Reactive Extrusion Process. Part II: Simulations and Verifications for the Twin-screw Extrusion*. Poly. Eng. Sci. 40. 2524-2538, 2000
3. T. Fukuoka, *Numerical Analysis of a Reactive Extrusion Process. Part I: Kinetics Study on Grafting of Vinylsilane to Polyethylene*, Poly. Eng. Sci. 40. 2511-2523, 2000
4. B. Vergnes, G. D. Valle, L. Delamare, *A Global Computer Software for Polymer Flows in Corotating Twin Screw Extruders*, Polym. Eng. Sci., 38, 1781, 1998

5. H. Kye and J. L. White, *Simulation of Reactive Extrusion: Polymerization of  $\epsilon$ -Caprolactam in A Modular Co-rotating Twin-screw Extruder*, Proceeding of SPE ANTEC, 309-313, 1996
6. L. Zhu and Kun Sup Hyun, *Numerical Simulation of Bulk Polymerization of  $\epsilon$ -caprolactone in Extrusion*, Proceedings of SPE ANTEC, xxx –xxx, 2002
7. Ph. Dubois, N. Ropson, R. Jérôme, and Ph. Teyssié, *Macromolecular engineering of polylactones and polylactides. 19. Kinetics of ring-opening polymerization of  $\epsilon$ -caprolactone initiated with functional aluminum alkoxides*, *Macromolecules*, 29, 1965-1975, 1996
8. J. Gimenez, P. Cassagnau, A. Michel, *Bulk Polymerization of  $\epsilon$ -Caprolactone: Rheological Predictive Law*, *J. Rheol.*, 44, 527-547, 2000