

## Modeling of polyurethane synthesis by reactive extrusion

Jean-Pierre Puaux<sup>a,\*</sup>, Philippe Cassagnau<sup>a</sup>, Grigore Bozga<sup>b</sup>, Iosif Nagy<sup>b</sup>

<sup>a</sup> *Laboratoire des Matériaux Polymères et Biomatériaux, Université Claude Bernard-Lyon1, 15 Bd Latarjet, 69622 Villeurbanne cedex, France*

<sup>b</sup> *University Politehnica of Bucharest, 313 Spl. Independentei, Sector 6, 060042 Bucharest, Romania*

Received 6 June 2005; received in revised form 21 November 2005; accepted 21 November 2005

Available online 28 December 2005

### Abstract

This paper describes a modeling and simulation study for the polyurethane synthesis by bulk copolymerization of dicyclohexylmethane 4,4'-diisocyanate with a mixture of a polyether diol and 1,4-butane diol, in a co-rotating twin-screw extruder. The process model is based on linear chain growth theory, a kinetic expression previously published in literature and the axial dispersion model, in both the hypothesis of non-segregated and totally segregated fluid structures. The numerical simulations evidenced that the effect of segregation phenomenon appears to be significant, particularly in the evaluation of the product polydispersity. Also, the polymerization process features an important sensitivity of the polymer molecular weight in respect to the inlet monomer molar ratio.

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**Keywords:** Polyurethane synthesis; Reactive extrusion; Polymerization

### 1. Introduction

The polyurethanes (PU) are copolymers presenting various practical applications in foams, elastomers, coatings, etc. Hepburn [1] described extensively the chemistry and engineering of polyurethanes synthesis.

The polymer synthesis by reactive extrusion presents significant advantages compared to the classical reactors. The most significant of these are the good control of the reaction time and temperature and the possibility to work at high conversions and high molecular weights, due to the improved capacity to transport and mixing of high-viscosity mixtures. The bulk PU synthesis by reactive extrusion was experimentally investigated by Hyun and Kim [2] in a single screw extruder, Cassagnau et al. [3,4] in a co-rotating twin-screw extruder and Bouilloux et al. [5] in a counter-rotating twin-screw extruder.

This work concerns the modeling and simulation of the bulk PU synthesis in a fully intermeshing co-rotating twin-screw extruder (TSE). Baird and Collias [6] and Brown [7] describe the constructive and functional principles of this apparatus, giving

also an extensive bibliography on reactive extrusion. The development of mathematical models with good predictive capability is a key element in the design and control of reactive extrusion processes. Despite of its high practical importance, there are a relatively small number of published works in the field of reactive extrusion modeling. A difficult problem in TSE modeling is the description of the flow and mixing of the material along the screw channels. This is very complex and the flow patterns are difficult to be mathematically predicted [6].

To describe the fluid flow and mixing in TSE two approaches are possible. The first one calculates the velocity and pressure profiles along the screw by solving the momentum balance equations. This approach is generally difficult to implement due to a number of complexities (change of rheological properties of the material along the screw, complex geometry of the flow, difficulties in the prediction of filling ratio levels in different zones or in the accurate description of the moving boundaries, etc.). The second approach describes the flow and mixing of the material in the TSE by the classical flow models currently used in chemical engineering. The parameters of these models are usually estimated from residence times distribution (RTD) data obtained from tracer experiments. In the present work we adopted the second approach, due to its relative simplicity and reasonable accuracy. A recent study published by Semsarzadeh et al. [8] concerning the synthesis of poly(urethane-isocyanurate) by reactive extrusion is based on the same approach.

*Abbreviations:* ADM, axial dispersion model; DP, average polymerization degree; MWD, molecular weights distribution; PDI, polydispersity index; PU, polyurethane; RTD, residence time distribution

\* Corresponding author.

*E-mail address:* [puaux@univ-lyon1.fr](mailto:puaux@univ-lyon1.fr) (J.-P. Puaux).

The process investigated is a PU synthesis by bulk copolymerization of dicyclohexylmethane, 4,4'-diisocyanate with a mixture of two diols: a long-chain polyether diol and 1,4-butane diol. To investigate the effect of micromixing on the polymerization progress along the screw, we used both non-segregated and completely segregated axial dispersion models. The reaction kinetics is taken from literature and the mixing parameter (Pe number) is evaluated from RTD experiments performed simultaneously with the polymerization process. The quality of the model predictions was tested by comparing the calculated and experimental values of the polymer average molecular weight in three points along the extruder barrel. This represents the classical approach devised by many monographs of chemical reactor engineering (Villermaux [9]).

## 2. Description of the twin-screw extruder experiments

The experimental data we used in this work were obtained by Cassagnau et al. [4]. The reagents used in the bulk polymerization process were a polyether soft segment (PEO) of functionality 2 and the molecular weight 1000 g/mol, dicyclohexyl-methane 4,4'-diisocyanate ( $H_{12}$ MDI) and 1,4-butane diol (BDO). The dibutyltin laurate was used as catalyst in a concentration of 0.000475 mol/l. The concentration of the diisocyanate monomer in the feeding mixture was 1.56 mol/l and the molar ratio BDO/PEO was 2:1 in all the experiments. The process was performed in an intermeshing self-wiping co-rotating TSE (Leistritz LSM-34; centerline distance 30 mm; screw diameter 34 mm; barrel length 1200 mm). The extruder barrel is divided into 10 equal zones, each one provided with individual temperature control systems. A “conveying” screw configuration was used and two intermediary ports were available to extract samples of the reaction mixture (Fig. 1). The molecular weights of the polymer samples, collected from two intermediary ports and at the extruder die, were measured by the size exclusion chromatography. A set of representative results obtained at a mass flow rate fixed to 3 kg/h and different screw speeds are presented in Table 1. To measure the RTD characteristics, pulse type experiments were performed and samples were collected every 10 s at the three points along the barrel (two intermediary ports and the die). Several experimentally determined curves are presented in Figs. 2 and 3. As observed from these figures, when increasing the speed of the screws the RTD moves to shorter times narrowing the distribution (Fig. 2). Also, the RTD

Table 1

Experimental values of the polymer number average molecular weight and polydispersity index (flow rate 3 kg/h)

Port #	Screw speed (rpm)	$T$ ( $^{\circ}$ C)	$M_n$ (kg/kmol)	PDI
1	20	162	9000	2.2
2	20	162	18700	1.99
3	20	162	25000	1.97
1	80	164	4500	2.35
2	80	164	10000	2.28
3	80	164	16000	1.96
1	200	166	4580	2.70
2	200	166	8800	2.13
3	200	166	15500	1.97

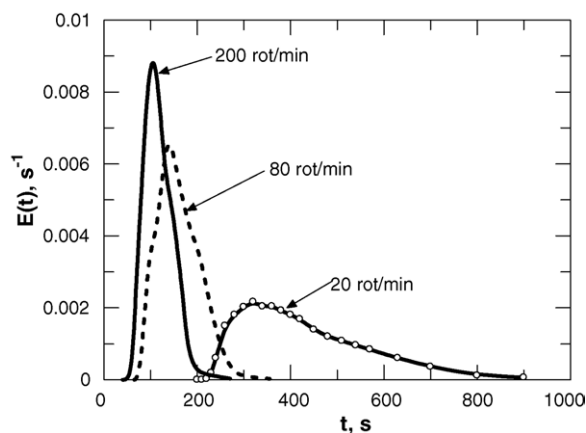


Fig. 2. Measured residence times distribution curves for different screw speeds.

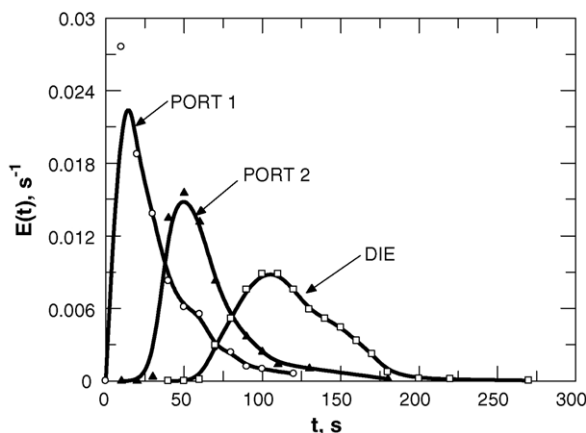


Fig. 3. Measured local residence times distribution curves along the screw (200 rpm).

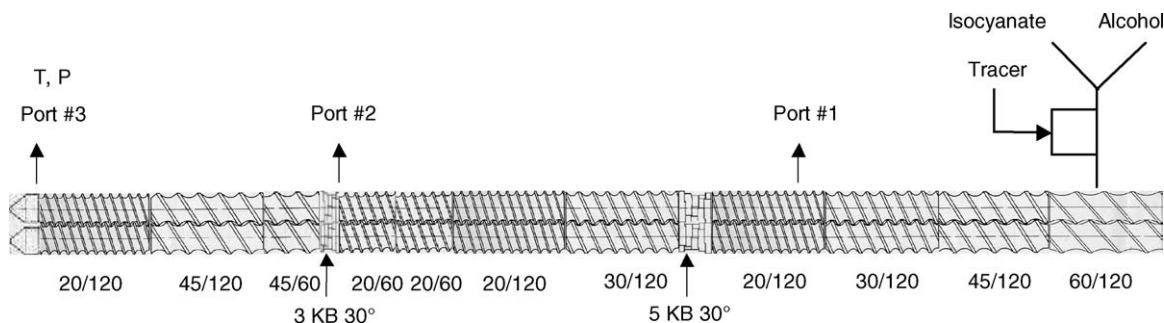


Fig. 1. Structure of the screw.

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