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PRELIMINARIES STUDIES ON THE SYNTHESIS OF A THERMOPLASTIC POYURETHANE FOR APPLICATION TO A REACTIVE EXTRUSION PROCESS

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Scientific topics: I.1

Abstract: This study deals with the determination of kinetic and rheological data of the formation of a thermoplastic polyurethane, which can be used in biomedical domain. The use of a twin-screw extruder as a continuous reactor of polymerisation is considered particularly in the point of view of the compatibility of the reaction and residence times.

Keywords: polyurethane, biomedical materials, kinetics, viscosity, modelling.

INTRODUCTION

Thermoplastic polyurethanes are widely used in medicine for over twenty years. Through the nature and stoichiometry of reactants, the structure of these polymers can easily be tailored to an important variety of applications. The last progress in the medical domain aims at improving their biostability (Coury et al., 1987). To develop these new polymers, it is necessary to settle a reliable process of synthesis. At the moment, the biomedical polyurethanes are carried out using batch reactors, which gives rise to heterogeneity from batch to batch due to a poor mixing. According to this problem, the use of a twin-screw extruder as bulk reactor is of a great interest since by its nature this apparatus is a high rate, continuous conveyor and an efficient mixer for high viscosity melt. However, reactive extrusion means certain requirements. Some difficulties to overcome are the reduced residence time of the reactants in the extruder and the exothermal control of the reaction. So, proper optimisation and control of the reactive extrusion require a good knowledge of the chemorheological behaviour of the reactants and products during the whole process. The main objective of this study is to determine kinetic and rheological data for the formation of thermoplastic polyurethane. These data could be then introduced in a complete model of the reactive extrusion process.

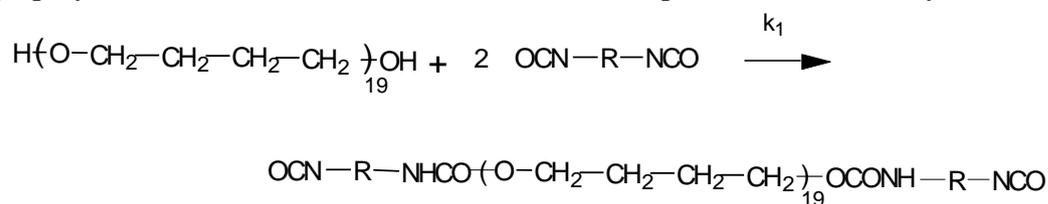
EXPERIMENTAL

1 Materials

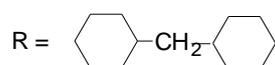
The thermoplastic polyurethane system chosen for this study consists of a polyether soft segment (poly(tetramethylene oxide) glycol (PTMG 1400) and a hard segment based on the chain extender 1,4-butanediol (BD). The third reactant is a liquid cycloaliphatic diisocyanate, the dicyclohexylmethane 4,4'-diisocyanate (HMDI). HMDI, PTMG and BD are used in a molar ratio of 2:1:1. The catalyst used is dibutyltin dilaurate (DBTDL) at concentration ranging between 0.001% and 1% by total weight.

2 Mechanisms

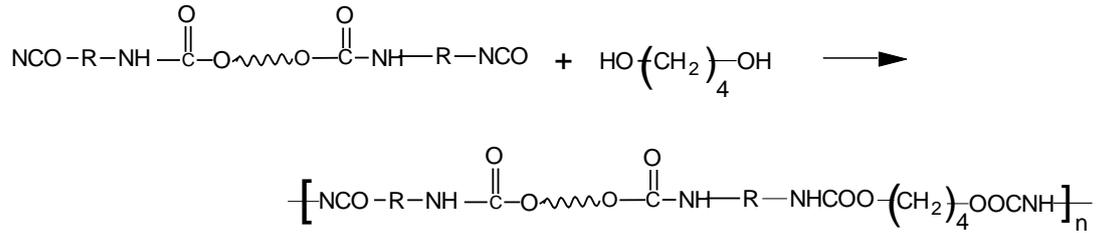
The polyurethane is obtained through a two-step procedure. In the first step, called prepolymerisation, PTMG reacts with HMDI in the presence of the catalyst:



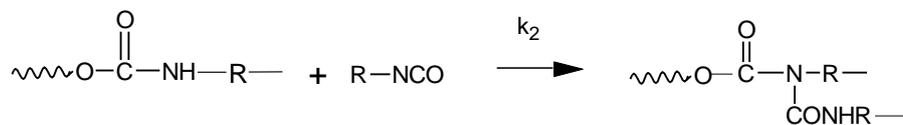
with



and in the second step, BD is added to the resulting prepolymer.



During the process, secondary reactions occur between isocyanate and active hydrogen-containing group in the polymer chain. During prepolymer formation the main secondary product formed is an allophanate group:



Because of this reaction and possibly other reactions, as, for instance, that between isocyanate groups and water, an excess of isocyanate is consumed during the reaction.

2 Measurements

On one hand, to follow the first step kinetics, the reaction is carried out in a batch reactor equipped with a four bladed impeller. Samples are taken out at various times and the concentration of unreacted isocyanate is determined by a back-titration method (Otey et al., 1964). An excess of a solution of dibutylamine in toluene is added to the sample. Isocyanate groups react with the dibutylamine to form urea and the residual dibutylamine is titrated with hydrochloric acid (0.1 N) by volumetric titration. The isocyanate number, I_{NCO} is then expressed by the following equation:

$$I_{NCO} = \frac{(V_{ref} - V) * N * 56.1}{m} \quad (1)$$

with V_{ref} : HCl volume to titrate 20 cm³ of dibutylamine
 V : HCl volume to titrate the sample
 N : acid normality
 m : weight of the sample

Viscosity changes with time during isothermal prepolymerisation are measured using a cone-and-plate rheometer (Rheometrics, Controlled Stress Laboratory Rheometer, model CSL-100). On the other hand, the complete polymerisation (first and second steps) is carried out in a Haake Rheomix 600 batch mixer equipped with two roller blades.

3 Analysis

The final average molecular weight of the polyurethane is determined by Size Exclusion Chromatography (SEC) using a Waters Model 150-C chromatograph.

RESULTS AND DISCUSSION

1 Kinetics and rheology of prepolymerisation

The first step of polymerisation has been carried out in batch reactor at 100°C for different catalyst concentrations. The change in concentration of NCO groups with time (figure 1) shows clearly that an excess of diisocyanate (with respect to polycondensation reaction between PTMG and HMDI) is consumed.

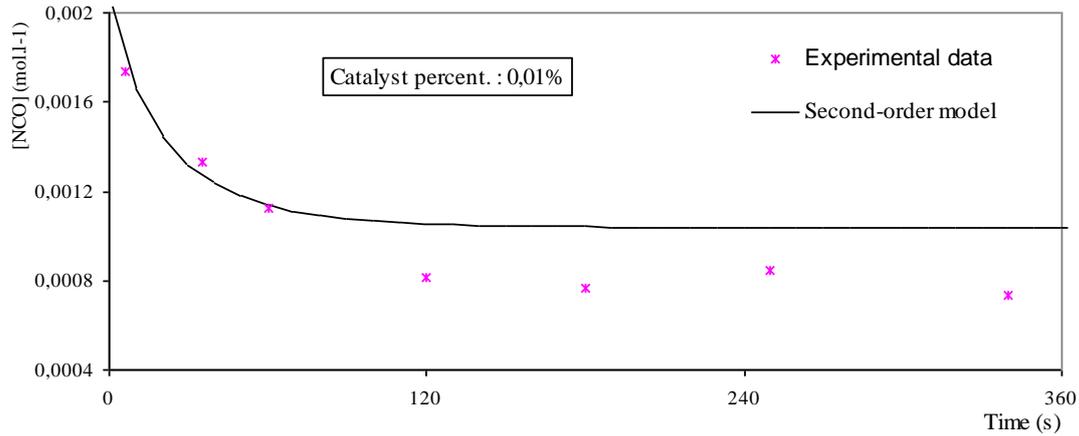


Figure 1 : Change in concentration of isocyanate groups with time for the reaction of HMDI with PTMG at 100°C.

With a model, which considers only the main reaction between the diisocyanates and the diols, the reaction rate can be expressed by the following equation:

$$R = -\frac{d[\text{NCO}]}{dt} = k_1[\text{NCO}] * [\text{OH}] \quad (2)$$

If a and b denote the initial concentrations of hydroxyl and isocyanate groups respectively and x denotes the isocyanate group concentration reacted with hydroxyl group, the equation (2) can be written:

$$R = -\frac{d(b-x)}{dt} = -k_1(b-x)(a-x) \quad (3)$$

Integrating equation 3 yields:

$$k_1 = [1/t(a-b)] \ln[b(a-x)/a(b-x)] \quad (4)$$

which can be resolved to give

$$x = \frac{b \left[e^{k_1 t(b-a)} - 1 \right]}{\left[\left(\frac{b}{a} \right) e^{k_1 t(b-a)} - 1 \right]} \quad (5)$$

Equation 5 gives the variation of reacted $-NCO$ against time without secondary reactions and represents the theoretical curve for the primary reaction. Theoretical curves of figure 2 is drawn using this second-order kinetic model. It is straight lines up to a determined reaction time, after which a deviation occurs.

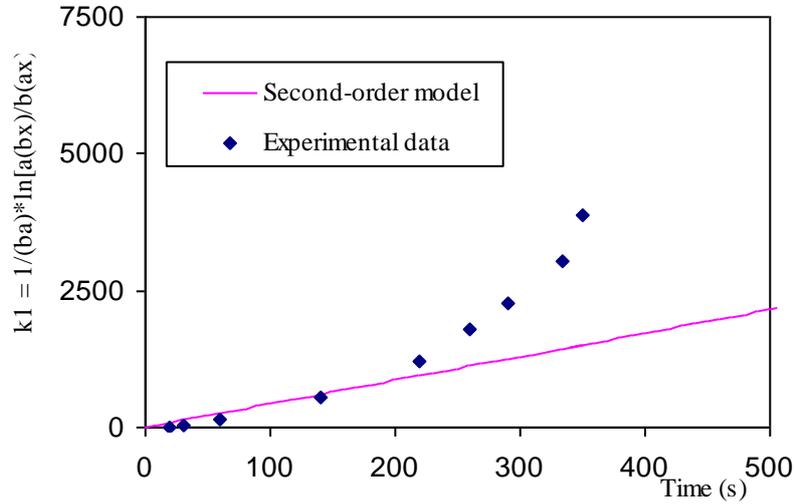


Figure 2: Second-order plots for the reaction the reaction of HMDI with PTMG at 100°C.

This deviation is due to the secondary reactions. To simplify the system, we have assumed that the main secondary reaction is the one between isocyanate and urethane groups giving rise to formation of allophanates. Therefore, the rate of disappearance of isocyanate groups can be expressed by the following equation:

$$d[NCO]/dt = k_1 [NCO] [OH] + k_2 [NHCOO] [NCO] \quad (6)$$

This equation may be written in the form

$$d(x-z)/dt = k_1 (b-x-z) (a-x) - k_2 (b-x-z) (x-z) \quad (7)$$

where z denotes the isocyanate group concentration reacted with urethane group.

The technique of the minimum squared deviation between experimental and theoretical values has been used to determine the two rate constants, k_1 and k_2 , of respectively primary and secondary reactions. It was found that k_1 depends on the catalyst concentration according to the following relation:

$$k_1 = 0.24 [Cat.] + 2.33 \text{ (kg.mol}^{-1} \cdot \text{s}^{-1}) \quad (8)$$

and that k_2 is constant and equal to $9.45 \cdot 10^{-3} \text{ kg/.mol}^{-1} \cdot \text{s}^{-1}$

The variations of conversion versus time calculated using this kinetic model including the secondary reactions are in a good agreement with experimental data (figure 3).

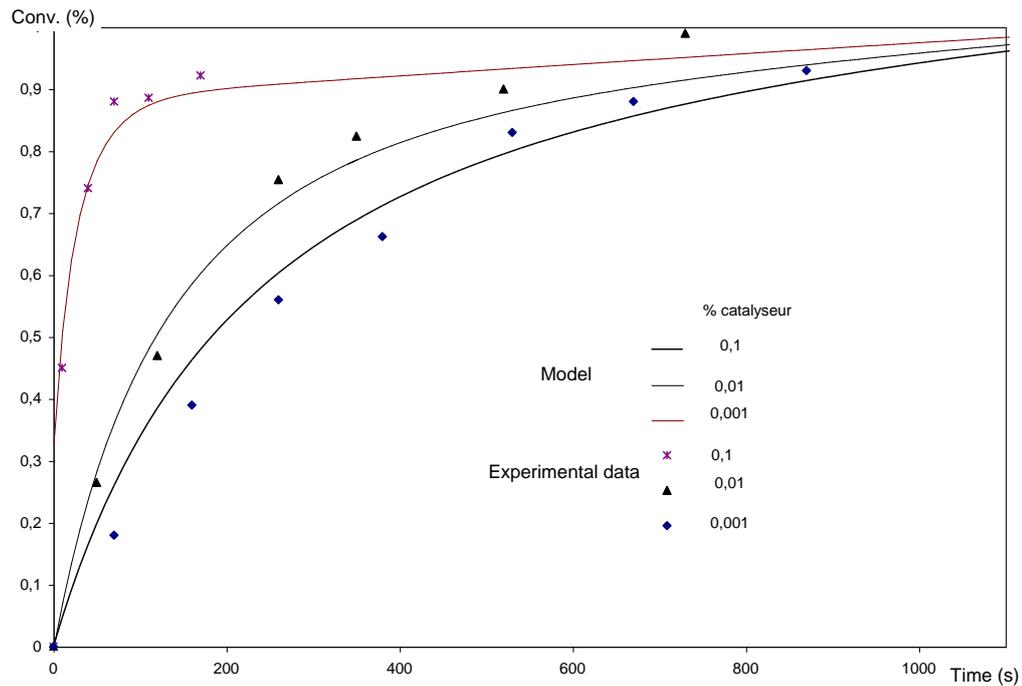


Figure 3: Experimental and theoretical curves of conversion versus time during prepolymerisation.

To follow the rheological behaviour of the reacting medium during the prepolymerisation, mixtures of PTMG and HMDI at three different catalyst concentrations have been placed in a cone-and-plate rheometer and heated at a temperature of 100°C. Changes in viscosity and shear stress have been recorded at a constant shear rate of 25 s⁻¹. The viscosity of the reaction mixture varies from 0.1 Pa.s up to a constant value of about 1 Pa.s (Figure 4). This level is reached even faster than the amount of the catalyst is high

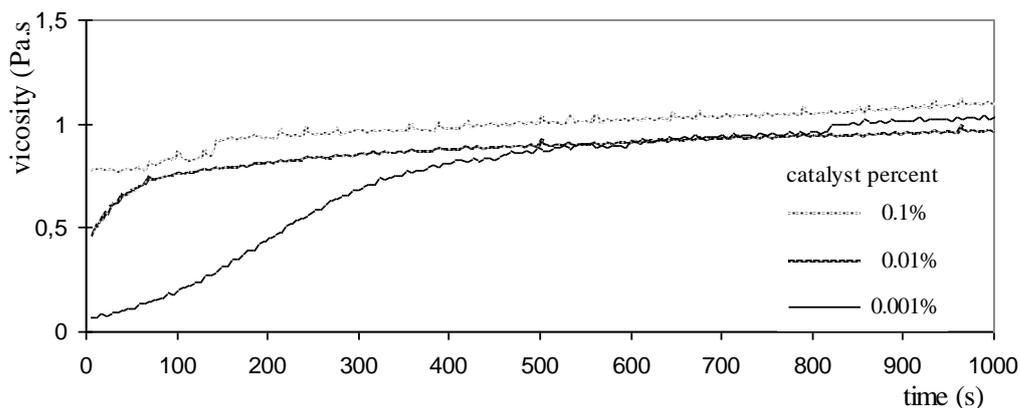


Figure 4: Changes in viscosity during the pre-polymerization.

2 Overall polymerisation

The overall polymerisation has been carried out using the internal mixer. In a first step, the two reactants PTMG and HMDI are added in the mixing chamber and heated at a temperature of 100°C then the catalyst (at a concentration of 0.1%) is introduced. After ten minutes of reaction (which corresponds to the maximum time to achieve the formation of the oligomers), the temperature is raised up to 160°C and BD is added. The mixing rate of the first step has been varied from 5 to 200 rpm and the mixing rate of the second step has been fixed at 160 rpm. The torque required to turn the roller rotors is continuously recorded. During reaction in the batch mixer, the molecular weight of the polyurethane increases and therefore the viscosity of the mixture. The mixing torque is thus an indirect measure of the progress of the reaction. Three areas can be observed. In the first part of curve, the value of the torque is near zero because of the low viscosity of the mixture. After the introduction of the BD, the curve exhibits a peak, which is due to a sudden increase of the viscosity. It corresponds to the formation of high molecular chains of macromolecules. After about five minutes, the reaction is complete and the torque reaches a constant value. The dependence of the value of this level with the mixing rates applied during the prepolymerisation can be explained by a difference in the viscosity of the obtained polyurethane. However, the values of the mean molecular weight of the product is equal to about 175 000 g.mol⁻¹ in all the cases. Further investigations on the properties of the final polyurethane must be done in a future work.

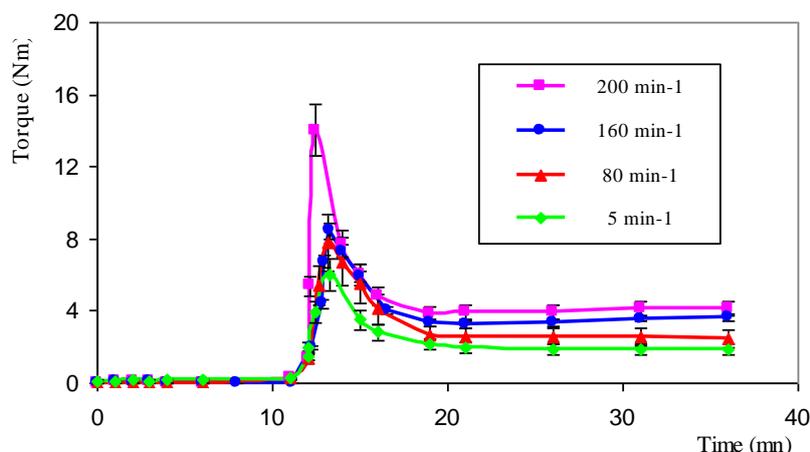


Figure 5: Experimental curves of torque versus time recorded during the overall polymerisation.

3 Polymerization in extruder

The aim of the work is to study the polyurethane formation in a fully intermeshing corotative twin-screw extruder. For a better control of the structure of the polymer, a two-step process has been considered. The prepolymerisation is carried out in a reactor, which feeds continuously the extruder. The chain extender is injected directly in the first zone of the extruder. One of the most important parameters of the process is the mean residence time inside the extruder, which depends of the operating conditions among them screw speed and flowrate. On the basis of a reaction time of about five

minutes (as determined previously), a first approximation of the operating conditions needed can be made using the following simplified relationship:

$$Q = N L \pi (D - H) H - \frac{D^2}{2} A \cos\left(1 - \frac{H}{D}\right) + \frac{D - H}{2} \sqrt{H(2D - H)} \quad (9)$$

with H : channel depth
D : Diameter of the screw
L : Length of the screw

A flowrate, Q, of 3.6 kg.h⁻¹ and screw speed, N, of 150 rpm are suitable to achieve a residence time of 5minutes.

CONCLUSION

A kinetic model of the formation of polyurethane has been developed. First results clearly show that is possible to find adequate operating conditions for which reaction time and residence time in an extruder would be compatible. Further developments include polymerisation experiments in a Clextral BC21 co-rotating extruder. The extruder could be used either alone or in tandem with a pre-reactor.

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