MATHEMATICAL MODELLING OF NYLON 6/6,6 COPOLYMERIZATION IN BATCH REACTOR

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Abstract

A mathematical model has been developed for the hydrolytic copolymerization of caprolactam with adipic acid and hexamethylene diamine in a 12 L batch reactor under isothermal operation. This model is a key step for determining kinetic expressions and parameter values that can be used to predict product properties and production rate in an industrial reactor train. The reaction mechanism described by the model includes hydrolysis of caprolactam and cyclic dimer, polycondensation, polyaddition, transamidation and ring formation via end biting and back biting. The polycondensation and ring-opening reactions are known to be catalyzed by a variety of acid compounds. Mass-transfer of water, caprolactam, cyclic dimer and hexamethylene diamine from the liquid phase into the reactor head space is accounted for in the model. The model predicts the degree of polymerization and dynamic changes in concentrations of water, caprolactam monomer, aminocaproic acid, cyclic dimer, carboxyl ends and amine ends in the molten polymer. It also accounts for accumulation of water in the headspace after the vent is closed during lab-scale reactions. Industrial data are being used to estimate model parameters and to test model validity.

Keywords

Polyamide, nylon, mathematical model, copolymerization

Introduction

Six reversible reactions shown in Table 1 are considered in the current model for nylon 6/6,6 copolymerization. The first reaction (R1) is ring-opening of caprolactam by water, and reverse R1 is an end-biting reaction to re-form caprolactam from aminocaproic acid. R2 is the amidation reaction and reverse R2 is hydrolysis of amide links. R3 is ring opening of caprolactam by amine end groups and reverse R3 is a back-biting reaction to produce caprolactam. R4 is ring opening of cyclic dimer by water and reverse R4 is end-biting by linear dimer to form cyclic dimer. R5 is ring opening of cyclic dimer by amine end groups and reverse R5 is a back-biting reaction that produces cyclic dimer. R1 to R5 were considered in the nylon 6 polymerization models of Arai and Tai et al. (1979, 1981). A simpler model by Reimschissel et al. (1959, 1969, 1977) considered only the first three reactions, neglecting the formation and consumption of cyclic dimer. R6, which accounts for transamidation, has been added to the current model for nylon 6/6,6 copolymerization because transamidation is known to occur and it has an

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important influence on randomizing the distribution of caprolactam, hexamethylene diamine and adipic acid units at the ends of the polymer chains and within the polymer chains. As a result, including R6 may lead to better model predictions.

Table 1. Reaction Scheme

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Mechanism</th>
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<tbody>
<tr>
<td>R1</td>
<td><img src="image" alt="Reaction Scheme R1" /></td>
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<tr>
<td>R2</td>
<td><img src="image" alt="Reaction Scheme R2" /></td>
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<td>R3</td>
<td><img src="image" alt="Reaction Scheme R3" /></td>
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<td>R4</td>
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<td>R5</td>
<td><img src="image" alt="Reaction Scheme R5" /></td>
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<tr>
<td>R6</td>
<td><img src="image" alt="Reaction Scheme R6" /></td>
</tr>
</tbody>
</table>

Model Development

15 ordinary differential equations (ODEs) were derived for total mass (m), caprolactam (M), aminocaproic acid (LM), hexamethylene diamine (HMD), adipic acid (ADA), linear dimer (LD), cyclic dimer (CD), water (W), amide links (L), amine ends (A), carboxyl ends (C), evaporated water, monomer, HMD and CD. Equation (1) is a mass balance on the monomer shown as an example:

\[
\frac{d[M]}{dt} = -k_{f1}[M][W] + k_{r1}[LM] - k_{f3}[M][A] + k_{r3}[A][L] + k_{r4}A_{c} \frac{k_{w}A_{c}([W] - [W]_{eq})MW_{w} + k_{r4}A_{c}M_{MWM} + k_{r6}A_{c}[HMD]M_{HMD}}{M} \tag{1}
\]

The first four terms on the right-hand side account for consumption of monomer by R1, production of caprolactam by reverse R1, consumption of monomer by R3 and production of monomer by reverse R3. The factor \( f_{1} \) appears because only amine ends on the polymer that are associated with caprolactam units are able to backbite to produce caprolactam. The fifth term on the right-hand side of the ODE accounts for evaporation of caprolactam. The final term accounts for the increase in caprolactam concentration associated with the loss in mass of the reactor. Expressions for \( f_{1} \) and for other similar factors that appear in the ODEs were derived and are included in the model. Selected simulation results are shown in Figure 1. The concentration of HMD falls quickly due to ring opening reaction R3.

Acknowledgments

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References


