Synthesis and Mathematical Modelling of Polyethylene Terephthalate via Direct Esterification in a Laboratory Scale Unit

Mohsen Mazloom, Mehdi Rafizadeh*, Vahid Haddadi-Asl, and Majid Pakniat

Polymer Engineering Department, Amirkabir University of Technology, P.O. Box: 15875/4413, Tehran, Iran

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ABSTRACT

Synthesis of polyethylene terephthalate (PET) in laboratory is a challenging task due to high reaction temperature up to 280ºC and high pressure in esterification step and low vacuum in polycondensation step. In this research, synthesis of PET, in a laboratory size unit was studied via direct esterification of terephthalic acid and ethylene glycol. Antimony oxide was added as catalyst for polycondensation. Mathematical model of process is presented based on the mass balance of different species such as acid and hydroxyl end groups, water output, diester groups during both esterification and polycondensation steps. Derived governing equations were integrated numerically using Runge-Kutta method. Reacting mixture mass variation was included in the model. Comparison of experimental and simulation results shows promising and good agreement. Hence, the model could be used as a powerful tool for engineering process. The model was applied to study different aspects of polymerization process.

INTRODUCTION

Production of polyethylene terephthalate (PET) has one of the fastest growing rates among thermoplastics during the last decades. PET has been produced mostly via direct esterification of terephthalic acid and ethylene glycol for a couple of decades. In the first step, esterification of terephthalic acid and ethylene glycol under goes reaction producing bishydroxyethyl terephthalate (BHET) as the main monomer for polycondensation. Regarding a reversible reaction, water, as side product should be extracted in order to perform reaction up to high conversions. In the second step, that is called polycondensation, oligomers and polymer chains under go reaction to
produce long polymer. The byproduct of polycondensation is ethylene glycol, which should be removed in order to increase the rate of polycondensation and chain length. To produce high molecular weight polymer and yarn, polymerization should be conducted in solid state [1-4]. Although PET has been produced for a long time, there are still different aspects such as modelling and mass transfer which need more research. Partial solubility of acid terephthalate (TPA) in ethylene glycol (EG) and diffusion of water and EG in polymer melt and mass transfer in liquid-gas phases are the main reasons of previous mentioned restrictions.

During the last two decades, some researchers have studied modelling of polyester polymerization. Ault et al. [5] studied a kinetic modelling of production of PET via dimethyl terephthalate (DMT) in a semi-batch reactor. Ravindranath et al. [6,7] published two review papers on various engineering aspects and mechanism of PET. Consequently, they published a series of considerable research works on PET that include seven papers [8-14]. In the first paper [8], a semi-batch reactor was modelled to produce PET via transesterification of DMT. They used zinc acetate as catalyst. Their published results are generally acceptable. The model was used to study the process and operation parameters on yield and production byproducts. The next paper was the extension of previous paper [9] for a continuous process with zinc acetate catalyst. In the next paper [10], they modelled a continuous prepolymerization process. Temperature and pressure were changed based on a predetermined pattern. The effect of adding DMT, during process was studied, as well. Ravindranath et al. [11] presented a mathematical model for continuous production of PET. Effects of process parameters, such as temperature distribution and residence time of BHET, and pressure on reactor performance were studied. Although, they did not validate their model, the results, however were physically meaningful. In the next research [12], a model of prepolymerization of BHET to PET in a series of continuous stirred tank reactors was presented. BHET was produced by transesterification of DMT. Ravindranath et al. [13], have modelled final stages of polycondensation in a continuous reactor. They were taken into account axial dispersion and suggested effective direction of mixing and other parameters. Although, their data were not in good agreement with experimental results, but they could be applied to process, qualitatively. In the last paper, Ravindranath et al. [14] presented a model for calculation of molecular weight distribution (MWD). Effects of byproducts and various reactions on MWD were introduced.

Kumar et al. [15] studied simulation of PET production in a homogeneous CSTR. Feed was included BHET and cetyl alcohol. Polycondensation of one functional compound reaction, redistribution and cyclization were taken into consideration. MWD Calculation shows importance of redistribution reactions. Calculations in semi-batch and CSTR show the latter, and give lower molecular weight average and polydispersity index (PDI). Kumar et al. [16] defined an objective function for maximizing conversion and minimizing byproduct production in a semi-batch reactor. They concluded that the temperature should be high in the beginning and then it should be decreased in order to reduce the byproducts production. Kumar et al. [17] applied Hamiltonian in a determined time interval model, and found optimum temperature trajectory in a semi-batch reactor.

Bhaskar et al. [18] presented a multi-objective optimization of an industrial PET reactor based model. Two objective functions were minimized in favour of acid and vinyl end groups concentrations. They incorporated an end-point constraint into optimization problem in order to produce polymer having a desired value of the degree of polymerization. Shin et al. [19] presented a minimization of the transesterification reaction in a semi-batch reactor, by using successive quadratic programming (SQP) and the cubic spline interpolation method. Therefore, there is a need to have better model of processing for the sake of process operation.

Reimschuessel et al. [20] studied equilibrium esterification-hydrolysis and condensation-glycolysis reactions among acid benzoic, ethane diol monobenzoate, ethane diol dibenzoate, and water in the presence of antimony catalyst. Kinetic studies showed that all rate constants are function of carboxyl group concentration. Antimony catalyst increases the condensation rate and has no effect on esterification reaction. They calculated all kinetic and thermodynamic parameters by non-linear regression. Reimschuessel
extended previous results to production of PET, considering: (1) esterification-hydrolysis, (2) polycondensation-glycolysis, and (3) transesterification-acidolysis reactions. These researchers used kinetic and thermodynamic parameters of the previous research [20], proving that condensation polymerization reaction among functional groups is important. Kang et al. [22] presented a model for esterification step. Effects of the monomer feed ratio, reaction temperatures, and oligomer addition on the conversion, degree of polymerization, and the formation of diethylene glycol were studied. El-Toufali et al. [23] studied chemical aspects of PET in the presence of antimony catalyst. They suggested formation of a ligand on antimony catalyst which includes terminated hydroxyl group and oxygen on the same end group. Configuration of the second chain on antimony determines polycondensation rate. El-Toufali et al. [24] studied the activity of hydrotalcite (HT) catalyst \([\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}]\) on polycondensation of BHET.

In this research, the synthesis of PET was studied in a laboratory scale unit via direct esterification of TPA and EG in the presence of antimony oxide catalyst. Then, a model of process was derived under esterification as well as polycondensation by applying mass balances for various species such as acid end groups, hydroxyl end groups, water, acid terephthalic concentration, ethylene glycol, ..., that is improvement of some previous models [22]. Output water in the esterification step and polymer intrinsic viscosity (molecular weight or degree of polymerization) were measured. Comparison of simulation and experimental results is in very good agreement. Solubility of TPA in reacting mixture is incorporated in the model. This is a new approach for modelling of PET production. Various aspects of model are presented by output results.

LABORATORY SCALE POLYMERIZATION UNIT

Figure 1 shows a schematic of PETSYN unit. Reaction unit consists of a 1 L stainless steel reactor, a condenser, two oil baths, and a cooling fan. Cooling section has a cooling bath down to -40ºC and vacuum pump. Digital control system has responsibility of...
transferring instruments signal to a computer (Pentium 4) and process control. Three PT100 temperature sensors were mounted inside reactor, in reactor jacket and oil bath. Reactor pressure was measured by a pressure transducer model 3248 from Tecsis Company. Ribbon type mixer was used in order to mix high viscous reactive mixture. A 1000 W bar type electrical heater was mounted around the reactor. Cooling of reactor was performed by air flow in a tube around reactor. On top of the reactor, there are six connections. These connections were used to mount temperature and pressure sensors, apply pressure by nitrogen, and connect vacuum pump. Motor mixer is a magnetic type that can tolerate 100 atm pressure and having 1.5 HP power could have 2500 rpm. Required vacuum was applied by a vacuum pump type JB-85N-250 from FastVac Company. All tasks of data acquisition were performed by computer via an I/O card model PCL-818L and corresponding terminal PCLD-8115 from AdvanTech.

**EXPERIMENTAL**

Terephthalic acid (TPA) and ethylene glycol (EG) were supplied by Tondgouyan Petrochemical Complex. Antimony oxide, supplied by Merck, was used as catalyst. Table 1 gives properties of raw materials. The synthetic procedure is as following: After weighing a required amount of each material, the first step was to dissolve antimony oxide in EG. Heating could increase the solvating rate. Then, TPA, EG, and antimony oxide were mixed gently to obtain a smooth and homogeneous mixture. The rest of mixing was performed in reactor at 40-60ºC. Air inside reactor was evacuated by nitrogen gas and mixing was performed under 4.5 atm and 60 rpm for 30 min. This step is normally called paste mixing. During paste mixing, EG is saturated by TPA as well as becoming as homogeneous as possible. Along paste mixing, temperature of condenser was set to 160ºC. This temperature is high enough to extract byproduct water in favour of esterification reaction, and is low enough for EG to return to reaction room. After mixing, reactor temperature was raised to 240ºC. Then, extracted water weight was measured and plotted as a measure of reaction extension. Esterification was completed when water weight reached a plateau. The time was normally 180 min. Finally, pressure was dropped and vacuum was applied to the reactor. At the same time, reactor temperature was raised to 280ºC. Figure 2 shows a typical temperature control result of the reactor and three steps of paste mixing, esterification, and polycondensation steps. Efforts for conden-
sation of EG were not successful. During this step, polycondensation reaction was dominant. After 150-180 min, the system was shut down and the product was evacuated via bottom valve. Product converted very fast to a crystalline state. However, it was evacuated in cold water to obtain amorphous polymer. Table 2 shows the results of some of the best runs. FTIR Test was performed in order to determine the nature of product. Figure 3 shows FTIR spectrum of polyethylene terephthalate product. A broad peak around 1100-1200 cm\(^{-1}\) indicates C-O bond. Carbonyl group, C=O bond, gives a peak in 1720-1730 cm\(^{-1}\). Hydroxyl group, O-H, gives broad peak in 2400-3400 cm\(^{-1}\) that has overlapped C-H peak. Aromatic C-H and C=H give a peak in 2969 cm\(^{-1}\) and 728 cm\(^{-1}\), respectively. Hence, it is a general polyester FTIR spectrum. Ubbelohde viscometer was used to determine intrinsic viscosity and molecular weight of product. Dichloroacetic acid along with 1C type Ubbelohde viscometer was used in 25 ± 0.1ºC. Figure 4 shows a typical Huggins and Kraemer plot that is measured for the produced PET. Consequently, molecular weight was calculated by Mark-Houwink formula.

\[
\eta_{\text{int}} = 0.0067 \left(\bar{M}_n\right)^{0.47}
\]

Table 3 shows the results of intrinsic viscosity (IV) and molecular weight.

### Reaction Mechanism

During esterification step, terephthalic acid reacts with ethylene glycol (eqn 1) [4]:

\[
\text{HO-CH}_2-\text{CH}_2-\text{OH} + \text{COOC}=\text{O} + \text{H}_2\text{O} \rightarrow \text{HO-CH}_2-\text{CH}_2-\text{O}-\text{COOC}=\text{O}
\]

**Table 2.** Conditions of experiments.

<table>
<thead>
<tr>
<th>Catalyst (ppm)</th>
<th>Sb(_2)O(_3) (g)</th>
<th>EG/TPA Ratio</th>
<th>EG (g)</th>
<th>TPA (g)</th>
<th>Run No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>0.1592</td>
<td>1.3</td>
<td>212.36</td>
<td>437.64</td>
<td>1</td>
</tr>
<tr>
<td>245</td>
<td>0.1592</td>
<td>1.3</td>
<td>212.36</td>
<td>437.64</td>
<td>2</td>
</tr>
<tr>
<td>245</td>
<td>0.1671</td>
<td>1.5</td>
<td>244.62</td>
<td>437.64</td>
<td>3</td>
</tr>
<tr>
<td>295</td>
<td>0.1918</td>
<td>1.3</td>
<td>212.36</td>
<td>437.64</td>
<td>4</td>
</tr>
</tbody>
</table>

**Figure 3.** FTIR spectrum of the polyethylene terephthalate product.

**Figure 4.** Typical Huggins-Kraemer plot for the produced PET.
In polycondensation, the following reaction occurs:

$$\text{tEG + tTPA} \rightarrow \text{tEG} + \text{tTPA + DEG} \quad (6)$$

Following side reactions were contributed in the model:

$$\text{tEG} \rightarrow \text{tTPA} + \text{AA} \quad (7)$$

$$\text{tEG} + \text{EG} \rightarrow \text{tTPA} + \text{DEG} \quad (8)$$

$$\text{tEG} + \text{tEG} \rightarrow \text{tTPA} + \text{tDEG} \quad (9)$$

All kinetic and thermodynamic parameters of rate equations were used as reported by Reimschuessel [21]. Law of mass action conservation was applied on undissolved terephthalic acid, dissolved terephthalic acid, ethylene glycol, diethylene glycol, water and polymer repeating unit, hydroxyl end group, and acid end group. General form of mass conservation law is:

$$\text{Accumulation} = \text{input} - \text{output} + \text{production} - \text{consumption} \quad (10)$$

**Mathematical Modelling**

Main reactions, which are involved in the model, are as following:

**Esterification:**

$$\text{EG} + \text{tTPA} \stackrel{k_1}{\longrightarrow} \text{tEG} + \text{W}$$

$$K_1 = \frac{k_1}{k_1^T} = \frac{[\text{tEG}][\text{W}]}{2[\text{tTPA}][\text{EG}]} \quad (4)$$

$$\text{tEG} + \text{tTPA} \stackrel{k_2}{\longrightarrow} \text{bEG} + \text{W}$$

$$K_2 = \frac{k_2}{k_2^T} = \frac{2[\text{bEG}][\text{W}]}{[\text{tTPA}][\text{tEG}]} \quad (5)$$

**Polycondensation:**

$$\text{tEG} + \text{tEG} \stackrel{k_3}{\longrightarrow} \text{bEG} + \text{EG}$$

$$K_3 = \frac{k_3}{k_3^T} = \frac{4[\text{bEG}][\text{EG}]}{[\text{tEG}]^2} \quad (6)$$

### Table 3. The results of intrinsic viscosity (IV) and molecular weight.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mn-Sim.</th>
<th>Mn-Exp.</th>
<th>IV-avg</th>
<th>IV-4</th>
<th>IV-3</th>
<th>IV-2</th>
<th>IV-1</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1978</td>
<td>2000</td>
<td>0.2385</td>
<td>0.237</td>
<td>0.2375</td>
<td>0.2390</td>
<td>0.2397</td>
</tr>
<tr>
<td>2</td>
<td>1576.5</td>
<td>1823.5</td>
<td>0.2284</td>
<td>0.2263</td>
<td>0.2284</td>
<td>0.2296</td>
<td>0.2292</td>
</tr>
<tr>
<td>3</td>
<td>1999.3</td>
<td>1823.5</td>
<td>0.2284</td>
<td>0.2263</td>
<td>0.2284</td>
<td>0.2296</td>
<td>0.2292</td>
</tr>
</tbody>
</table>

It should be mentioned that Reimschuessel [21] reported kinetic and thermodynamic parameters based on the mass of reactive mixture. Therefore, this point should be taken into consideration in the modelling.

**Mass balances are:**

$$\frac{d[\text{COOH}]}{dt} = -R_1 - R_2 + R_4 + R_5 + R_6 \quad (11)$$

$$\frac{d[\text{OH}]}{dt} = R_1 - R_2 - 2R_3 - R_4 - R_5 - R_6 \quad (12)$$

$$\frac{d[\text{bEG}]}{dt} = R_2 + R_3 \quad (13)$$

$$\frac{d[\text{W}]}{dt} = R_1 + R_2 - \dot{m}_W(t) \quad (14)$$

$$\frac{d[\text{EG}]}{dt} = -R_1 + R_3 - \dot{m}_{\text{EG}}(t) \quad (15)$$
RESULTS AND DISCUSSION

The above governing equations are highly non-linear ordinary differential equations. Moreover, changing reacting mixture is an algebraic equation. The fourth order Runge-Kutta method along with variable rate constant was applied to integrate equations numerically. Due to restriction in existing software, code for solving equations was written internally. The code was written using MATLAB. It should be emphasized that MATLAB command, for ODE solution, was not applied. Figure 5 shows the flow chart of solution. Upon definition of initial conditions, calculations of the esterification step start. Mass of reacting mixture was variable due to solubility of BHET and oligomers in EG. Hence, more TPA was dissolved in reacting mixture. Finally, calculation of the polycondensation step was performed. Figure 6 shows the comparison of simulated and measured water output. Results are in very good agreement. Difference between water output results could be explained by variation in pressure during the reaction (Figure 5). This suggests that control of pressure should be considered that is not an easy task. However, model prediction could improve by taking into consideration interfacial mass transfer. Most of published modelling results [8-14] were related to PET synthesis via DMT with zinc acetate catalyst. Other published results either were not compared by experimental results [11] or were given the model of esterification step [22]. Therefore, there is a need for improved model such as the above. Due to tough processing conditions, it is not easy to obtain sample during the course of reaction. Therefore, water output and molecular weight (via intrinsic viscosity) were available. Table 3 gives intrinsic viscosity results. Figure 7 shows other model outputs. Water production rate increases and then decreases. Furthermore, there is no significant water production during polycondensation. Ethylene glycol amount decreases gradually and during polycondensation there is more or less no ethylene glycol. There is, however, an increase in diethylene glycol and acetaldehyde during polycondensation. It could be concluded that temperature or some processing conditions should be controlled in order to avoid byproducts. It is interesting to consider the increase in reactive mass due to gradual solution of terephthalic acid in ethylene glycol and oligomers. After finishing TPA, there is a decrease in reactive mass. Acid end group
Figure 6. Comparison of experimental and simulation water output.

Figure 7. Model output of different parameters: (a) water and ethylene glycol output rates; (b) diethylene and acetaldehyde rates; (c) reacting mixture mass; and (d) acid end groups.
amount decreases along the reaction. Figure 8 shows variation amounts of acid terephthalic and hydroxyl end group. By decreasing the amount of TPA, reactive mixture weight increases. Hydroxyl end group shows a jump onset of vacuum. Due to equilibrium nature of reaction, there is an increase in rate in the beginning of polycondensation.

CONCLUSION

There is still a need for investigation in area of polymerization leading to polyethylene terephthalate. Hence, a laboratory scale unit was manufactured for synthesizing of PET. Polyethylene terephthalate was produced under various conditions. Mass balance was applied for different species. Finally, a set of non-linear ordinary differential equations were derived. These differential equations were integrated numerically by the fourth order Runge-Kutta method. Terephthalic acid, hydroxyl end group, diester group, water, ethylene glycol, diethylene glycol, acetaldehyde, reactive mixture mass, and acid end group concentrations are output of the written code. The results of simulated and measured value are in very good agreement.

ACKNOWLEDGEMENT

Authors would like to express their appreciation to Petrochemistry Research and Technology Company for providing financial support of this research.

ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>polyethylene terephthalate</td>
</tr>
<tr>
<td>BHET</td>
<td>bishydroxyl ethyl terephthalate</td>
</tr>
<tr>
<td>TPA</td>
<td>terephthalic acid</td>
</tr>
<tr>
<td>EG</td>
<td>ethylene glycol</td>
</tr>
<tr>
<td>DMT</td>
<td>dimethyl terephthalate</td>
</tr>
<tr>
<td>MWD</td>
<td>molecular weight distribution</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index</td>
</tr>
<tr>
<td>W</td>
<td>water</td>
</tr>
<tr>
<td>AA</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>DEG</td>
<td>diethylene glycol</td>
</tr>
<tr>
<td>tDEG</td>
<td>diethylene glycol terminated chain</td>
</tr>
<tr>
<td>COOH</td>
<td>carboxy acid</td>
</tr>
<tr>
<td>OH</td>
<td>hydroxyl group</td>
</tr>
</tbody>
</table>

NOMENCLATURE

\[
\begin{align*}
\dot{m}_{\text{AA}} & : \text{acetaldehyde output} \\
\dot{m}_{\text{EG}} & : \text{ethylene glycol output} \\
\dot{m}_{\text{W}} & : \text{water output} \\
\dot{r}_f & : \text{forward reaction rate equation} \\
\dot{r}_r & : \text{backward reaction rate equation} \\
R & : \text{overall reaction rate equation} \\
[x] & : \text{concentration of species}
\end{align*}
\]

REFERENCES


