Simulation and optimization of polyethylene terephthalate (PET) reactors*

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Abstract. Recent developments in the area of polymerization reactor design and optimization have been highlighted using polyethylene terephthalate (PET) as an example. Both the DMT and the TPA routes for its manufacture have been discussed and it has been demonstrated that a good understanding of the various physical processes present in industrial reactors is required before good models can be developed. The simulations carried out have been tested on some industrial scale reactors as well as pilot plants and improvements have been suggested based on these studies.

Keywords. Simulation; polymerization reactors; polyethylene terephthalate.
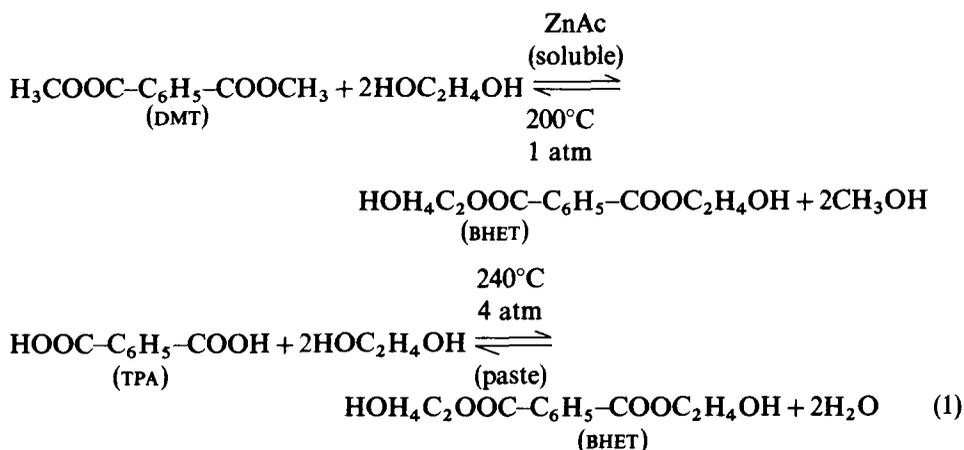
1. Introduction

Recently, a considerable amount of work has been reported on the simulation and optimization of industrial polymerization reactors. (Gupta and Kumar 1983a; Mashelkar 1983; Ray 1972; Ray and Laurence 1977; Reimschuessel 1977; Throne 1979). This is not unexpected since a large number of chemical industries are involved with polymers in some way or the other.

The major thrusts in the research in polymerization reaction engineering have proceeded along the following four directions: (a) various physical effects present on an industrial scale have been modelled successfully. These include the effects of imperfect mixing of the fluid elements, variations in the reaction times of the different fluid elements (residence time distribution) in flow reactors, spatial variation of temperature and vacuum, etc., on the course of polymerization (b) the effect of side reactions on the polymer manufactured (c) optimization of polymerization reactors using temperature, vacuum, feed concentration, etc., as control variables (d) optimal control of reactor operation near the design-conditions in spite of unplanned variations in the input variables like cooling-water temperature, etc. In this paper, some of the above aspects are discussed for one particular polymer, polyethylene terephthalate (PET), sold commercially as terene, dacron, etc.
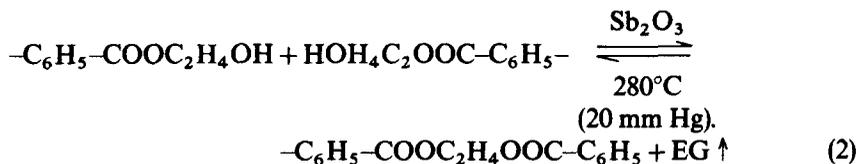
Two routes have been industrially used to manufacture PET. The major one uses dimethyl terephthalate (DMT) and ethylene glycol (EG). The other is from terephthalic acid (TPA) and EG which is now preferred. Polymerization is carried out in three stages because the equilibrium of the reaction is unfavourable for the formation of high molecular weight polymer and different conditions must be used as the polymerization progresses. In the first stage, DMT or TPA reacts with EG in a molar ratio of about 1 : 2 for 2–3 hr and the major reactions taking place are

$$\underset{\text{(DMT)}}{H_3COOC-C_6H_5-COOCH_3} + 2HOC_2H_4OH \underset{\substack{200°C \\ 1 \text{ atm}}}{\overset{\substack{\text{ZnAc} \\ \text{(soluble)}}}{\rightleftharpoons}}$$

$$\underset{\text{(BHET)}}{HOH_4C_2OOC-C_6H_5-COOC_2H_4OH} + 2CH_3OH$$

$$\underset{\text{(TPA)}}{HOOC-C_6H_5-COOH} + \underset{\text{(paste)}}{2HOC_2H_4OH} \overset{\substack{240°C \\ 4 \text{ atm}}}{\rightleftharpoons}$$

$$\underset{\text{(BHET)}}{HOH_4C_2OOC-C_6H_5-COOC_2H_4OH} + 2H_2O \qquad (1)$$

Under the conditions used, the condensation product (methanol or water) vaporizes along with EG. However, the vapours are distilled and the EG recycled to the reactor as shown in the flow sheet of figure 1. The main product of the first stage is BHET, though some higher oligomers are also formed.

In the second stage, the product of the first stage is subjected to a vacuum (pressure ~ 20 mm Hg) so that the following reaction takes place in the forward direction:

$$-C_6H_5-COOC_2H_4OH + HOH_4C_2OOC-C_6H_5- \overset{\substack{Sb_2O_3 \\ 280°C \\ (20 \text{ mm Hg}).}}{\rightleftharpoons}$$

$$-C_6H_5-COOC_2H_4OOC-C_6H_5 + EG \uparrow \qquad (2)$$

The above reaction is written in terms of reactive functional groups, which is the common practice in polymer engineering (Kumar and Gupta 1978). The residence time in this stage is about 2 hr. In the third stage, the reaction is the same as above, but a still
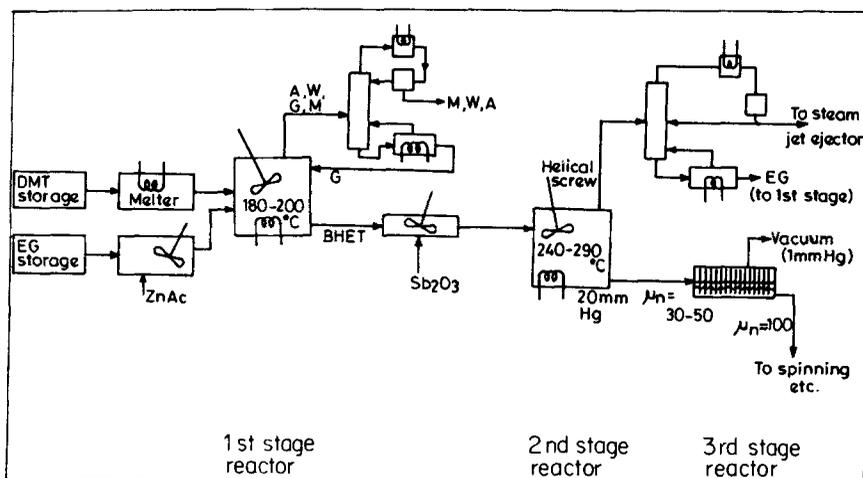

Figure 1. Flow chart of manufacture of PET from DMT + EG.

higher vacuum (0·5–1 mm Hg) is necessary to drive off the EG from the viscous reaction mass (which has the consistency similar to the dough required for making bread). Various devices are used to expose thin layers of the reaction mass to vacuum for a short period after which these are mixed with the bulk of the reaction mass—this process being repeatedly carried out. Figure 1 shows these stages in the form of a flow chart.
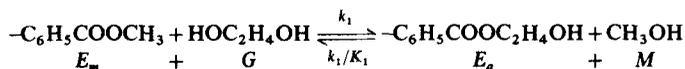
2. Simulation of the first stage reactor for the DMT route

The various reactions (including important side reactions) for all the stages are given in table 1 in terms of functional groups (Ravindranath and Mashelkar 1981). The formation of acetaldehyde (A) leads to discoloration of the final polymer and is, therefore, undesirable. Similarly, the diethylene glycol (DEG) and its end groups E_D lower the melting point and the tensile strength of the polymer while simultaneously improving its dyeability. Its concentration must therefore be kept below certain levels. The acid end groups (E_c) poison the catalyst and the water vapour W creates design
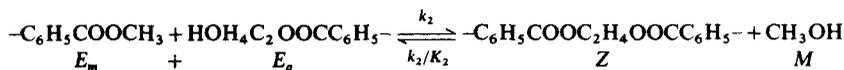
Table 1. Reactions occurring in PET manufacturing (Ravindranath and Mashelkar 1981).
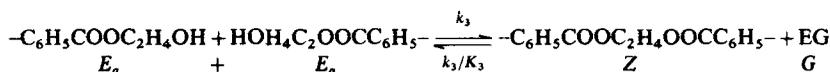
Major Reactions

1. Ester Interchange:

$$-C_6H_5COOCH_3 + HOC_2H_4OH \underset{k_1/K_1}{\overset{k_1}{\rightleftharpoons}} -C_6H_5COOC_2H_4OH + CH_3OH$$
$$\quad E_m \quad\quad + \quad G \quad\quad\quad\quad E_g \quad\quad + \quad M$$

2. Transesterification:

$$-C_6H_5COOCH_3 + HOH_4C_2OOCC_6H_5- \underset{k_2/K_2}{\overset{k_2}{\rightleftharpoons}} -C_6H_5COOC_2H_4OOCC_6H_5- + CH_3OH$$
$$\quad E_m \quad\quad + \quad\quad E_g \quad\quad\quad\quad\quad Z \quad\quad\quad\quad M$$

3. Polycondensation:

$$-C_6H_5COOC_2H_4OH + HOH_4C_2OOCC_6H_5- \underset{k_3/K_3}{\overset{k_3}{\rightleftharpoons}} -C_6H_5COOC_2H_4OOCC_6H_5- + EG$$
$$\quad E_g \quad\quad + \quad\quad E_g \quad\quad\quad\quad\quad Z \quad\quad\quad\quad G$$

Side Reactions

4. $-C_6H_5COOC_2H_4OH \xrightarrow{k_4} -C_6H_5COOH + CH_3CHO$
$\quad E_g \quad\quad\quad\quad E_c \quad + \quad A$

5. $-C_6H_5COOC_2H_4OH + HOC_2H_4OH \xrightarrow{k_5} -C_6H_5COOH + HOC_2H_4OC_2H_4OH$
$\quad E_g \quad\quad + \quad G \quad\quad\quad\quad E_c \quad + \quad DEG$

6. $-C_6H_5COOC_2H_4OH + HOH_4C_2OOCC_6H_5- \xrightarrow{k_6} -C_6H_5COOH + -C_6H_5COOC_2H_4OC_2H_4OH$
$\quad E_g \quad\quad + \quad\quad E_g \quad\quad\quad\quad E_c \quad\quad\quad\quad E_D$

7. $-C_6H_5COOH + HOC_2H_4OH \underset{k_7/K_7}{\overset{k_7}{\rightleftharpoons}} -C_6H_5COOC_2H_4OH + H_2O$
$\quad E_c \quad + \quad G \quad\quad\quad\quad E_g \quad\quad + \quad W$

8. $-C_6H_5COOH + HOH_4C_2OOCC_6H_5- \underset{k_8/K_8}{\overset{k_8}{\rightleftharpoons}} -C_6H_5COOC_2H_4OOCC_6H_5- + H_2O$
$\quad E_c \quad + \quad\quad E_g \quad\quad\quad\quad\quad Z \quad\quad\quad\quad + \quad W$

9. $-C_6H_5COOC_2H_4OOCC_6H_5- \xrightarrow{k_9} -C_6H_5COOH + -C_6H_5COOCH=CH_2$
$\quad\quad Z \quad\quad\quad\quad\quad\quad E_c \quad\quad\quad\quad E_v$

10. $-C_6H_5COOC_2H_4OH + H_2C=HCOOC_6H_5- \xrightarrow{k_3} -C_6H_5COOC_2H_4OOCC_6H_5- + CH_3CHO$
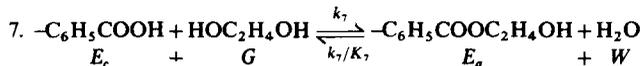$\quad E_g \quad\quad + \quad E_v \quad\quad\quad\quad\quad\quad Z \quad\quad + \quad A$
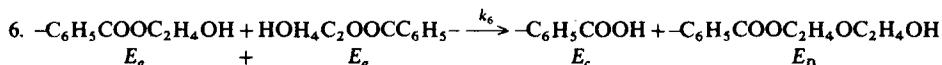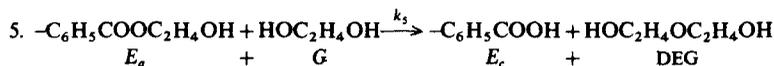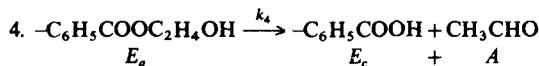
Table 2. Reaction rate and equilibrium constants.

Reaction number	Activation energy (Kcal/mol)	Frequency factor lit/mol. min or l/min	Equilibrium constants (independent of T)
1	15	4×10^4	0·3
2	15	2×10^4	0·15
			$K_2 = K_1 K_3$
3	18·5	$6·8 \times 10^5$	0·5
4, 5 and 6	29·8	$2·17 \times 10^9$ (ZnAc)	
		$4·16 \times 10^7$ (Sb_2O_3)	—
7	17·6	1×10^6	2·5
8	17·6	1×10^6	1·25
9	37·8	$3·6 \times 10^9$	—

$k_i = k_i^0 \exp(-E_i/RT)$. Data on rate constants from Fontana (1968) and Yokoyama *et al* (1978). Those on equilibrium constants from Challa (1960) and Chegyola *et al* (1979)

problems in the vacuum-system and so must also be controlled. The corresponding rate and equilibrium constants have been compiled in table 2.

Appropriate mass balance equations may be written for the various functional groups and the products of the reaction based on the kinetic scheme of table 1. In writing these equations, two important facts must be kept in mind. The first is that the volume of the reaction mass is a function of time because of vaporization and the other is that the concentration of the volatile products of the reaction (glycol, acetaldehyde, water and methanol) in the vapor phase are at thermodynamic equilibrium with the liquid phase. A simple application of Raoults law has been attempted, though better equations for thermodynamic equilibria of polymer solutions (like the Flory-Huggin's theory etc.) would be more appropriate (Ravindranath and Mashelkar 1982c). Detailed equations are available in Ravindranath and Mashelkar (1981, 1982a,c). Results for the first-stage reactor using typical industrially encountered temperature histories and feed (subscript 0) concentrations are shown in figure 2. It may be mentioned that some of these results have been found to match some industrial data but for proprietary reasor ɔ, details are not available.

With the mathematical model thus confirmed, the effect of changes in the operating conditions can be studied on the computer and based on these simulation studies, changes can be suggested to improve the performance of the plant.

3. Simulation of the second stage reactor (DMT Route)

The kinetic scheme used for the second stage (Ravindranath and Mashelkar 1982b) reactor is the same as that for the first stage but the rate constants corresponding to Sb_2O_3 catalyst (as given in Table 2) must be used. The mass-balance equations are also the same since the mass transfer rates are still fairly rapid, compared to the reaction rates. Figure 3 shows results for the following industrially encountered temperature
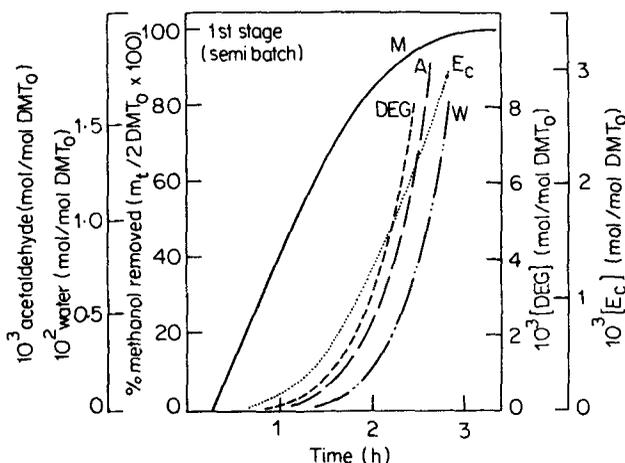
Figure 2. Results for stage I DMT + EG reactor. $[EG]_0/[DMT]_0 = 2$, ZnAc $= 5\cdot6 \times 10^{-4}$ mol/l, $T_0 = 140°C$, increased linearly at $30°C/hr$.

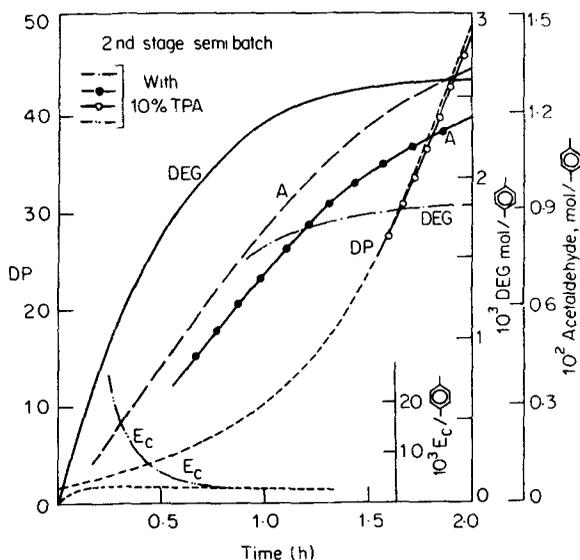**Figure 3.** Results for stage II DMT + EG reactor. T, p as in equation (3).

and pressure histories

$$T(°C) = 290 - 50 \exp[-1\cdot2\,t\,(hr)]$$

$$P(mm\,Hg) = 760 \exp[-1\cdot8587\,t + 1\cdot776\,t^2 - 1\cdot2527\,t^3] \tag{3}$$

The number-average chain length, μ_n (or DP), increases with time to about 50 in 2 hr, this variation being quantitatively confirmed. The addition of small amounts of TPA to the feed does not affect μ_n significantly, but leads to lower concentrations of E_c and thus to improved product quality (figure 3).

In a simultaneous study of the simulation of PET reactors, Kumar *et al* (1982a,b; 1983a) have incorporated the redistribution reaction

$$P_m + P_n \xrightarrow{k_r} P_{m+n-r} + P_r,$$ (4)

where P_m is a polymer molecule having m repeat units, as well as the cyclization reaction

$$P_m \rightleftharpoons C_m + G, m \geqslant 2,$$
$$P_m \rightleftharpoons C_{m-n} + P_n, m \geqslant 3,$$ (5)

and have computed the entire molecular weight distribution of the polymer formed. Reaction (4) does not alter the monomer conversion or the number-average chain length but does effect the molecular-weight distribution of the polymer, and so the product properties, whereas the cyclic oligomers C_m formed by reaction (5) give problems in the spinning of the fibre and must be suppressed. These workers found that the incorporation of these reactions led to significant lowering of the polydispersity index of the product. The rate constants used, however, were those for uncatalyzed reactions and so their study is not directly applicable to industrial plants. However, computationally efficient mathematical techniques to compute the polydispersity index of the polymer have been established by these workers.

4. Simulation of the third-stage reactor

The simulation of the third stage reactor poses the most formidable challenge in polymer reactor modelling. Several models have been developed (Amon and Denson 1980; Ault and Mellichamp 1972; Ghosh *et al* 1983; Gupta *et al* 1983b) to account for the complex interplay of fluid-flow phenomena, diffusion and chemical reaction. A simplified model has been used with the kinetic scheme for PET polymerization and the method of orthogonal collocation used to solve the set of mass-balance equations to obtain μ_n and the polydispersity index ρ as a function of the axial position in the reactor (Kumar *et al* 1983b). The rate constants for the catalyzed system have been used in generating the results. It is found that the final values of μ_n increases as the pressure is lowered but below a certain pressure, this effect is minimal. A curve-fit parameter is used by Ravindranath and Mashelkar (1983d) to explain some pilot-plant data of Yokoyama *et al* (1978). More work, however, is required in this area.

5. Optimization of PET (DMT route) reactors

Now that good models at least for the first and second stages of PET polymerization have become available, the stage is ready for optimization studies. For a design engineer, an appropriate objective function, I, to be minimized for stage I is

$$I = \alpha_1 [E_m]_{t_f}^2 + \alpha_2 \{([DEG] + [E_D])^2 + [E_v]^2 + [E_c]^2\}_{t_f},$$ (6)

where t_f is the reaction time and α_1 and α_2 are the weightage functions. The minimization of I maximizes the conversion of DMT while simultaneously minimizing the undesirable side products. Optimization techniques discussed by Denn (1969) may be used with the mass balance equations (state variables) to compute the optimal
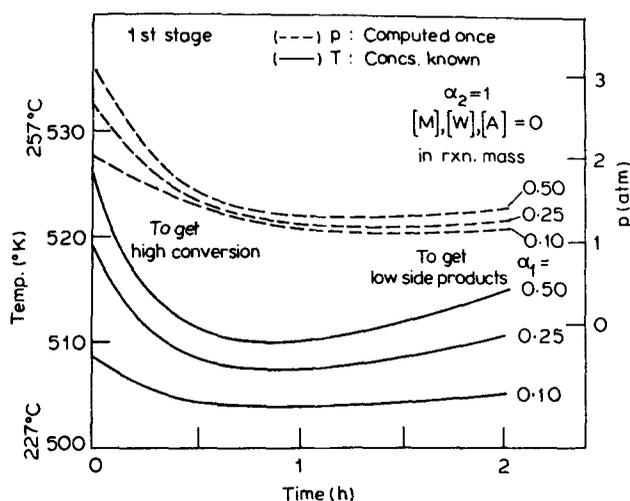
Figure 4. Optimal temperature profiles for stage 1 reactor. Reaction scheme of table 1 used (total pressure not constrained to be 1 atm.).

temperature history, $T(t)$. Figure 4 (Kumar *et al* 1983c) shows that higher temperatures should be used initially to speed up the monomer conversion, and then the temperature lowered to prevent the side-product concentrations from building up to very high levels. To keep the computations within manageable levels, the concentrations of M, W and A in the reaction mass were fixed at zero and Raoults law was used to compute the total pressure corresponding to the optimal temperature. It may be difficult to achieve high initial temperatures industrially and a more meaningful optimization problem would be to determine the optimal flow-rate history of the heating fluid and treat the temperature also as a state variable. Studies along these lines are in progress (Kumar *et al* 1983d). Similar optimal temperature histories for stage 2 polymerization have also been worked out, assuming that a *constant* vacuum is applied to the reaction mass.

6. PET from TPA Route

The kinetic scheme used for simulating the first stage of the polymerization of PET from TPA and EG (see equation (1)) is simpler and comprises of reactions 7, 8, 3, 4, 5 and 6 of table 1. However, the modelling of this reactor is far more difficult because the reaction mixture is a two-phase system, with the solid TPA being only slightly soluble in EG or the reaction medium. In addition, the acid end groups present in the reaction mass catalyze the various reactions. Kemkes (1969), found that the concentration of the –COOH groups in the liquid phase does not vary with time till the reaction mass is heterogeneous. This means that the rate of dissolution and diffusion of the TPA is very rapid and as soon as it is depleted by chemical reaction in the liquid phase, it is made up by dissolution from the solid phase. This behaviour is analogous to what happens in emulsion polymerization.

Mass balance equations for the first-stage reactor are more difficult than for the corresponding reactor from the DMT route and have been solved recently

(Ravindranath and Mashelkar 1982e). Information on the solubility of TPA in the reaction medium and on vapour pressures (required for flash computations as previously) has been incorporated. Similar results on the second-stage reactor *via* this route have also been presented recently (Ravindranath and Mashelkar 1982c). It has been found that sequences of stirred tank reactors operating at different temperatures are more useful than single reactors. Optimal studies for this route have yet to be carried out.

7. Conclusions

Recent efforts on the simulation and optimization of industrial polyethylene terephthalate reactors have been described. Some of the models developed have been tested on industrial reactors and based on simulation studies on a computer, changes in operating conditions can be suggested to improve the performance of the reactors. Future trends along these lines would include the simulation of solid-state polymerization, optimal control of existing reactors and the design of better reactors in the future.

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