

Kinetics and Thermodynamics of Hydrolytic Depolymerization of Poly(ethylene terephthalate) at High Pressure and Temperature

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ABSTRACT: Hydrolytic depolymerization of PET (polyethylene terephthalate) waste in excess of water was studied using a 0.5-L stirred high-pressure autoclave at temperatures of 100, 150, 200, and 250°C and at 200, 300, 400, 500, 700, and 800 psi (pounds per square inch) pressure. Velocity constants of hydrolysis were calculated from the experimental data obtained. Maximum depolymerization (91.38%) of PET into monomer was obtained at 250°C and 800 psi. However, the maximum rate of reaction was recorded at 200°C and 500 psi temperature and pressure,

respectively. The energy of activation and frequency factor were calculated, as 64.13 KJ/g mol and $7.336 \times 10^4 \text{ min}^{-1}$, respectively, for higher pressure and temperature conditions. It was also reported that the hydrolytic depolymerization is first order with the velocity constant $1.773 \times 10^{-2} \text{ min}^{-1}$ at 250°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3305–3309, 2003

Key words: activation energy; polyesters; thermodynamics; monomers

INTRODUCTION

Chemical recycling of waste polyester has attracted great attention in recent years as a means of obtaining valuable products.¹ In chemical recycling, PET is treated chemically to depolymerize it into TPA (terephthalic acid) or other useful oligomers.

Polyester waste can be depolymerized by alcoholysis,^{2,3} transesterification,^{4–6} and hydrolyses^{7–10} as a chemical recycling. The processes of acid, alkali, and water hydrolyses of PET waste in organic solvents have been reported by several researchers.^{11–16} The kinetics of glycolysis of PET waste powder at moderate pressure and temperature has been studied by Mishra et al.¹⁷ The kinetics of hydrolysis of PET in nitric acid could be explained by a modified shrinking-core model of a chemical reaction control in which the effective surface area is proportional to the degree of unreacted PET, affected by the deposition of the product TPA.¹³ Hydrolysis in sulfuric acid was accelerated because of an increase in the specific surface area of PET by formation and growth of pores and cracks.^{11,14,18}

The kinetics of PET hydrolysis in water has been studied at higher temperature and pressure. Ther-

mal and hydrolytic depolymerization of PET melt has also been studied.¹⁹ However, little effort has been made to study the kinetics and thermodynamics of depolymerization of PET waste at higher temperature and pressure conditions. In the present study, the kinetics and thermodynamics of PET hydrolysis are studied using a high-pressure autoclave at higher temperature.

EXPERIMENTAL

The PET used in all experiments is polyester waste obtained from Garware Polyester, Aurangabad, Maharashtra, India. The molecular weight of PET measured by a viscosity method in 3 : 5 (v/v) phenol-tetrachloroethane was 17,500.¹⁶ Water used was of high purity HPLC grade. The PET waste was chilled for its brittleness and grounded into desired a particle size (425 μm) to create the maximum surface area for heat and mass transfer in the reaction vessel. A 0.5-L capacity high-pressure autoclave was used for all hydrolytic depolymerization experiments. The autoclave was well equipped with a constant rotating stirrer at the speed of 500 rpm, which ensures the proper mixing of the reaction mixture.

The PET waste and water were charged in a vessel of the autoclave in the ratio of 1 : 30 (w/w). The vessel was heated for 2 h. After the specified time interval and the reaction temperature, the vessel was removed from the heating collar and cooled

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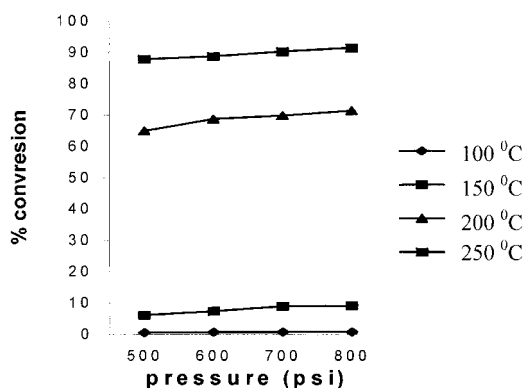
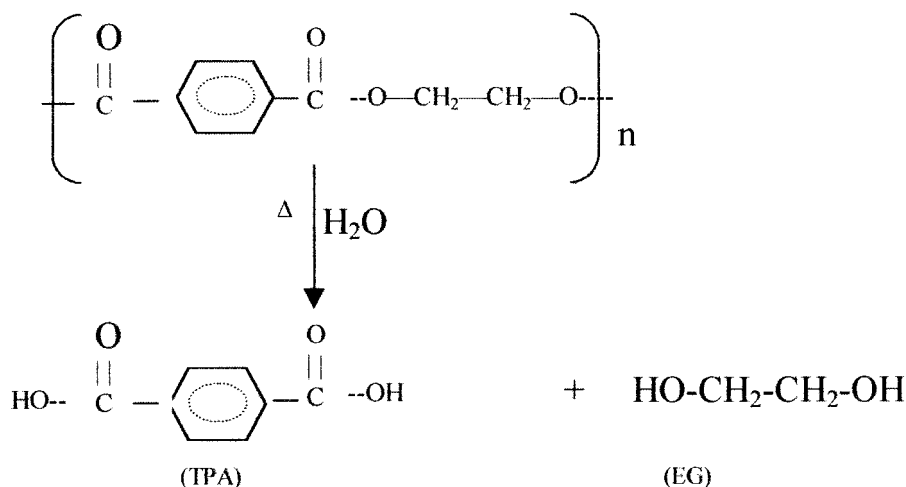


Figure 1 Effects of pressure on depolymerization of PET waste at 2 h reaction time and various temperatures.

suddenly. The vessel was subsequently opened and the product was removed. It was treated with sodium hydroxide to form a sodium salt of



Effect of temperature and pressure on hydrolytic depolymerization of PET waste

Figure 1 represents the effect of pressure on depolymerization of PET waste at 2 h reaction time and various temperatures. It evidents that at 100°C the depolymerization is negligible. Also, there is no significant effect on depolymerization. It has also been proven by constant values of the frequency factor and energy of activation at different pressures. At the above temperature, the percent conversion only increases from 0.52 to 0.85 by varying the pressure from 500–800 psi.. The percent conversion increases significantly from 62.00 to 91.38% at and above 200°C temperature by varying the pressure from 500 to 800 psi. At 250°C and 800 psi pressure the maximum conversion (91.38%) is recorded. However, a little effect of pressure on depolymerization is observed for a spe-

terephthalic acid, then acidified with hydrochloric acid; a white pure precipitate of TPA was obtained. It was filtered, dried, and weighed. Sodium hydroxide treatment followed by hydrochloric acid was given to obtain pure TPA. After drying, it was grounded up to fine powder using mortar and pestle. The TPA was analyzed by recording its FTIR spectra on a Hyper-IR from Shimadzu.

A similar experimental procedure was repeated for various pressures from 100 to 800 psi at 100, 150, 200, and 250°C separately. Similarly, for kinetic and thermodynamic studies, the experiments were carried out for the reaction time 30, 60, 90, 120, and 150 min at 200 and 250°C maximum temperatures.

RESULTS AND DISCUSSION

The reaction mechanism for depolymerization is represented below

cific temperature. The percent conversion increases drastically from a temperature of 150 to 200°C, and beyond that, there is less increment in depolymerization.

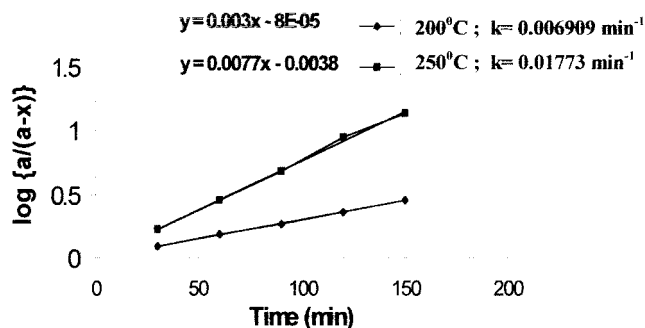


Figure 2 Variation of velocity constants with time at 200 and 250°C temperatures.

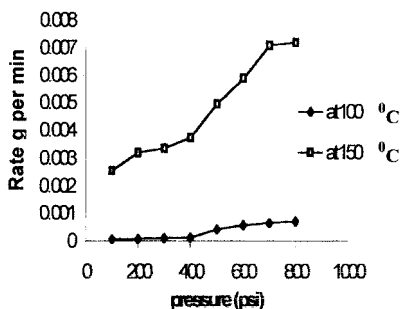


Figure 3 Variation of rate of reaction with pressure at 100 and 150°C temperatures.

Kinetics of hydrolytic depolymerization of PET waste

The kinetic study of depolymerization was undertaken on the basis of product depolymerized and its residue. The velocity constant of depolymerization was calculated by using formula $k = [2.303/t] \log [a/(a-x)]$, where a = initial weight of PET waste in grams, x = the amount of PET depolymerized in grams at time t , and k = the velocity constant of the reaction.

On the basis of results obtained, the velocity constant $1.773 \times 10^{-2} \text{ min}^{-1}$ is recorded for the depolymerization reaction at 200 and 250°C temperatures for 200 and 500 psi pressures, respectively (Fig. 2). The straight lines in the graph of $\log \{a/(a-x)\}$ vs time in minutes, which almost pass through the origin and slope, give the values of velocity constants 1.773×10^{-2} and $6.909 \times 10^{-2} \text{ min}^{-1}$, respectively, and show the first-order reaction kinetics.

The value of velocity constant (k) was employed in the law of mass action $R = k[\text{PET}]$, where R is the rate of reaction, and $[\text{PET}]$ is the concentration of PET at time t . Because k is constant, therefore, the rate of the reaction is directly proportional to the concentration of PET. The rate was calculated by

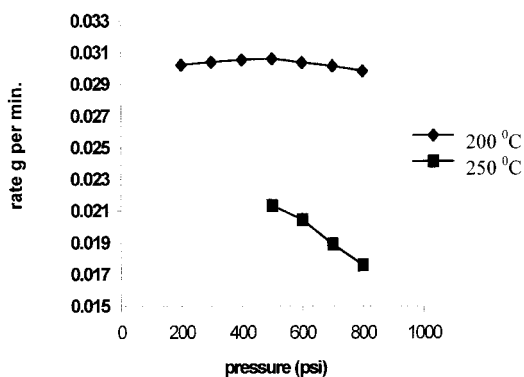


Figure 4 Variation of rate of reaction with pressure at 200 and 250°C temperatures.

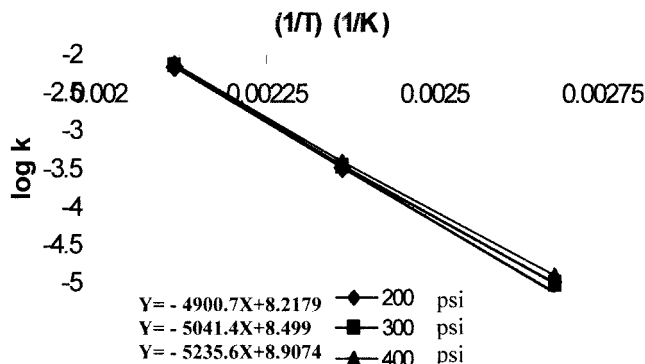


Figure 5 Variation of log k with 1/T at 200, 300, and 400 psi pressures.

carrying out the reactions at various temperatures, i.e., 100 to 250°C for pressures ranging from 100 to 800 psi (Figs. 3 and 4). The preheating periods of time for 200 and 250°C are 20 and 25 min, respectively, which are excluded from the reaction time. It is revealed from Figure 3 that at 100°C the increment in the rate of the reaction is gradual up to 500 psi, and beyond this pressure there is an increment in the rate of the reaction. However, the rate of reaction at 100°C is very low, which ranges from 0.0001 to 0.0007 g min⁻¹. On increasing the reaction temperature up to 150°C, the rate of reaction increases about 10 times to that of pressure applied at 100°C. Nevertheless, there is a gradual increment in the rate of the reaction unlike the reaction that occurs at 100°C. At higher temperatures, i.e., 200 and 250°C, the rate of the reaction is more or less 10 times more than recorded at 150°C for the respective pressure. It attains a maximum value at 200°C and 500 psi pressure, and then subsequently there is a decrease in the rate of the reaction with an increase in the pressure (Fig. 4). Thus, critical condition is obtained at 200°C and 500 psi for the maximum rate of the reaction. Above these conditions of pressure and temperature, the decrement in the rate of the reaction is due to the decrement in PET concentra-

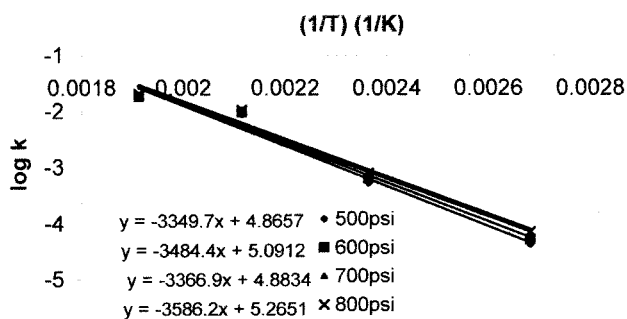


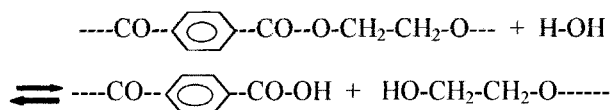
Figure 6 Variation of log k with 1/T at 500, 600, and 800 psi pressures.

tion, and generated TPA tends to adhere to the surface of PET particles.

Thermodynamics of hydrolytic depolymerization of PET waste

The energy of activation and frequency factor are obtained by plotting the Arrhenius graph $\log k$ vs $1/T$ at various pressures, as shown in Figures 5 and 6. The intercept and slope of the Arrhenius plot give a frequency factor and energy of activation, respectively. These two thermodynamic parameters at various pressures are shown in Table I. It is clear from above results that there is no significant increase in values of energy of activation and frequency factor with varying the pressure from 500 to 800 psi. Like the energy of activation, a change in enthalpy, Gibb's free energy, and entropy variations from 500 to 800 psi pressure are remarkable in decreasing order. Thus, 500 psi pressure for 200°C reaction temperature is the optimum condition (Table I).

As shown in the reaction, each chain scission utilizes one water molecule to form one each of carboxylic acid and ethylene glycol end groups. Therefore, the progress of the reaction was studied by measuring the concentration of the carboxylic group after a definite reaction time.



On the basis of work of Campanelli et al.,¹² the rate of carboxylic acid end group formation is expressed as

$$d[\text{COOH}]/dt = K C_{\text{PET}} \cdot C_{\text{water}} - k' C_{\text{COOH}} \cdot C_{\text{OH}} \quad (1)$$

$$Ke = k/k' \quad (2)$$

where k = the rate of the forward reaction (depolymerization), k' = the rate of the reverse reaction (condensation), Ke = the equilibrium constant, and C_{PET} = the concentration of PET.

$$Ke = \frac{[\text{COOH}][\text{OH}]}{[\text{PET}][\text{H}_2\text{O}]} \quad (3)$$

Because each hydrolytic chain breaking forms one molecule of carboxyl and one hydroxyl group, i.e., equimolar quantities of carboxyl group and hydroxyl group, eq. (3) therefore reduces to

$$Ke = \frac{[\text{COOH}]^2}{[\text{PET}][\text{H}_2\text{O}]} \quad (4)$$

Equations (2) and (3) were used to calculate the rate constant for the condensation reaction and equilibrium constant, respectively. Results are summarized in Table I.

CONCLUSION

The following conclusions can be drawn from this study:

1. The conversion of PET up to 150°C recorded less than 10%, while at 200°C and above, the temperature depolymerization increases with an increase in pressure from 62 to 91.38%.
2. The rate of depolymerization up to 150°C increases with an increase in pressure. But at 200°C and above, the increment in the rate is recorded up to 500 psi. Beyond it, the decrement is due to the deposition of TPA on PET particles as well as a decrement of concentration of PET.
3. The equilibrium constant Ke increases from 200 to 800 psi.
4. Energy of activation (E_a), change in enthalpy (ΔH), Gibb's Free energy (ΔG), and entropy (ΔS) decrease with an increase in pressure.
5. Negligible changes in the above parameters beyond 500 psi pressure result, as 500 psi is an optimum pressure at 200°C temperature.

TABLE I
Thermodynamic Parameters at 200°C for Various Pressures

Sr. no.	Pressure Psi.	E_a KJmol ⁻¹	ΔH KJmol ⁻¹	ΔG KJmol ⁻¹	ΔS KJmol ⁻¹	Ke	k' min ⁻¹	k min ⁻¹	Frequency factor (A) min ⁻¹
1	200	9135	9127	5.278	19.28	0.2613	0.02678	0.00699	8.076×10^8
2	300	8796	8788	4.801	18.57	0.2950	0.02472	0.00729	3.155×10^8
3	400	8551	8543	4.682	18.05	0.3041	0.02499	0.00759	1.651×10^8
4	500	6257	6249	2.579	13.21	0.5197	0.01683	0.00875	1.841×10^5
5	600	6079	6071	1.390	12.83	0.7023	0.01364	0.00958	1.233×10^5
6	700	5874	5866	0.859	12.39	0.8037	0.01241	0.00997	0.765×10^5
7	800	5844	5836	0.268	12.33	0.9339	0.01114	0.01041	0.734×10^5

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