

Kinetics of Neutral Hydrolytic Depolymerization of PET (Polyethylene Terephthalate) Waste at Higher Temperature and Autogenous Pressures

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ABSTRACT: Neutral hydrolytic depolymerization of PET (Polyethylene terephthalate) waste was studied using 0.5-L high pressure autoclave at the temperatures 100, 150, 200, 230, and 250°C at autogenous pressures 15, 80, 230, and 451 psi (pound per square inch) and time intervals of 60, 90, 120, and 150 min, respectively. The obtained terephthalic acid (TPA) was characterized by measuring its acid value and recording FTIR spectra. Depolymerization of the PET by neutral hydrolysis was found to be first order with velocity constant in the order of 10^{-2} min^{-1} . Energy of activation and frequency factor were obtained by slope and intercept of Arrhenius plot, which

were found to be $99.58 \text{ KJ mole}^{-1}$ and $2.9 \times 10^8 \text{ min}^{-1}$ respectively. Effect of temperature on rate of depolymerization reaction was also studied and optimized: rate of reaction increased drastically on increase in temperature from 150 to 200°C. Modified shrinking core model based on acid values focused the light on depolymerization of the PET into TPA by fragmentation due to formation of pores and cracks. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2179–2183, 2008

Key words: hydrolysis; depolymerization; kinetics; PET; TPA

INTRODUCTION

Chemical recycling of polyester waste, a method of obtainable valuable products has been of great attention in recent years.¹ In chemical recycling, PET is treated chemically to get depolymerized into TPA (terephthalic acid) or other useful oligomers. Polyester waste can be depolymerized by alcoholysis,^{2,3} *trans*-esterification^{4–6} and hydrolysis.^{7–10} Several researchers^{11–16} have reported processes of acid, alkali, and water hydrolysis of PET waste in organic solvents.^{11–16} Kinetics of glycolysis of poly (ethylene terephthalate) waste powder at moderate pressure and temperature has been studied by Mishra Goje.¹⁷ Kinetics of hydrolysis of PET in nitric acid has been explained by a modified shrinking-core model by Yashioka et al.,¹³ in which effective surface area is proportional to the degree of unreacted PET that affected by the deposition of the product TPA.

Besides kinetics of PET hydrolysis in water has been studied at higher temperature and autogenous pressure, thermal and hydrolytic depolymerization of PET melt has also been studied.¹⁸ Salting out method was used for recovery of ethylene glycol

(EG).¹⁹ However little efforts have been made to study the kinetics and thermodynamics of depolymerization of PET waste at higher temperature and autogenous pressure conditions. In present study, kinetics and thermodynamics of PET hydrolysis are studied at higher temperature and autogenous pressures using a high-pressure autoclave. We also propose the modified shrinking core model on the basis of measurements of acid values of depolymerized product during the course of depolymerization reaction.

EXPERIMENTAL

Depolymerization of PET waste at high temperatures and autogenous pressures

Polyethylene terephthalate (PET) waste obtained from Garware Polyester, Aurangabad (M. S.) was chilled for its brittleness then it was ground and sieved into 150- μm mesh size. About 10 g of PET waste of 150- μm mesh size and 250-mL distilled water were charged into the reactor of 0.5-L capacity high-pressure autoclave equipped with constant rotating stirrer at the speed of 600 rpm for the proper mixing of reaction mixture. The vessel was heated to various temperatures i.e., 100, 150, 200, 230, and 250°C for 120-min reaction time. Autogenous pressure developed at particular temperature in the vessel was responsible to increase the rate of

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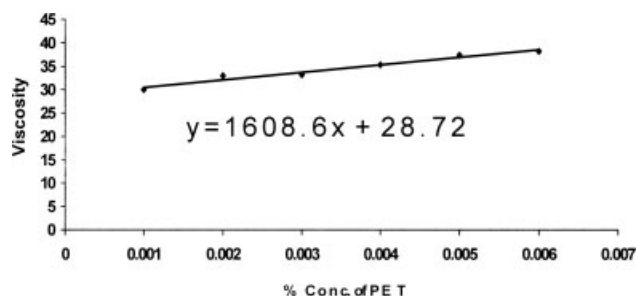


Figure 1 Variation of viscosity versus percent concentration (before hydrolysis).

depolymerization. After the specified time interval, the vessel was cooled suddenly by circulating cold water in vessel through inner coil. The vessel was opened by removing collar of the high-pressure autoclave. Product TPA was removed from the vessel. Obtained product was treated with the sodium hydroxide to form sodium salt of terephthalic acid then precipitated again as TPA by concentrated hydrochloric acid. A milky white precipitate was filtered, dried and weighed. After drying, it was ground to fine powder using mortar and pestle. The TPA obtained was characterized by recording the FTIR spectra on the Hyper FTIR of SHIMADZU make.

Percent depolymerization of PET waste

All neutral hydrolysis reactions were carried out in a batch reactor at various temperatures and times. Residual PET was washed with water, dried and weighed. Percent depolymerization of PET was determined by gravimetry and defined in following ways.

Percent depolymerization of PET

$$= \{(W_{(\text{PET})_0} - W_{(\text{PET})_t}) / (W_{(\text{PET})_0})\} \times 100 \quad (1)$$

where, $W_{(\text{PET})_0}$ is initial weight of PET and $W_{(\text{PET})_t}$ is weight of unreacted PET.

Determination of rate of reaction

The rate of reaction was experimentally determined by measuring the concentration of PET waste at various times. Law of mass action $R = k [\text{PET}]$ was used to calculate the rate of reactions.

Determination of molecular weight after and before hydrolysis

The viscosity average molecular weight of Polyester waste obtained from industrial waste was determined by using Ostwald's viscometer. About 0.1 g of PET powder of particle size 425 μm was dissolved

in the 100-mL solvent (3 : 5 v/v phenol and tetrachloroethane). To ensure the complete dissolution, solution was mildly heated on water bath; the solution formed was of 0.01% concentration. Using this solution, concentration of 0.001, 0.002, 0.003, 0.004, 0.005, and 0.006 were prepared. The time of flow for solvent and solutions were recorded in seconds. The graph of viscosity (η_{sp}/C) versus concentration (C) was plotted (Fig. 1). Intercept of the graph was 28.72. Intrinsic viscosity " η " is viscosity as concentration tends to zero, i.e., $(\eta_{\text{sp}}/C) = \eta$ as $C \rightarrow 0$, which is intercept of the graph. Molecular weight (M) was calculated by the formula

$$\eta = kM^\alpha \quad (2)$$

where, k and α values of solvent are 22.9×10^{-3} and 0.73, respectively. The molecular weight was recorded 17,500.

Similarly the molecular weight of PET was obtained after hydrolysis of PET waste. The intrinsic viscosity (intercept = 21.24) of the graph (Fig. 2) " η_{sp}/C " versus concentration " C " was used to calculate molecular weight of PET bottle sample, using formula $\eta = k M^\alpha$, where symbols have their usual meanings. k and α values of above solvent are 22.9×10^{-3} and 0.73, respectively. The molecular weight was recorded as 11,609.

Determination of acid value

The acid value determination was carried out with 1 g of material by using suitable solvent. The sample was titrated with standard solution of KOH using phenolphthalein indicator. Following relationship was used to calculate the acid value.²⁰

Acid value =

$$\frac{5.61 \times \text{volume of N/10 KOH required in mL}}{\text{Weight of the sample taken in gram}} \quad (3)$$

Similar experimental procedure was repeated for various temperatures such as 150, 200, and 250°C. Experiments were carried out in batches for reaction time viz 30, 60, 90, 120, and 150 min to study the kinetics of depolymerization reaction.

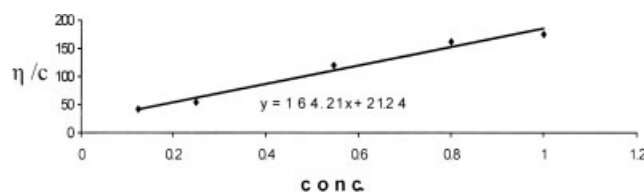


Figure 2 Variation of viscosity versus percent concentration (after hydrolysis).

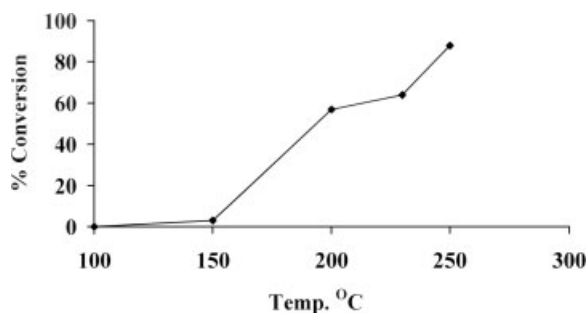
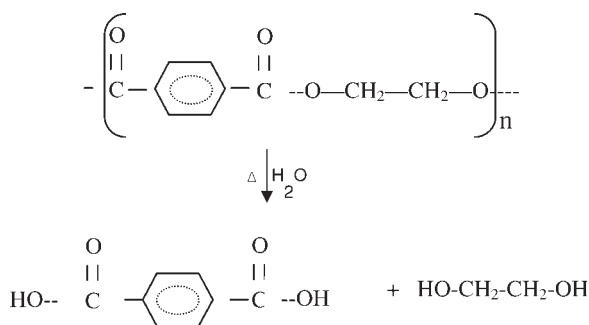


Figure 3 Variation in percent conversion of PET on hydrolytic depolymerization with temperatures.

RESULTS AND DISCUSSION

The reaction mechanism for depolymerization is represented below



Effect of temperature and autogenous pressure on depolymerization of PET waste

Figure 3 represents the effect of temperature at autogenous pressure on depolymerization of PET waste at 2-h reaction time. It is evident from the figure that percent conversion at 100°C is negligible (0.08%), and increases very slowly from 100 to 150°C (from 0.08 to 3.08%). But percent conversion increases very sharp, up to 56%, on increasing temperature from 150 to 200°C. Further, increment in rate of percent conversion is less due to increase in temperature from 200 to

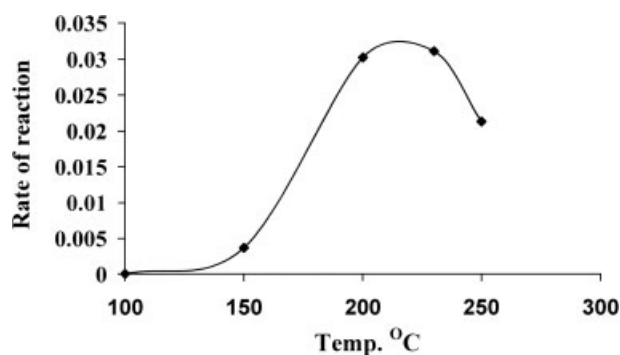


Figure 4 Variation in rate of reaction of hydrolytic depolymerization of PET with temperatures.

TABLE I
Kinetics of Neutral Hydrolytic Depolymerization of PET Waste at 200°C Temperature and at Autogenous Pressure

Time (min)	[PET] ₀ (g)	[PET] _t (g)	Velocity constant (k) min ⁻¹
30	10	7.168	1.11 × 10 ⁻²
60	10	5.138	1.111 × 10 ⁻²
90	10	3.716	1.100 × 10 ⁻²
120	10	3.618	1.111 × 10 ⁻²
150	10	1.864	1.120 × 10 ⁻²

250°C. However percent conversion of PET is recorded maximum as 87.83% at 250°C temperature. It is due to very fast reaction at high temperature, hence maximum conversion occurs at shorter period of time. Moreover, the conversion of PET starts from 150°C, which is onset of conversion; therefore reaching to a certain temperature i.e., 200, 230, and/or 250°C, the reactant gets converted proportionally. Because, according to the law of mass action, the rate of reaction is directly proportional to concentration of reactants. Hence rate of reaction decreases at higher temperatures. This is due to reduced concentration with reduced surface area of the reactant (PET) left and also deposition of terephthalic acid (TPA) particles on unreacted PET. Yashioka et al.¹⁴ have observed the deposition of TPA particles on unreacted PET that hinders the depolymerization of PET. It has also been studied by us taking a single particle for depolymerization under the condition of with and without stirring. It has been observed that the particle size reduces more under the stirring condition, and depolymerized TPA amount was found less on the surface of particle. While without stirring condition, it is *vice versa*.

Kinetics and thermodynamics of neutral hydrolytic depolymerization of PET waste

Kinetics of depolymerization of PET waste was studied by measuring the amount of TPA obtained and PET residue left after the depolymerization reaction.

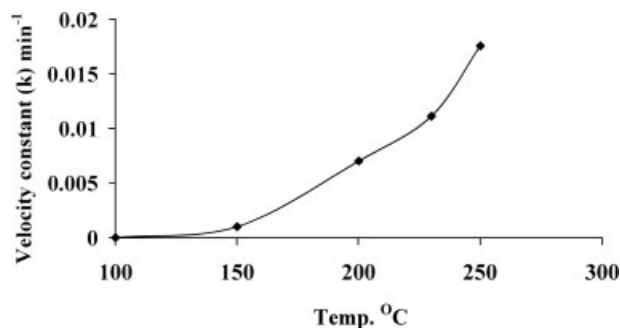


Figure 5 Variation in velocity constants of PET on hydrolytic depolymerization with temperatures.

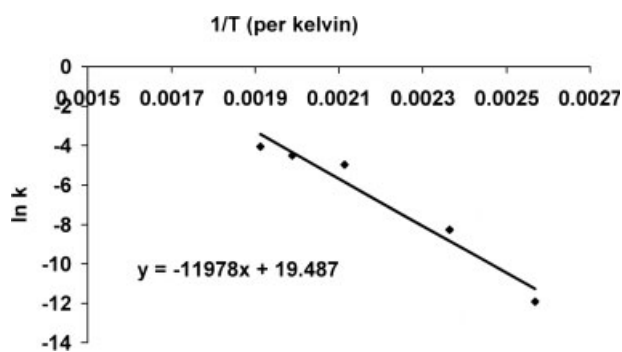


Figure 6 Arrhenius plot for hydrolytic depolymerization of PET waste.

The values of velocity constant (k) of depolymerization reaction were calculated by the formula,

$$k = \frac{2.303}{t} \log \frac{[\text{PET}]_0}{[\text{PET}]_t} \quad (4)$$

where, $[\text{PET}]_0$ is initial weight of PET waste in gram. $[\text{PET}]_t$ is weight of PET waste at time “ t .”

The values obtained for velocity constant indicate that the above formula fits for the depolymerization reaction. Like Figure 3 the rate of reaction increases very fast from 150 to 230°C (Fig. 4). However further increase in temperature up to 250°C, the rate of reaction decreases unlike percent conversion of PET. As discussed earlier in the text, the reaction of PET conversion starts from 150°C and rate of reaction is proportional to temperature. Therefore, from 150°C to the desired temperature i.e., 250°C, the depolymerization reaction is occurring which is not included in present study. The rate of reaction and velocity constant are accounted for period of particular temperature, therefore the velocity constants are continuously increasing, while rate of reaction shows decrement after 250°C. Based on the optimization of temperature, 200°C is the optimum temperature. The

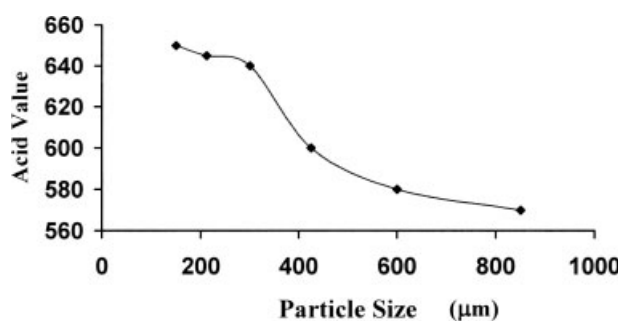


Figure 8 Variation in acid values on hydrolytic depolymerized product of PET with particle size of PET.

reaction time was also optimized, maintaining 200°C reaction temperature, ranging from 30 to 150 min at the interval of 30 min (Table I). Result shows that depolymerization reaction is of first order with the velocity constant in the order of 10^{-2} min^{-1} . Figure 5 shows increase in velocity constant with temperature. It is evident from the figure, the velocity constant of the reaction is in the order of 10^{-6} min^{-1} up to 150°C temperature, and it is recorded in range of 10^{-3} min^{-1} from 150 to 200°C. Further, velocity constant increases linearly up to a temperature of 250°C. Velocity constant at 250°C is found to be maximum as $1.757 \times 10^{-2} \text{ min}^{-1}$.

Energy of activation and frequency factor are obtained by plotting Arrhenius graph $\ln k$ versus $1/T$. Intercept and slope of the graph (Fig. 6) provide frequency factor and energy of activation, respectively. The energy of activation and frequency factor are found to be $99.58 \text{ KJ mole}^{-1}$ and $2.9 \times 10^8 \text{ min}^{-1}$, which show that the hydrolytic depolymerization reaction, at autogenous pressure, is faster at lower energy of activation with high degree of collision of reacting molecules. The FTIR spectra of TPA obtained during depolymerization reaction and control TPA were recorded and found to be identical as shown in Figure 7.

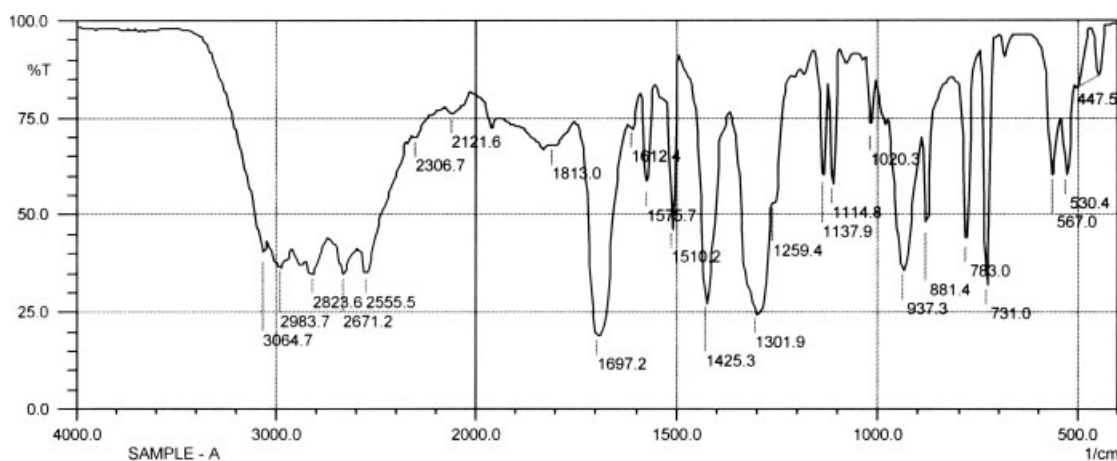


Figure 7 IR spectra of TPA obtained during hydrolytic depolymerization of PET waste.

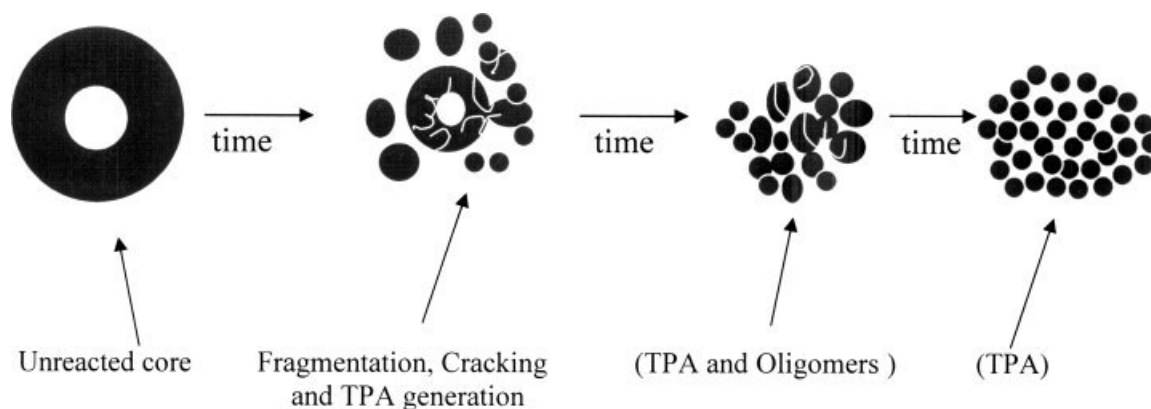


Figure 9 Simultaneous fragmentation and depolymerization model.

Modified shrinking core model

The PET waste of different particle sizes was depolymerized by neutral hydrolysis. Acid value of obtained depolymerized product (TPA) was measured,²¹ which was found to be in the range of 650–570. The acid value of pure TPA of S. D. Fine chemicals was recorded as 655. Figure 8 shows the significant depolymerization for the smaller particles size, and hence have greater acid value. But as the particle size increases, the acid value decreases due to lower rate of depolymerization. Acid values are inversely proportional to the particle of PET waste. Increase in depolymerization of the PET waste of smaller particle size may be due to formation of pores on the surface of PET particles and their fragmentation. The simultaneous depolymerization and fragmentation of PET is illustrated in Figure 9. Kurokawa et al.²² have determined the molecular weight of the depolymerized PET chains into oligomers by GPC, which occurs in second step. The depolymerization is at random position on polymer chains. In the third step oligomers convert into monomers, which is in presence of aluminum triisopropoxide (AIP) catalyst.

CONCLUSIONS

Following conclusions can be drawn from this study.

1. Hydrolytic depolymerization PET is negligible up to 150°C; beyond 150°C there is significant percent conversion observed (i.e., 87.83%).
2. Hydrolytic depolymerization of PET at autogenous pressure is first order reaction with velocity constant of the order of 10^{-2} min^{-1} .
3. Rate of reaction increases from 150 to 200°C, which is due to initially higher concentration of PET; further decrement in rate on increase in temperature is due to less concentration of PET and deposition of TPA on fragmented PET particles.
4. The energy of activation ($99.58 \text{ KJ mole}^{-1}$) and frequency factor ($2.9 \times 10^8 \text{ min}^{-1}$) show

requirement of less energy for hydrolytic depolymerization with a high degree of collisions.

5. Acid values recorded for the depolymerized product strengthen the modified shrinking core model with simultaneous fragmentation and depolymerization.

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