

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Alkaline Hydrolysis of Waste Poly(Ethylene Terephthalate): A Modified Shrinking Core Model

Santosh Kumar^a; Chandan Guria^a

^a Department of Polymer Engineering, Birla Institute of Technology, Ranchi, India

To cite this Article Kumar, Santosh and Guria, Chandan(2005) 'Alkaline Hydrolysis of Waste Poly(Ethylene Terephthalate): A Modified Shrinking Core Model', Journal of Macromolecular Science, Part A, 42: 3, 237 – 251

To link to this Article: DOI: 10.1081/MA-200050346

URL: <http://dx.doi.org/10.1081/MA-200050346>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Alkaline Hydrolysis of Waste Poly(Ethylene Terephthalate): A Modified Shrinking Core Model

SANTOSH KUMAR AND CHANDAN GURIA

Department of Polymer Engineering, Birla Institute of Technology, Ranchi, India

Hydrolytic decomposition of waste poly(ethylene terephthalate) (PET) is studied in the presence of an aqueous potassium hydroxide solution. A modified shrinking core model with a depleting product layer of waste PET is developed under finite solution volume conditions. An analytical solution is obtained for the model based on average molar distribution coefficient of aqueous potassium hydroxide solution. This model assumes the first order depolymerization kinetics with respect to the concentration of potassium hydroxide solution. The conversion of the waste PET is determined after filtration of the unreacted PET left after depolymerization. The conversion of PET is also compared with the amount of terephthalic acid obtained after acidification of the filtrate. Infra red (IR) spectroscopy studies of unreacted PET samples at different hydrolysis time intervals are carried out. It is observed that the transmittance at $\sim 1700\text{ cm}^{-1}$ decreases gradually with reaction time, which confirms the increased concentration of carbonyl group generated from aryl carboxylic acid group and the major reaction is occurring on the polymer chain end on the solid PET surface. Average molar distribution coefficient of aqueous potassium hydroxide solution, intrinsic PET depolymerization rate constant, frequency factor and activation energy of PET depolymerization are estimated based on the modified shrinking core model.

Keywords waste PET, recycle, depolymerization, hydrolysis, shrinking core model

Introduction

Poly(ethylene terephthalate) (PET) is a thermoplastic saturated polyester and is largely consumed in textile industries for fabrics, electronic industries for audio-video tapes, and the packaging industry for soft drink bottles. Wide applications of PET in the packaging industries is mainly due to its high strength, low weight, low permeability to gases (mainly CO_2), good light transmittance, smooth surface and no side effects on human bodies. To prevent ecological imbalance, the main interest in PET recycling is continuously increasing due to its substantial production in waste stream and its high resistance to the atmospheric and biological agents. Considering the economic aspects, chemical recycling of waste PET, a post consumer condensation polymer, has been gaining growing attention in recent years (1). The common methods of chemical recycling or depolymerization of waste PET is reviewed by Paszun and Szychaj (2) and

Received and accepted June 2004

Address correspondence to Chandan Guria, Department of Polymer Engineering, Birla Institute of Technology, Mesra-835215, Ranchi, India. Fax: +91-0651-2275401. E-mail: guria@iitk.ac.in

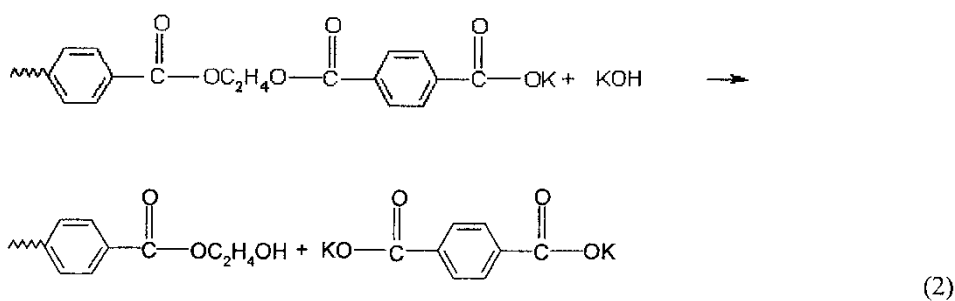
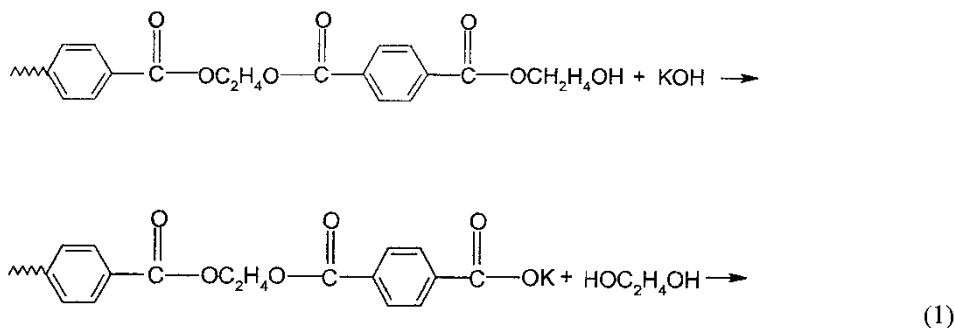
these methods are methanolysis, glycolysis, and hydrolysis of which hydrolysis of PET to terephthalic acid (TA) and mono ethylene glycol (MEG) is the prime importance. In hydrolytic decomposition, TA and MEG are recovered and can be used directly for the synthesis of virgin bottle grade PET (3–5). Industrial hydrolytic decomposition of PET is carried out at a high temperature, which is usually above the melting point of the resin using zinc acetate as a catalyst (6–8). Hydrolysis of PET is usually carried out in the presence of strong acids (e.g. sulphuric acid (9–13), nitric acid (14) and hydrochloric acid (15, 16)) and strong bases (e.g. sodium hydroxide (17, 18) and potassium hydroxide. (18–20)) Neutral hydrolysis (21–23) is also reported in the presence of water and/or steam. Hydrolytic decompositions of waste PET with strong acid is usually carried out at a high temperature for a prolonged period to get reasonable conversion of PET (12–16). Decompositions of waste PET particles with a strong base is usually carried out at a high temperature under autogeneous pressure (17, 18). Alkaline hydrolysis of PET in the presence of an organic solvent is also reported in the literature (24–27). However, very few have studied the reaction kinetics of alkaline hydrolysis (18) of PET. Zeronian et al. (28, 29) have studied PET depolymerization kinetics at ambient temperature with sodium hydroxide and fails to predict the high conversion of PET depolymerization. Wan et al. (17) have studied the solid-state hydrolysis by NaOH and KOH and concluded that hydrolysis by KOH is superior over NaOH due to improved conversion. They have also reported the kinetic parameters for the PET depolymerization at elevated pressure in aqueous KOH solution (18). The existence of a moving boundary during hydrolytic decomposition of PET particles in acid and alkaline medium is reported by Yoshioka (13, 14) and Wan et al. (18), respectively. A kinetic model based on alkaline hydrolysis is developed by Wan et al. (18) and assumes a negligible change in the surface area of the reacting PET particles during hydrolysis, which is not true during hydrolysis of PET particles. Moreover, this model does not hold well at complete conversion of the PET particles. The proposed model of Wan et al. (18) gives the contradicting relationship between conversion and size of the PET particles, which is not in accord with solid-liquid non catalytic reactions (30, 31). This model also assumes the identical KOH concentration at the bulk and surface of PET particles. It is not applicable at low bulk concentration of the aqueous KOH solution, as well as at higher PET conversion. Therefore, the present work involves the development of a moving boundary transport model for hydrolytic depolymerization of waste PET particles considering the shrinking core behavior of reacting PET particles with a continuous depleting product layer (i.e., formation of MEG and salt of TA) accounting for the effect of surface concentration (molar distribution coefficient) of aqueous KOH solution under finite solution volume conditions. The effects of particle size, molar ratio between PET repeating units to potassium hydroxide, and the reaction temperature on PET depolymerization are also studied. Depolymerization parameters like intrinsic reaction rate constant, frequency factor and activation energy for PET decomposition are estimated through the proposed modified shrinking core model. This model also predicts the average molar distribution coefficient of aqueous KOH solution during PET depolymerization.

Experimental

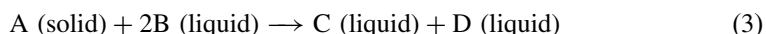
Model Development

The possibility of the moving boundary process in hydrolytic decomposition of waste PET arises when conversion of PET to potassium salt of TA and MEG involves

the consumption of alkaline hydroxide. In this moving boundary problem under finite solution volume conditions, depolymerization products are completely soluble in an aqueous alkali solution and shrinking behavior arises due to the gradual depletion of solid PET materials from the surface. Depolymerization of PET in the presence of aqueous potassium hydroxide solution occurs via random scission of ester linkage on the solid PET surface and requires two moles of potassium hydroxide for disappearance of each mole of PET repeating unit. However, the decomposition reaction of PET repeating units proceeds according to Eqs. (1) and (2) (18):



Here, the first reaction indicates the formation of potassium salt at the polymer chain end, whereas the second reaction shows the complete dissociation of one PET repeating unit giving MEG and potassium salt of TA. Assuming Eq. (1) is the rate-determining step (18), depolymerization of PET follows first order kinetics with respect to the potassium hydroxide concentration. The overall hydrolytic decomposition of PET can be written in the following simplified form:



where, A, B, C, and D are the PET repeating unit, KOH, MEG and potassium salt of TA, respectively. In order to describe the moving boundary process of PET depolymerization kinetics with a depleting soluble product layer under finite solution volume conditions, the following assumptions and simplifications are made in the present work:

The depolymerization of PET is a slow process and overall hydrolysis is kinetically controlled.

Reaction takes place at the boundary of the liquid and solid.

Reversible reaction of PET decomposition is neglected due to the formation of soluble salt of TA and MEG.

The PET particles consist of isotropic spherical particles of equal constant diameter. The PET particles are considered as quasi-homogeneous phase for mathematical treatment.

Molar distribution coefficient of aqueous KOH solution remains constant during a given set of depolymerization experiment.

The PET particles undergo negligible swelling during depolymerization.

Net reaction volume is constant throughout the depolymerization process.

According to assumptions 1–8, the rate of depolymerization reaction (13, 14, 18) ($-r_A$) of waste PET through alkaline hydrolysis (or the rate of formation of MEG or the salt of TA) can be written in the following form (30, 31):

$$-\frac{1}{4\pi r^2} \frac{dN_A}{dt} = -\frac{b}{4\pi r^2} \frac{dN_B}{dt} = bk \bar{C}_B \quad (4)$$

Where, N_A is the number of moles of PET repeating units present in the polymer chain, N_B is the number of moles of KOH, r is the radius of the PET particles (moving reaction front), \bar{C}_B is the molar concentration of aqueous KOH solution at the surface of the PET particles, k is the intrinsic depolymerization rate constant, t is the depolymerization time and b is a constant, which is related to the stoichiometric coefficient in the PET depolymerization reaction in Eq. (3) Writing Eq. (4) in terms of the shrinking core radius (r) gives:

$$-\rho_A \frac{dr}{dt} = bk \bar{C}_B \quad (5)$$

where, ρ_A is the molar density of PET particles.

KOH concentration at the PET surface can be correlated with the bulk concentration of KOH using following equilibrium relation:

$$\bar{C}_B = \lambda C_B \quad (6)$$

where, λ is the molar distribution coefficient of aqueous KOH solution. Here it is assumed that instantaneous equilibrium is established at the PET interface during a slow depolymerization reaction.

Substituting $C_B = [N_{A0}(M - 2X_A)]/V_0$ and $r = r_0(1 - X_A)^{1/3}$, one can obtain the following expression for the conversion of PET particles (X_A) using Eqs. (5) and (6):

$$\frac{dX_A}{dt} = K(M - 2X_A)(1 - X_A)^{\frac{2}{3}} \quad (7)$$

where, K is a modified first order depolymerization rate constant and is given by:

$$K = \frac{3b\lambda k N_{A0}}{\rho_A r_0 V_0} \quad (8)$$

Here, V_0 is the total volume of the reaction mixture at the start of the batch, N_{A0} is the initial number of moles of PET repeating units, r_0 is the initial size of PET particles M is the initial molar ratio of potassium hydroxide to PET repeating units, respectively. Assuming the molar distribution coefficient is independent of the change in the concentration of KOH during the hydrolytic decomposition of PET for a given set of experiments,

Eq. (7) can be integrated for $M > 2$ and/or $M < 2$ with the appropriate initial conditions (i.e., at $t = 0$ and $X_A = 0$) to yield:

$$\begin{aligned} & \frac{1}{4c^2} \ln \left\{ \frac{(c \pm z)^3}{c^3 \pm z^3} \right\} \pm \frac{\sqrt{3}}{2c^2} \arctan \left(\frac{2z \mp c}{c\sqrt{3}} \right) \\ & = -Kt + \frac{1}{4c^2} \ln \left\{ \frac{(c \pm 1)^3}{c^3 \pm 1} \right\} \pm \frac{\sqrt{3}}{2c^2} \arctan \left(\frac{2 \mp c}{c\sqrt{3}} \right) \end{aligned} \quad (9)$$

where,

$$c^3 = \left| \frac{(M-2)}{2} \right| \quad (10)$$

$$z = (1 - X_A)^{\frac{1}{3}} \quad (11)$$

Here, the upper sign is applicable to $M > 2$ and the lower one for $M < 2$. If $M = 2$, Eq. (9) can be integrated to yield:

$$\frac{1}{(1 - X_A)^{2/3}} = \frac{4}{3}Kt + 1 \quad (12)$$

Equations (9) and (12) represent the conversion of PET particles as a function of time at any given value of the molar ratio. The left hand side of Eqs. (9) and (12) can be plotted against t , and K can be evaluated from the slope of the linear plot. Hence, the values of λk for different molar ratio of KOH to PET repeating units can be evaluated for values b , N_{A0} , ρ_A , r_0 and V_0 .

Commercially available mineral water, beverage and soft drink bottles, which constituted the bulk of waste PET, were used to carry out the depolymerization experiments. These waste PET bottles were cut into small pieces by kneaders. To determine the depolymerization rate, PET particles were sieved to obtain four fractions (I-IV) with average particle diameters (r_0) 0.00168, 0.0012, 0.0010, and 0.00070 m. Size fraction III constituted the bulk of the waste PET particles and the density of these particles was found to be 1385.40 kg m⁻³. Intrinsic viscosity, $[\eta]$ of waste PET particles was measured in a 6:4 (w/w) phenol/1,1,2,2 tetrachloroethane solution at 30°C using Ubbelohde viscometer and was estimated as 0.8085 dL g⁻¹ (Fig. 1). The average molecular weight (\overline{MW}) of the waste PET particles is determined from the Mark-Houwink equation (18) Eq. (13) and was found to be 26.468 kg mol⁻¹.

$$\overline{MW} = 3.61 \times 10^4 [\eta]^{1.46} \quad (13)$$

PET depolymerization was carried out in a standard glass lined micro-autoclave. The micro-autoclave was dipped in a silicon oil bath equipped with an agitator and automatic temperature controller to maintain a constant temperature for depolymerization. The waste PET particles with the desired particle size and aqueous KOH solution with fixed molar ratio (PET repeating units to KOH) were charged together into the autoclave and placed into the thermostatic bath at the desired temperature. For molar ratio of 1:4, 1.0 gm of PET particles ($r_0 = 0.001$ m) and 1.1667 gm dry KOH were added in 10 mL of double distilled water to the autoclave. At regular time intervals, the depolymerization mixture was taken out and quickly quenched to room temperature by spraying cold water. The cooled reaction mixture was filtered to complete the removal of the potassium salt of TA and MEG by washing with double distilled water. Unreacted PET was dried under

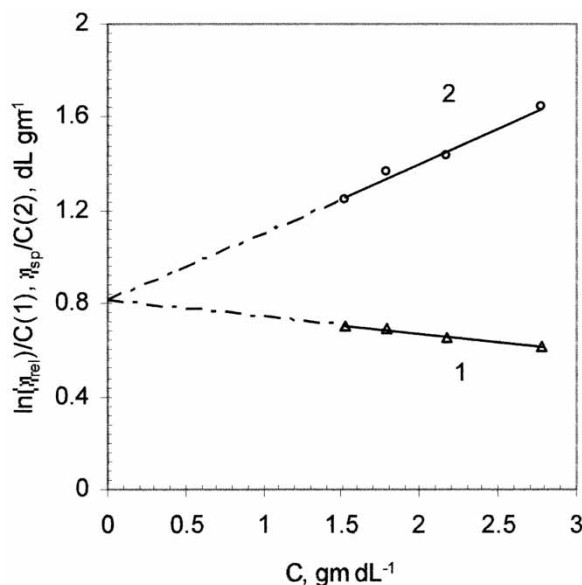


Figure 1. Intrinsic viscosity of waste PET particles.

vacuum at 80°C for 24 h and weighed. The filtrate was acidified with dilute acetic acid to get the precipitate of TA, which was then dried under vacuum at 80°C for 24 h. Conversion of the waste PET was calculated from the decrease in the weight of PET particles and was confirmed with the amount of terephthalic acid produced after precipitation. Unreacted PET samples ($r_0 = 0.001$ m and molar ratio = 1 : 4) at different time intervals (at 0, 4 and 8 h, respectively) were also analyzed by a Perkin-Elmer 1430 infra red (IR) spectrometer (see Fig. 2). The IR film was made by dissolution of unreacted PET with phenol and 1,1,2,2 tetrachloroethane. It was observed that all transmittance peaks were identical except the peak at $\sim 1700\text{ cm}^{-1}$ and the transmittance at this position decreased with the depolymerization time (20). The decreased transmittance at $\sim 1700\text{ cm}^{-1}$ was due to the increasing surface concentration of the $>\text{C}=\text{O}$ group, which is generated from a substituted aryl carboxylic acid group ($-\text{COOH}$). This proves that the major hydrolytic decomposition reaction occurs at the polymer chain end section of the PET surface and increases the concentration of aryl carboxylic acid.

To find the effect of particle size, the depolymerization rates were measured for each particle size fraction (I-IV) and the conversion of PET particles vs. the decomposition time were plotted in Fig. 3. Here, the molar ratio of PET repeating units to KOH was taken as 1 : 4 for all size fractions. In each experiment, 1.1667 gm of dried KOH was taken per gm of waste PET particles. 10 mL of twice distilled water was taken for each experiment and temperature was kept at 403 K. A logarithmic plot of quarter time ($t_{1/4}$) for PET depolymerization vs. initial radius (r_0) of PET particles is shown in Fig. 4 at 403 K. It was found that the rate of depolymerization was inversely proportional to the initial size of the PET particles. An inverse relationship proves that depolymerization kinetics was controlled by chemical reaction alone (30, 31), whereas the model developed by Wan et al. (18) gives an inverse relationship between the square of the radius and the depolymerization time, which is not consistent with the present test results.

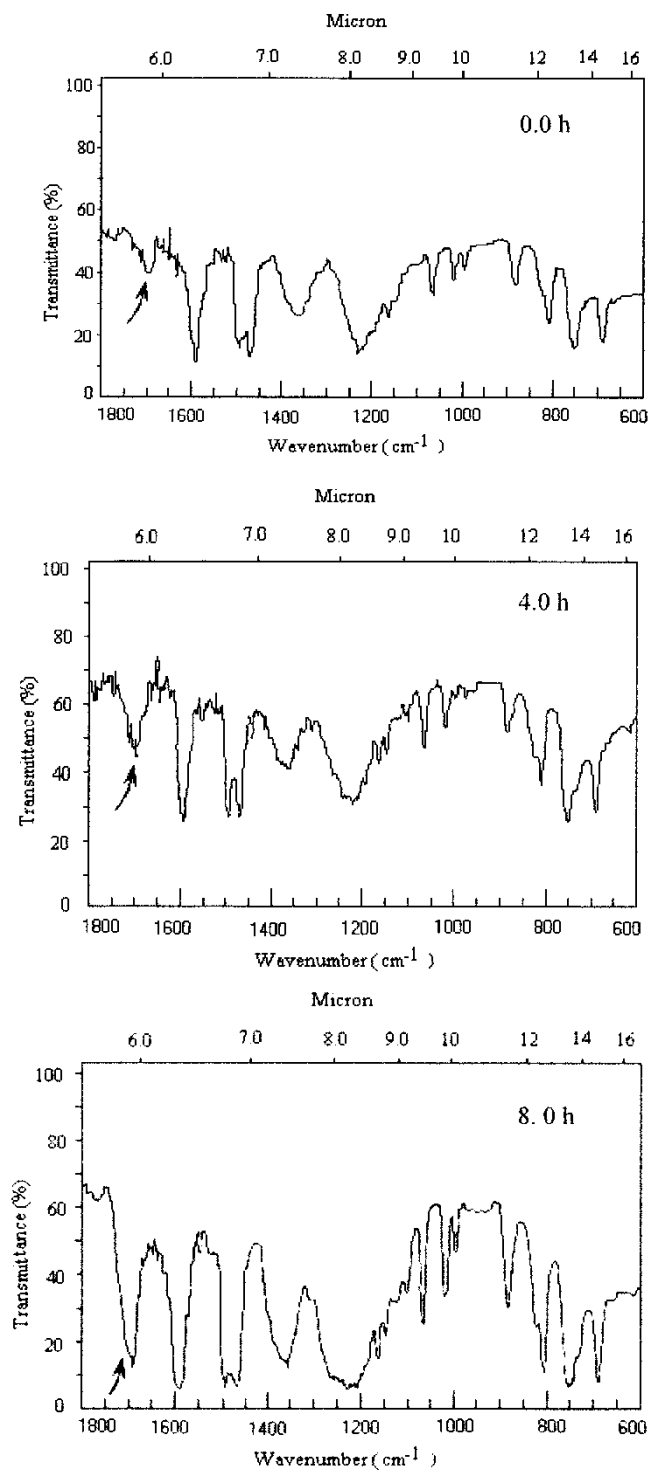


Figure 2. IR analysis of unreacted waste PET particles ($M = 1 : 4$, $r_0 = 0.001$ m, $t = 0.0$ h, 4.0 h and 8.0 h, $T = 403$ K).

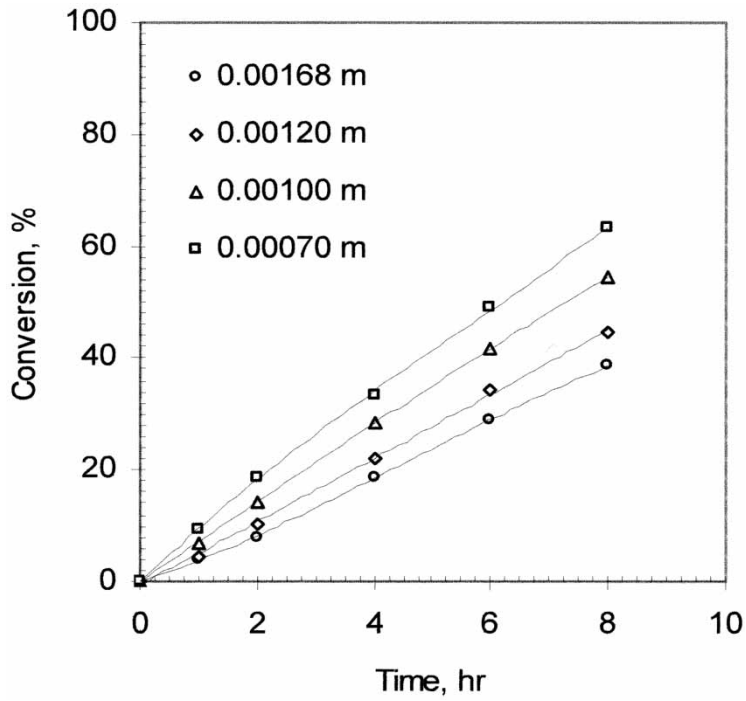


Figure 3. Effects of PET particle size on depolymerization ($M = 1:4$; $T = 403$ K).

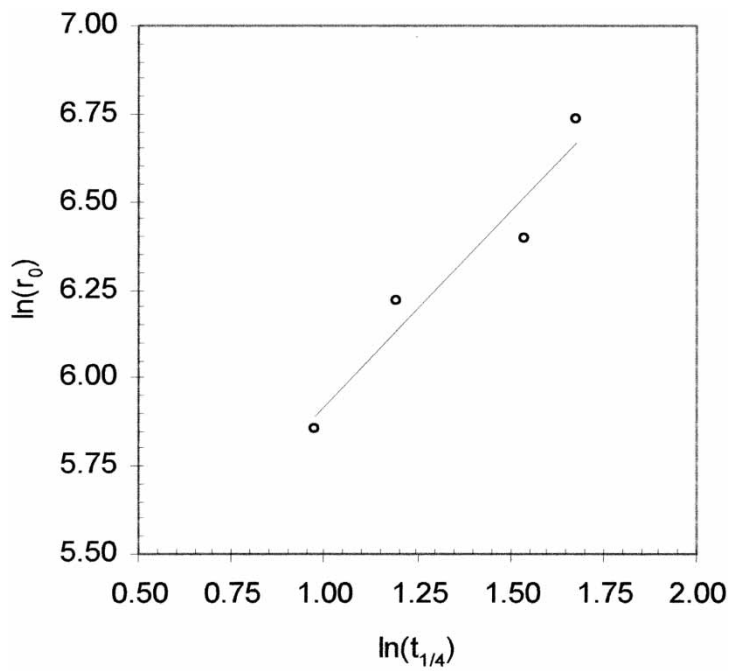


Figure 4. Plot of $\ln(r_0)$ vs. $\ln(t_{1/4})$.

The effect of the molar concentration of KOH on the depolymerization kinetics was measured with PET particles having size fraction III ($r_0 = 0.001$ m) at 403 K. Here, molar ratios of PET repeating units to KOH were taken to be 1 : 6, 1 : 4, 1 : 2, and 1 : 1. The results were shown in Fig. 5 and showed that bulk concentration has a marked effect on depolymerization kinetics, which is in accord with the kinetically controlled model.

The effect of temperature on depolymerization kinetics was studied at four different temperatures (383 K, 393 K, 403 K, and 408 K) for size fraction III ($r_0 = 0.001$ m) and 1 : 4 molar ratio of PET repeating units to KOH. The conversion of PET to reaction time is shown in Fig. 6 and the rate of depolymerization increases with an increase in reaction temperature.

Results and Discussion

The shrinking core model with depletion of a soluble product developed above was tested. Bear in mind that in developing the mathematical model for hydrolytic decomposition of PET, the constancy of molar distribution coefficient λ was assumed in order to facilitate the analytical integrations for a given initial bulk concentration of KOH. As λ is more sensitive to dilute solution (i.e., λ increases with an increase in the dilution), this assumption is true only at higher molar concentrations of KOH where the change of λ is negligible, and at lower conversions of PET particles. Therefore, it is assumed that an average molar distribution coefficient ($\bar{\lambda}$) exists during any given set of depolymerization experiment.

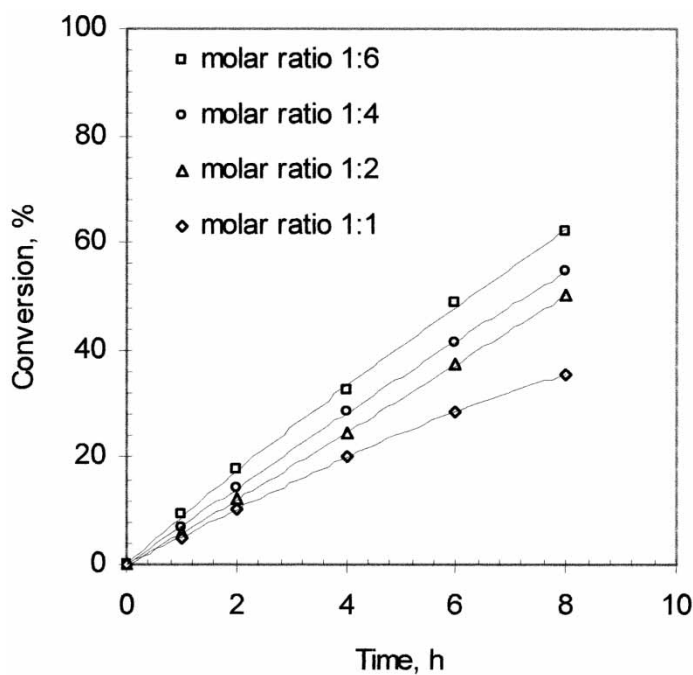


Figure 5. Effects of bulk concentration of KOH solution on PET depolymerization ($r_0 = 0.001$ m; $T = 403$ K).

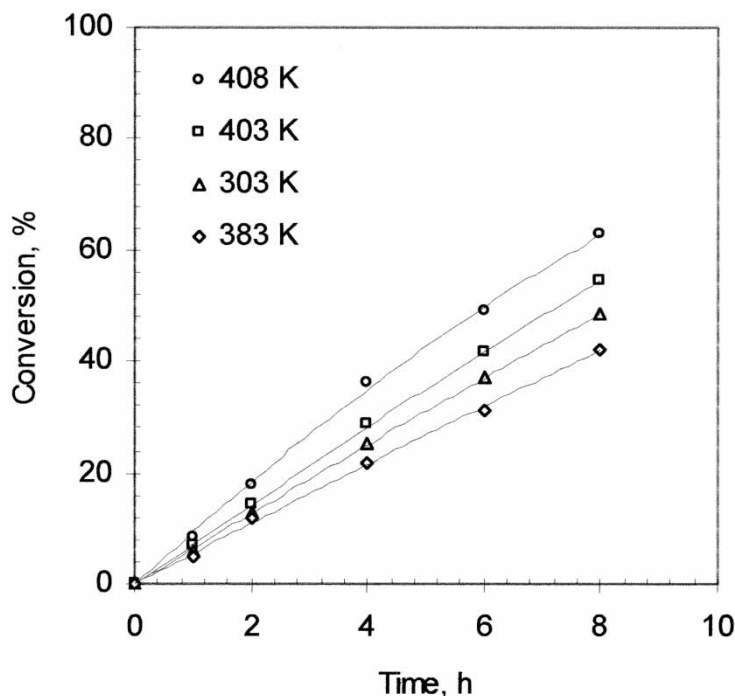


Figure 6. Effects of temperature on PET depolymerization.

To test the modified shrinking model with a depleting product layer (consisting of potassium salt of TA and MEG), the left hand sides of Eqs. (9) and (12), which are functions of the PET conversion, were evaluated and plotted against the depolymerization time (t) based on Fig. 3 for four different particle sizes at 403 K and 1 : 4 molar ratio of PET repeating units and KOH (Fig. 7). The slope of the linear plot (Fig. 7) will give the different values of K . Substituting appropriate values r_0 , V_0 , b , N_{A0} and ρ_A ($V_0 = 10^{-5} \text{ m}^3$, $b = 0.5$, $N_{A0} = 5.2085 \times 10^{-3} \text{ mol}$ and $\rho_A = 52.3426 \text{ mol m}^{-3}$) in Eq. (8), individual values of $\bar{\lambda}k$ for four different particle sizes are calculated and almost identical values of $\bar{\lambda}k$ (average value $1.68 \times 10^{-6} \text{ m h}^{-1}$) is obtained (Fig. 8). This indicates that at a given bulk concentration of aqueous KOH and reaction temperature, $\bar{\lambda}$ is constant for the given value of k . Similarly, using Eq. (9) ($M \neq 2$) and Eq. (12) ($M = 2$), K values are obtained from the slope of the linear plot (Fig. 9) based on the data of Fig. 5 at different molar ratios of PET repeating unit to KOH under isothermal condition ($r_0 = 0.001 \text{ m}$ and $T = 403 \text{ K}$). The corresponding values of different $\bar{\lambda}k$ are obtained at four different values of molar bulk concentration of aqueous KOH solution. The plot of $\bar{\lambda}k$ vs. C_{B0} (Fig. 10), gives an idea to estimate the value of the intrinsic reaction rate constant (k) and hence, the average molar distribution coefficient ($\bar{\lambda}$). It is observed that in Fig. 10 as C_{B0} increases, $\bar{\lambda}k$ decreases and reaches a constant value asymptotically, which indicates that the value of $\bar{\lambda}$ approaches unity at higher bulk molar KOH concentrations, and is independent of the bulk concentration of aqueous KOH solution. Therefore, at the limiting value of C_{B0} , the value of $\bar{\lambda}k$ will be equal to k , which helps calculate the intrinsic depolymerization rate constant at the given temperature. The intrinsic depolymerization rate constant (k) at the limiting C_{B0} is $1.30 \times 10^{-6} \text{ m h}^{-1}$ at 403 K and limiting C_{B0} is found to be 4000 mol m^{-3} . Thus, $\bar{\lambda}$

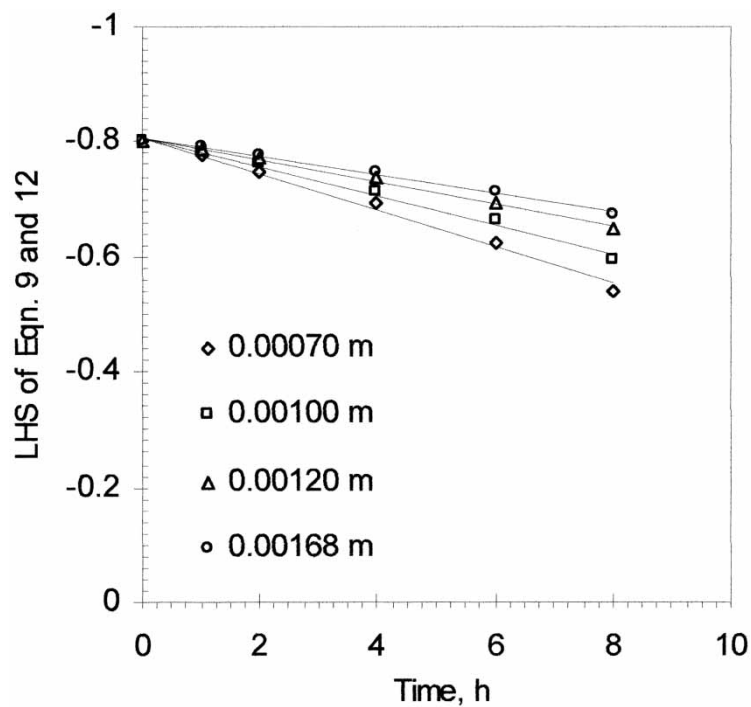


Figure 7. Test of Eqs. (9) and (12) for different particle size of PET on depolymerization ($M = 1 : 4$; $T = 403$ K).

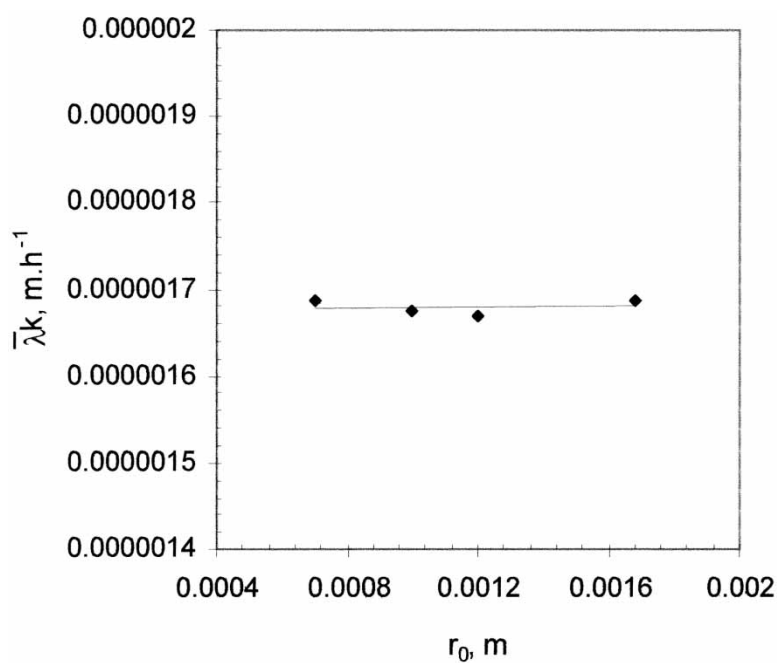


Figure 8. Variation of $\bar{\lambda}k$ with particle size of PET particles ($M = 1 : 4$, $T = 403$ K).

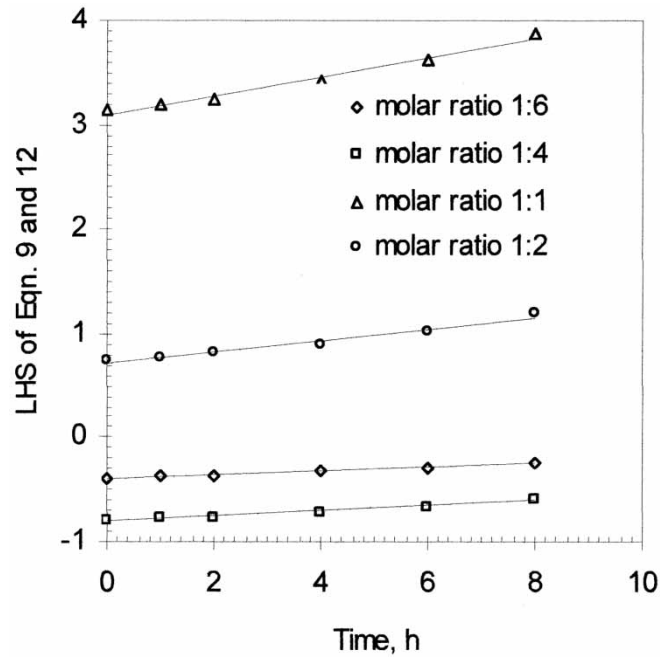


Figure 9. Test of Eqs. (9) and (12) for different initial bulk concentration of KOH solution ($r_0 = 0.001$ m; $T = 403$ K).

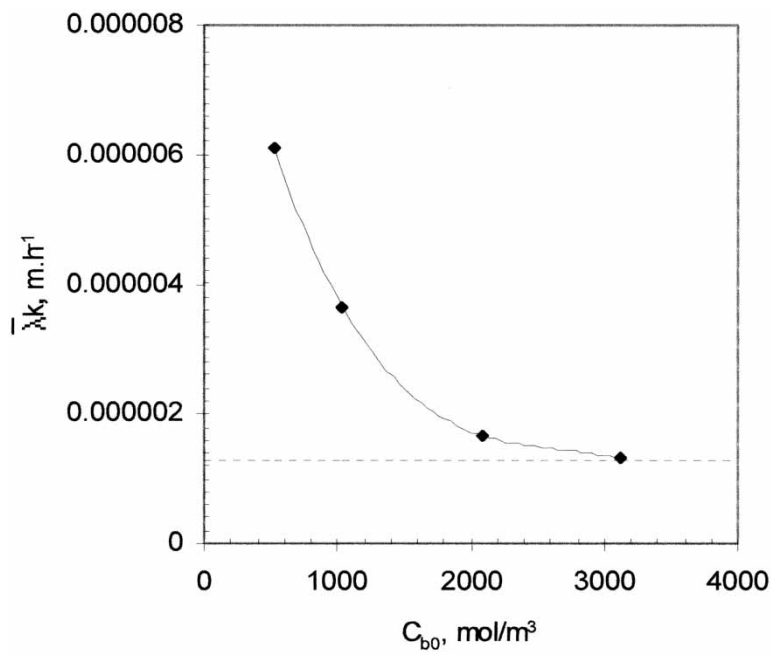


Figure 10. Variation of $\bar{\lambda}k$ with initial bulk concentration of KOH solution ($r_0 = 0.001$ m; $T = 403$ K).

corresponding to each experiment (for different C_{B0}) was evaluated by knowing the values of k . The values of $\bar{\lambda}$ for molar ratio 1:6, 1:4, 1:2, and 1:1 calculated as 1.005, 1.288, 2.798, and 4.690, respectively. The effect of temperature on the intrinsic PET depolymerization rate constant (k) can be evaluated by knowing $\bar{\lambda}$ (independent of temperature) at given C_{B0} (molar ratio of PET repeating units to KOH = 1:4). For given $\bar{\lambda}$ (1.288), k values at different temperatures (i.e., 408 K, 403 K, 393 K, and 383 K) were evaluated, the slope of Eqs. (9) and (11) (Fig. 11) for the data based on Fig. 6 and the corresponding values of the intrinsic reaction rate constant (k) are determined as: 1.66×10^{-6} , 1.30×10^{-6} , 1.12×10^{-6} , $9.10 \times 10^{-7} \text{ m h}^{-1}$, respectively. Arrhenius plot (Fig. 12) was made to evaluate the frequency factor (k_0) and $\Delta E/R$, where ΔE is the activation energy and R is the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$). The value of k_0 and $\Delta E/R$ are evaluated as $0.009178 \text{ m h}^{-1}$ and 3537.7 K , respectively.

Conclusions

The hydrolytic depolymerization of waste PET, with an aqueous potassium hydroxide solution, was investigated. An IR spectroscopy study of unreacted PET samples shows that the major decomposition reaction occurring on the polymer chain end section on the solid PET surface. An improved moving boundary transport model (modified shrinking core model) for kinetically controlled depolymerization of PET particles was developed to account the continuous depletion of the product layer by incorporating the molar distribution coefficient. Kinetic parameters, i.e., the intrinsic rate constant (k),

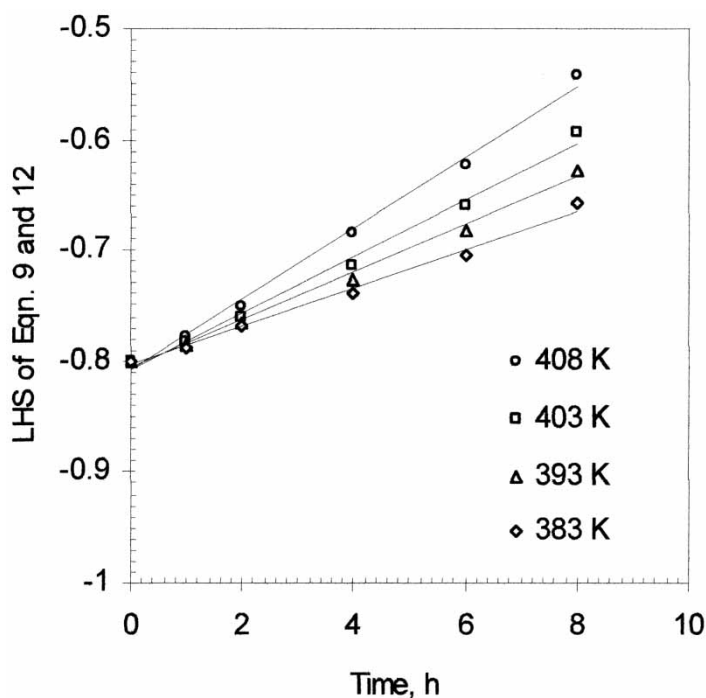


Figure 11. Test of Eqs. (9) and (12) at different PET depolymerization temperatures ($r_0 = 0.001 \text{ m}$; $M = 1:4$).

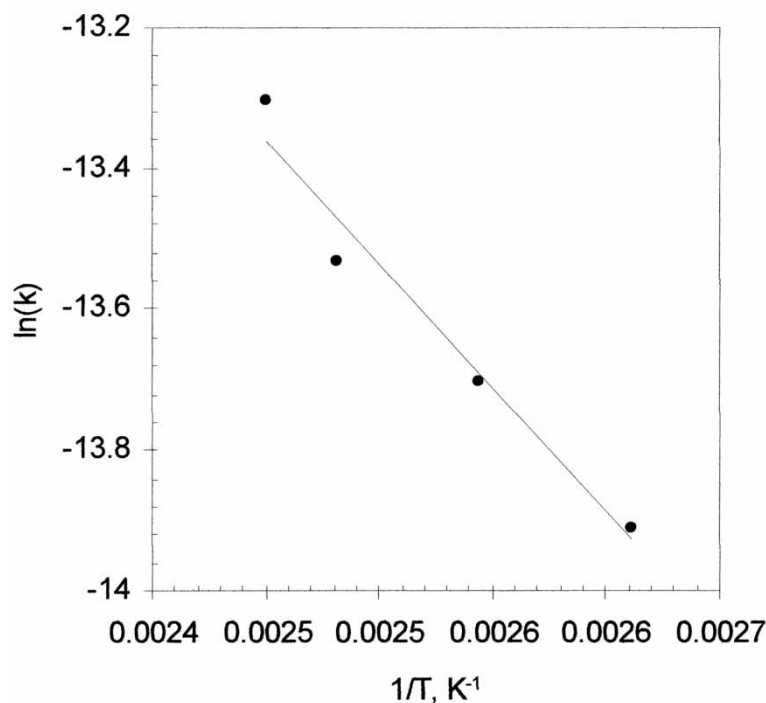


Figure 12. Arrhenius plot for PET depolymerization ($r_0 = 0.001$ m; $M = 1:4$).

frequency factor (k_0), activation energy of depolymerization (ΔE) and the average molar distribution coefficient of aqueous KOH solution ($\bar{\lambda}$) were evaluated based on the above model.

References

1. Nir, M.M., Miltz, J., and Ram, A. (1993) Update on plastics and the environment: progress and trends. *Plast. Eng.*, 49 (3): 75–93.
2. Paszun, D. and Spychaj, T. (1997) Chemical recycling of poly(ethylene terephthalate). *Ind. Eng. Chem. Res.*, 36 (4): 1373–1383.
3. Cudmore, W.J.G. (1986) Poly(ethylene terephthalate) Saponification. U.S. Patent 4 578 502.
4. Doerr, M.L. (1986) Process for minimizing formation of low molecular weight oligomers during hydrolytic depolymerization of condensation polymers. U.S. Patent 4 578 510.
5. Rosen, B.J. (1991) Preparation of purified terephthalic acid from waste PET. U.S. Patent 5 095 145, CA 123: 257937.
6. Campanelli, J.R., Kamal, M.R., and Copper, D.G. (1993) A kinetic study of hydrolytic degradation of poly(ethylene terephthalate) at high temperatures. *J. Appl. Polym. Sci.*, 48 (3): 443–451.
7. Campanelli, J.R., Copper, D.G., and Kamal, M.R. (1994) Catalyzed hydrolysis of poly(ethylene terephthalate) melts. *J. Appl. Polym. Sci.*, 53 (8): 985–991.
8. Kao, C., Wan, B., and Cheng, W. (1998) Kinetics of hydrolytic depolymerization of melt poly(ethylene terephthalate). *Ind. Eng. Chem. Res.*, 37 (4): 1228–1234.
9. Brown, G.E., Jr.; O'Brien, R.C. (1976) Method of recovering terephthalic acid and ethylene glycol from polyester materials. U.S. Patent 3 952 053.

10. Pusztaszeri, S.F. (1982) Method for recovery of terephthalic acid from polyester scrap. U.S. Patent 4 355 175.
11. Sharma, N.D.; Vaidya, A.A.; Sharma, P. (1985) Recovery of pure terephthalic acid from polyester materials. Ind. Patent 163 385, CA 112: 76613d.
12. Yoshioka, T., Sato, T., and Okuwaki, A.J. (1994) Hydrolysis of waste PET by sulphuric acid at 150°C for Chemical recycling. *J. Appl. Polym. Sci.*, 52 (9): 1353–1355.
13. Yoshioka, T., Motoki, T., and Okuwaki, A.J. (2001) Kinetics of hydrolysis of poly(ethylene terephthalate) powder in sulfuric acid by a modified shrinking-core model. *Ind. Eng. Chem. Res.*, 40 (1): 75–79.
14. Yoshioka, T., Okayama, N., and Okuwaki, A. (1998) Kinetics of hydrolysis of PET powder in nitric acid by a modified shrinking-core model. *Ind. Eng. Chem. Res.*, 37 (2): 336–340.
15. Ravens, D.A.S. (1960) The chemical reactivity of poly(ethylene terephthalate): heterogeneous hydrolysis by hydrochloric acid. *Polymer*, 1: 375–383.
16. Davies, T., Goldsmith, P.L., Ravens, D.A.S., and Ward, M.I. (1962) The Kinetics of the hydrolysis of poly(ethylene terephthalate) film. *J. Phys. Chem.*, 66 (1): 175–176.
17. Kao, C., Cheng, W., and Wan, B. (1998) Investigation of alkaline hydrolysis of poly(ethylene terephthalate) by differential scanning calorimetric and thermo- gravimetric analysis. *J. Appl. Polym. Sci.*, 70 (10): 1939–1945.
18. Wan, B., Kao, C., and Cheng, W. (2001) Kinetics of depolymerization of poly(ethylene terephthalate) in a potassium hydroxide solution. *Ind. Eng. Chem. Res.*, 40 (2): 509–514.
19. Mandoki, J.W.. Depolymerization of condensation polymers. U.S. Patent 4 605 762, 1986.
20. Guclu, G., Yalcinyuva, T., Ozgumus, S., and Orbay, M. (2003) Hydrolysis of waste poly(ethylene terephthalate) and characterization of products by differential scanning calorimetry. *Thermochimica Acta*, 404 (1–2): 193–205.
21. Sammon, C., Yarwood, J., and Evarall, N. (2000) An FT-IR study of the effect of hydrolytic degradation of on the structure of thin PET films. *Polym. Degrad. Stab.*, 67 (1): 149–158.
22. Launay, A., Thominet, F., and Verdu, J. (1994) Hydrolysis of poly(ethylene terephthalate): a kinetic study. *Polym. Degrad. Stab.*, 46 (3): 319–324.
23. Kao, C., Wan, B., and Cheng, W. (1998) Kinetics of hydrolytic decomposition of melt poly(ethylene terephthalate). *Ind. Eng. Chem. Res.*, 37 (4): 1228–1234.
24. Kirby, J.R., Baldwin, A.J., and Heigener, R.H. (1965) Experimental reactor thermal-neutron activation analysis sensitivities. *Anal. Chem.*, 37 (1): 129–132.
25. Namboori, C.G.G. and Haith, M.S. (1968) Steric effects in the base hydrolysis of poly(ethylene terephthalate). *J. Appl. Polym. Sci.*, 12 (9): 1999–2005.
26. Tindall, G.W.; Perry, R.L. (1991) Ester hydrolysis and depolymerization of polyester and polycarbonate polymers. U.S. Patent 5 045 122.
27. Tindall, G.W.; Perry, R.L.; Spaugh, A.T. (1994) Depolymerization of substantially amorphous polyester. U.S. Patent 5 328 982.
28. Collins, M.J. and Zeronian, S.H.J. (1992) The molecular weight distribution and oligomers of sodium hydroxide hydrolyzed poly(ethylene terephthalate). *J. Appl. Polym. Sci.*, 45 (5): 797–804.
29. Holmes, S.A. and Zeronian, S.H.J. (1995) Surface area of aqueous sodium hydroxide hydrolyzed high-speed spun poly(ethylene terephthalate) fibers. *J. Appl. Polym. Sci.*, 55 (11): 1573–1581.
30. Carberry, J.J. (1976) *Chemical and Catalytic Engineering*; McGraw-Hill: New York.
31. Levenspiel, O. (1999) *Chemical Reaction Engineering*; Wiley: New York.