

# Production of Agrochemical from Waste Polyesters

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**ABSTRACT:** In this study, agrochemical was produced from waste polyesters. Reactions of waste polyesters [poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT)] powder with ethylene glycol (EG) in the presence of tetrahydrofuran (THF) using 0.003 mol lead acetate as a catalyst were carried out in a batch reactor at 470 K and at atmospheric pressure conditions. Reactions were undertaken with various particle size ranges from 50 to 512.5  $\mu\text{m}$ , and reaction time from 30 to 70 min for reactions of polyesters. Low molecular weight product of polyester was obtained during this process. In the next stage, hydroxylamine hydrochloride (HAHC), cyclohexylamine (CHA), and potassium hydroxide (KOH) solution were introduced to convert low molecular weight product of polyester into terephthalohydroxamic acid (TPHA) by introduction of HCl (Hydrochloric Acid) as per stoichiometric requirement. TPHA can be used as an agrochemical (insecticide) with appreciable

efficiency. To increase the polyester conversion rate, external catalyst (0.003 mol lead acetate) was introduced during the reaction. The product was deposited on the surface of unreacted polyester, which was removed from the surface by introducing dimethyl sulfoxide (DMSO). To accelerate the reaction rate, DMSO, CHA, and THF were introduced during the reaction, which has an industrial significance. Depolymerization of polyester was proportional to the reaction time. Depolymerization of polyester was inversely proportional to the particle size of polyester. Analyses of value-added product (TPHA) and byproducts [EG and BD (1,4-butanediol)] as well as polyesters were undertaken. A kinetic model is developed, and experimental data simulated with it, which was consistent with the model. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2504–2510, 2006

**Key words:** PET; PBT; agrochemical; catalyst; kinetics

## INTRODUCTION

There are various agrochemicals that could be applied as insecticides. But, terephthalohydroxamic acid (TPHA) is a very effective and an expensive agrochemical that could be used as an insecticide. TPHA can be produced from expensive fine chemicals; hence, its production cost is very high. To reduce the production cost of TPHA, it could also be produced from waste polyesters (PET and PBT). The thermoplastic polyester group of polymers includes saturated polyesters like PET and PBT that are most important polyesters, which are principally recognized for its use as consumer materials. The current usage of PET/PBT has been as engineering thermoplastic. Poly (ethylene terephthalate) is a polyester of terephthalic acid (or dimethyl terephthalate) and ethylene glycol. Poly (butylene terephthalate) is polyester of terephthalic acid and butylene glycol (or dimethyl terephthalate and 1,4-butanediol). The growing interest in PET/PBT recycling is due to widespread use of fiber, film, and packaging with PET/PBT, and a further increase in its application is predicted. Ecological as well as eco-

nomical considerations advocate introduction of wide-scale PET/PBT recycling. Recycling of waste PET/PBT can be carried out in many ways. Availability of a wide spectrum of depolymerizing agents and a large variety of products, e.g., monomers for polymer and resin synthesis and other additives for polymeric materials, are some of the advantages of PET/PBT chemical recycling.<sup>1,2</sup>

Chemical recycling processes for polyester implemented nearly parallel to the manufacture of polyester on a commercial scale. Initially, chemical recycling found an application as a way to utilize wastes arising in polyester production cycle. Historical and practical reasons cause processes of chemical depolymerization of polyester to be usually divided as methanolysis, glycolysis, hydrolysis, ammonolysis, aminolysis, and other processes.<sup>3,4</sup> Second most important method in chemical processing of polyester is glycolysis. This process is used widely on a commercial scale. Polyester degradation is carried out most frequently using ethylene glycol.<sup>5–11</sup> Very few researchers were devoted to kinetics of glycolysis reactions,<sup>7,11</sup> but their rates were very low and could not have any industrial significance. Chen et al.,<sup>10</sup> have concluded that the glycolysis rate was second order with respect to EG concentration, and that EG thus acts as both reactant and catalyst in glycolysis of PET. It contradicts with

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the earlier findings of Challa.<sup>12</sup> Baliga and Wong<sup>7</sup> found that glycolysis reaction was first order with respect to EG concentration during depolymerization of PET. Yields of monomeric products were almost consistent with PET waste conversion.<sup>13–15</sup>

In the past, there were no detailed required data available about product characterization and kinetics that were necessary for process development of glycolytic-aminolysis of polyester to obtain TPHA as an insecticide. In the absence of a reliable model and reaction data, reaction engineers are forced to scale-up and to establish the reactors with economy. Available reaction data are insufficient for designing new reactor concepts with justifiable expenditure.

To obtain high quality of an insecticide as an agrochemical with the high value-added product, this study was undertaken. TPHA is used as an insecticide, and it is highly expensive. TPHA was produced from expensive fine chemicals, and hence, its production cost was very high. In this study, TPHA is produced during depolymerization of waste polyesters and the manufacturing cost is comparatively very low; hence, it has an industrial significance. Polyester particle size and reaction time were optimized. A kinetic model was developed and validated with our own experimental data. Glycolysis rate was improved significantly by addition of CHA, THF, and DMSO to EG, which resulted in appreciable amount of conversion of polyester with lesser time.

## EXPERIMENTAL

### Material, chemicals and reagents

Waste PET/PBT used were procured from local market, Aurangabad, M.S., (India). Here, waste just means materials left over after some products were made from raw material. The other materials used were neutral water, methanol, calcium oxide (CaO), sodium sulfate, ethylene glycol (EG), lead acetate, hydroxylamine hydrochloride (HAHC), cyclohexylamine (CHA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and potassium hydroxide (KOH) etc., obtained from s. d. fine chemicals (India). These chemicals were used as received without further purification.

### Glycolytic-aminolysis of polyesters (PET/PBT)

Glycolysis was undertaken in a 500-mL four-necked round bottom flask equipped with a temperature sensor, a stirrer, and two reflux condensers at 470 K and at atmospheric pressure conditions. Reaction was carried out by taking 10 g PET/PBT in 40 mL EG with 5 mL THF and 5 mL DMSO, using 0.003 mol lead acetate as catalyst with 4 pieces of porcelain for different periods of reflux time ranging from 10 to 70 min at the interval of 10 min. Different particle sizes ranging

from 50 to 512.5  $\mu\text{m}$  of PET/PBT were taken for this reaction (separately). After completion of glycolysis reaction, batch reactor was removed from heating mantle and unreacted PET/PBT whether any was separated, collected, and washed with neutral water and then with alcohol to remove deposition on the PET/PBT surface, if any. Collected unreacted PET/PBT was dried in a controlled oven at 353 K until their constant weights were recorded.

After removing unreacted polyester if any, the resulting liquid phase was taken in the batch reactor, which was kept in an ice-bath to cool to 288 K for 5 min. In this reaction mixture, 12 g HAHC with 50 mL neutral distilled water, 1 mL CHA, and 12 g KOH with 50 mL neutral distilled water were introduced. It was stirred at 288 K until it turns to pale yellow, which takes about 10 min. It was again kept in an ice-bath to cool to 273 K for 5 min. The reaction mixture was neutralized by introduction of stoichiometric amount (as per requirement) of HCl, which formed white precipitates. The resulting white precipitates of TPHA were separated from rest of the materials. It was washed with hot neutral water, and then with alcohol to remove the catalyst and other impurities away from TPHA. Collected TPHA was dried in a controlled oven at 353 K until constant weight was recorded.

From the resulting waste liquid phase, EG/1,4-butanediol (BD) was recovered using salting-out method by introduction of sodium sulfate. Reaction products (TPHA, EG and BD) were analyzed qualitatively and quantitatively. Percent depolymerization of PET/PBT, yield of TPHA, yield of EG, and yield of BD were determined by gravimetry and defined in the following ways:

Depolymerization of PET (%) =

$$\{(W_{\text{PET},i} - W_{\text{PET},R})/W_{\text{PET},i}\} \times 100.$$

Depolymerization of PBT (%) =

$$\{(W_{\text{PBT},i} - W_{\text{PBT},R})/W_{\text{PBT},i}\} \times 100.$$

$$\text{Yield of TPHA (\%)} = \{m_{\text{TPHA},O}/m_{\text{PET},i}\} \times 100.$$

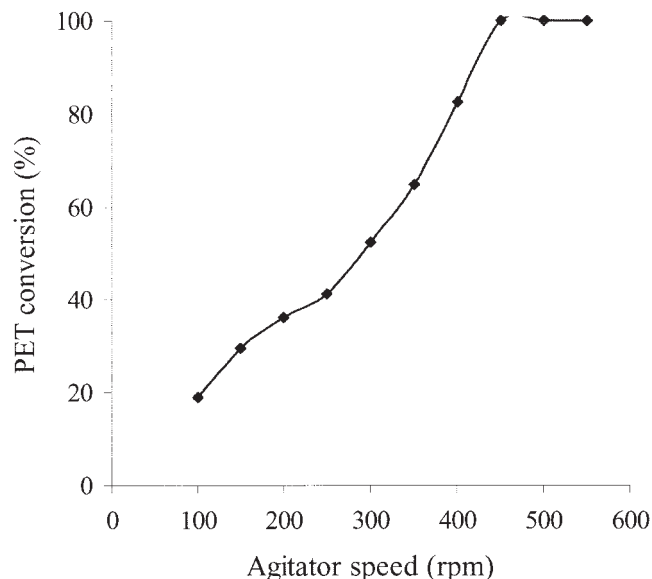
$$\text{Yield of TPHA (\%)} = \{m_{\text{TPHA},O}/m_{\text{PET},i}\} \times 100.$$

$$\text{Yield of EG (\%)} = (m_{\text{EG},O}/m_{\text{PET},i}) \times 100.$$

$$\text{Yield of BD (\%)} = (m_{\text{BD},O}/m_{\text{PBT},i}) \times 100.$$

where  $W_{\text{PET},i}$  is the initial weight of PET,  $W_{\text{PET},R}$  is the weight of unreacted PET,  $W_{\text{PBT},i}$  is the initial weight of PBT,  $W_{\text{PBT},R}$  is the weight of unreacted PBT,  $m_{\text{TPHA},O}$  is the number of moles of TPHA,  $m_{\text{EG},O}$  is the number of moles of EG,  $m_{\text{PET},i}$  is the initial number of moles of PET monomers,  $m_{\text{BD},O}$  is the number of moles of BD, and  $m_{\text{PBT},i}$  is the initial number of moles of PBT monomers.





**Figure 2** Effect of agitator speed (rpm) on the PET conversion (%) for 20 min at 470 K with 127.5  $\mu\text{m}$  particle size of the waste PET and at atmospheric pressure.

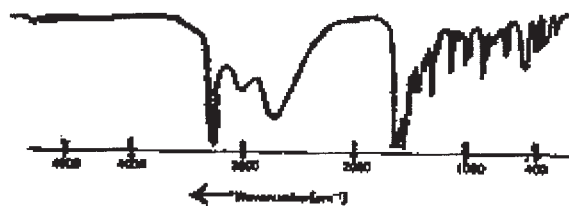
#### Optimization of agitator speed for PET conversion

Maintaining 127.5  $\mu\text{m}$  particle size of PET at 470 K temperatures for 20 min of operation time at atmospheric pressure, PET conversion was undertaken at various agitator speeds (100–550 rpm) at the interval of 50 rpm. Effects of various agitator speeds on PET conversion (%) are shown in Figure 2. It showed that PET conversion (%) was increased upto 450 rpm and later it was constant. Optimal agitator speed was recorded as 450 rpm.

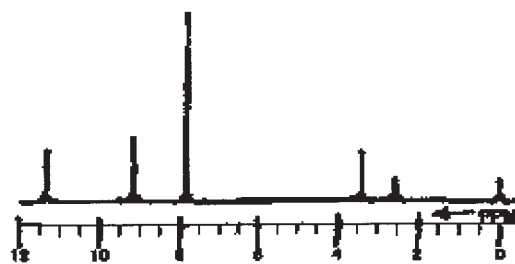
#### Analysis of products (EG, BD and TPHA)

Liquid product obtained from glycolytic-aminolysis of PET was analyzed by determining its weight per mL (1.113), boiling point (470 K), and molecular weight (62  $\text{g mol}^{-1}$ ). These results were close to values of EG.

The liquid product obtained from depolymerization of PBT was analyzed by determining its weight per mL (1.017 g), boiling point (230°C), melting point (16°C), molecular weight (90  $\text{g mol}^{-1}$ ), and refractive index (1.445). These results were close to the values of 1,4-butanediol (BD).



**Figure 3** IR spectra (KBr) of TPHA.



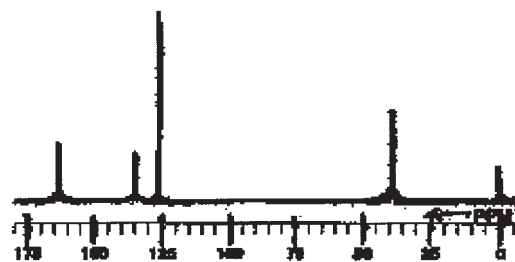
**Figure 4**  $^1\text{H}$  NMR spectra ( $\text{DMSO-}d_6$ ) of TPHA.

Solid product obtained from glycolytic-aminolysis of PET/PBT was analyzed, melted at 575 K, and molecular weight was 196  $\text{g mol}^{-1}$ . These results were close to values of TPHA.

Figure 3 shows FTIR (KBr) spectral absorption with wave numbers 1503, 1560, and 1650  $\text{cm}^{-1}$  for aromatic group, amide group first, and amide group second, respectively. Figure 4 shows  $^1\text{H}$  NMR spectra with  $\delta$  value 7.81 ppm for aromatic protons,  $\delta$  value 9.14 ppm for hydroxyl protons, and  $\delta$  value 11.33 ppm due to the presence of amide protons. Figure 5 shows  $^{13}\text{C}$  NMR spectra with  $\delta$  value 126.8 ppm for ArC—H,  $\delta$  value 135 ppm for ArC—CO, and  $\delta$  value 163 ppm for CO group. Various spectra's (FTIR in Fig. 3,  $^1\text{H}$  NMR in Fig. 4, and  $^{13}\text{C}$  NMR in Fig. 5) of solid product confirms the product TPHA. These results clearly indicate that TPHA was the solid product obtained from glycolytic-aminolysis of waste PET/PBT.

#### Optimization of particle size of PET/PBT for glycolytic-aminolysis

Results of optimization of particle size of PET/PBT for glycolytic-aminolysis were shown in Figure 6 (for 20 min of reflux time in the presence of cyclohexylamine). Particle sizes from 50 to 512.5  $\mu\text{m}$  were taken and it was observed that with greater particle size, PET/PBT conversion was decreased. Initially, PET/PBT conversion was constant and maximum (100, 26.3% respectively) for particle of 50, 64, 90, and 127.5  $\mu\text{m}$ . But later, PET/PBT conversion was decreased with higher particle size (181, 256, 362.5, and 512.5  $\mu\text{m}$ ). It indicates that PET/PBT conversion was



**Figure 5**  $^{13}\text{C}$  NMR spectra ( $\text{DMSO-}d_6$ ) of TPHA.

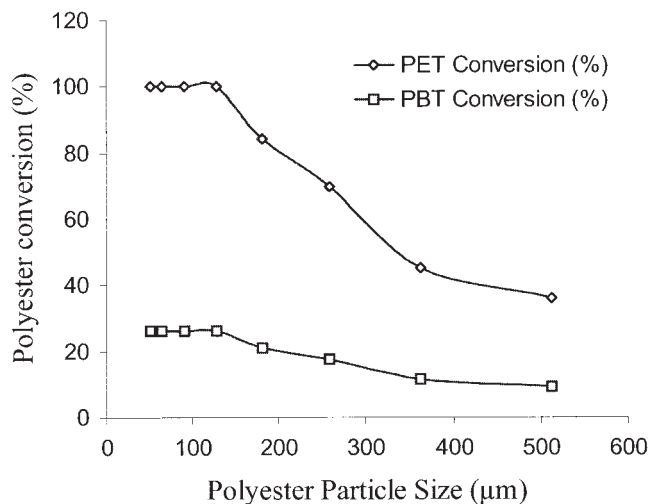
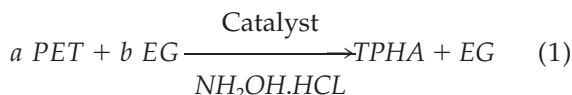
inversely proportional to particle size of PET/PBT. Optimal PET/PBT size is the maximum particle size at which PET/PBT conversion is maximum. Optimal PET/PBT size was recorded as 127.5  $\mu\text{m}$  (Fig. 6).

### Optimization of reaction time for glycolytic-aminolysis of PET/PBT

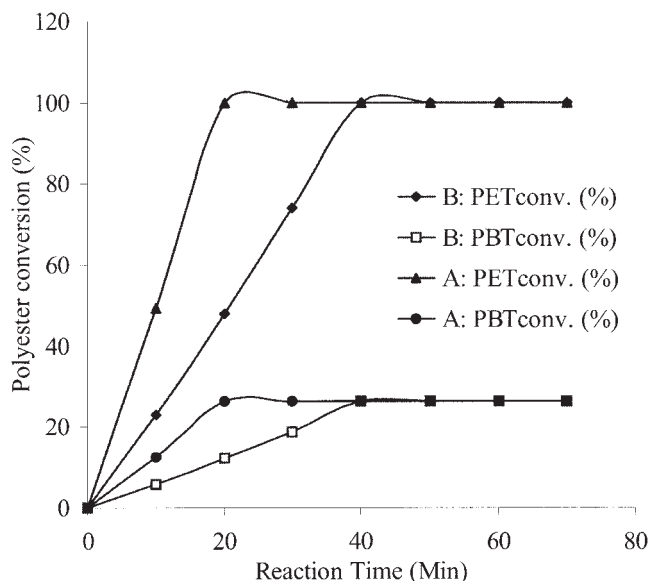
Maintaining particle size of PET/PBT 127.5  $\mu\text{m}$ , reaction time was optimized varying from 10 to 70 min for depolymerization of PET/PBT with (A) and without (B) introduction of CHA. Results were shown in Figure 7. Initially, PET/PBT conversion was less, further with increasing time, PET/PBT conversion was found to increase upto reaction time periods of 20 min (A) and 40 min (B), respectively. After 20 min (A) and 40 min (B) of reaction time, there was no increase in PET/PBT into products, respectively. Optimal PET/PBT conversion was recorded at 20 min (A) and 40 min (B), respectively, for glycolytic-aminolysis of PET/PBT into optimal recovery of products (Fig. 7). It clearly indicates that PET/PBT conversion into products was proportional to the reaction time. Optimal time is the time at which the PET/PBT conversion is maximum and there after it remains constant. Optimal PET/PBT conversion was recorded at 20 min (A) and 40 min (B), respectively.

### Kinetic modeling and simulation of glycolytic-aminolysis of PET

Glycolytic-aminolysis of PET takes place at equilibrium with reverse reaction that is given here.



**Figure 6** Optimization of particle size of PET/PBT for glycolytic-aminolysis.



**Figure 7** Optimization of reaction time for glycolytic-aminolysis of PET. (A: with cyclohexylamine and B: without cyclohexylamine).

For the initial time periods of reaction, the reverse reaction is not important because its rate is very low, and can be omitted. Thus, rate of disappearance of polyester EDE groups is equal to the rate of formation of product TPHA, which is given here by the stoichiometric eq. (2).

$$-r_{\text{EDE}} = -dC_{\text{EDE}}/dt = dC_{\text{TPHA}}/dt = kC_{\text{EG}}C_{\text{EDE}} \quad (2)$$

$$dC_{\text{TPHA}}/dt = dx/dt = kC_{\text{EG}}C_{\text{EDE}} \quad (3)$$

where  $C$ , concentration; PET, poly (ethylene terephthalate), EG, ethylene glycol; TPHA, terephthalohydroxamic acid;  $\text{NH}_2\text{OH.HCL} = \text{HAHC} = \text{hydroxylamine hydrochloride}$ ; EDE, ethylene diester groups in PET;  $-r_{\text{EDE}}$ , rate of reaction of depolymerization;  $-dC_{\text{EDE}}/dt$ , rate of disappearance of EDE groups;  $dC_{\text{TPHA}}/dt$ , rate of formation of product TPHA;  $k$ , second order rate constant of reaction;  $t$ , reaction time;  $x$  = moles of EDE groups of PET or EG in time  $t$  = degree of depolymerization of PET;  $a$ , initial concentration of EDE groups of polymer PET;  $b$ , initial concentration of EG;  $(a-x)$ , concentration of EDE groups of polymer PET left behind at time  $t$ ;  $(a-b)$ , concentration of EG left behind at time  $t$ .

Separating the variables in eq. (3), it gives:

$$dx/[(a-x)(b-x)] = kdt \quad (4)$$

Resolving into partial fractions for  $b > a$ , it gives:

$$1/[(a-x)(b-x)] = [1/(b-a)] \times [1/(a-x) - 1/(b-x)] \quad (5)$$

Using this result, eq. (4) can be integrated as follows:

$$\int dx/[(a-x)(b-x)] = [1/(b-a)] \left[ \int dx/(a-x) - \int dx/(b-x) \right] = k \int dt \quad (6)$$

Carring out the integration, it gives:

$$[1/(b-a)] \{ -\ln(a-x) - [ -\ln(b-x) ] \} = kt + IC$$

$$[1/(b-a)] \{ \ln[(b-x)/(a-x)] \} = kt + IC \quad (7)$$

where *IC* is the integration constant. To determine value of *IC*, consider that at *t* = 0, *x* = 0. Hence, from eq. (7),

$$IC = [1/(b-a)] [\ln(b/a)] \quad (8)$$

Substituting this value of *IC* in eq. (7), it gives:

$$[1/(b-a)] \{ \ln[(b-x)/(a-x)] \} = kt + [1/(b-a)] [\ln(b/a)]$$

Rearranging and solving for *kt*, it gives:

$$[1/(b-a)] \{ \ln[(b-x)/(a-x)] - [\ln(b/a)] \} = kt$$

$$kt = [1/(b-a)] \{ \ln[(a/b)(b-x)/(a-x)] \} \quad (9)$$

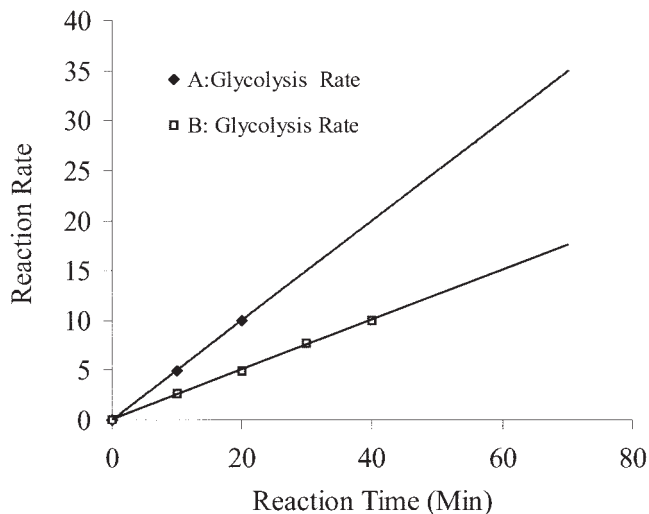
In general, eq. (9) can be written as:

$$(1/B) \ln[1/(1-x)] = kt \quad (10)$$

where *B* = *b* - *a* = difference in initial concentrations of EG and EDE groups,  $[1/(1-x)] = [(a/b)(b-x)/(a-x)]$  for the initial time periods, and  $(1/B) \ln [1/(1-x)]$  is the reaction rate of depolymerization.

We see that eq. (10) is the eq. of a straight line that passes through the origin (viz., *y* = *mx*), where *y* =  $(1/B) \ln [1/(1-x)]$ , *m* = *k*, and *x* = *t*.

Variable *x* takes a value of 0 at reaction time *t* = 0, and with a value of 1 for complete (100%) conversion of PET. Reaction time 0 is considered to be time when the desirable reaction temperature was first obtained in the reaction vessel. Reaction rate constant was obtained by plotting  $(1/B) \ln [1/(1-x)]$  verses *t*, as shown in Figure 8. Initial rate with eq. (10) is seen to provide a good fit for our own experimental data. Hence, from Figure 8, the glycolytic-aminolysis rate of PET expressed in eq. (10) was applicable and consistent with simulated data. Slope of line in Figure 8 predicted value of rate constant as 0.0005 and 0.0002501 (L/min mol) for A and B, respectively, for PET depolymerization at 470 K and atmospheric pres-



**Figure 8** The effect of reaction time on glycolytic-aminolysis rates with model eq. (13) at 470 K using lead acetate catalyst with (A), and without (B) cyclohexylamine at atmospheric pressure for 127.5 μm particle size. (A: with cyclohexylamine and B: without cyclohexylamine).

sure. In an identical manner, the modeling and simulation can be done for PBT. Rate of reaction was improved significantly by addition of CHA with EG.

**Analysis of PET sample**

Analyses of PET samples were undertaken wiz molecular weight (16,703 g mol<sup>-1</sup>), density (1.41 g/cc), melting range (523–537 K), thermoplastic polyester, water absorption (0.5%), and breaking strength (50 MPa). These values were almost identical with literature.<sup>18</sup>

**Analysis of PBT sample**

Analyses of PBT samples were undertaken wiz molecular weight (22,116 g mol<sup>-1</sup>), measured density (1.34 g/cc), melting point (331°C), thermoplastic polyester, glass-transition temperature (59°C), yield strength (51 MPa), dielectric constant (3.3 MHz), and breaking strength (54 MPa). These values were almost identical with those in the literature.<sup>18</sup>

**CONCLUSIONS**

Glycolytic-aminolysis of PET/PBT revealed that it is possible to obtain appreciable amount of PET/PBT conversion into value-added agrochemical (TPHA) and monomers as by products (EG/BD). Optimal reactant size and reflux time are recorded as 127.5 μm and 20 min, respectively. Glycolytic-aminolysis of PET/PBT was proportional to reaction time. Glycolytic-aminolysis of PET/PBT was inversely proportional to particle size of PET/PBT. A kinetic model developed and simulated was consistent with own

experimental data. Reaction rate is significantly improved by addition of THF, CHA, and DMSO to EG-resulted appreciable amount of conversion of PET/PBT into value-added product (TPHA) and monomers as by products (EG and BD) with lesser reaction time. The kinetic model for the glycolytic-aminolysis of PET was found close to first order in both EG and ethylene diester concentrations.

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