

Alkaline hydrolysis of poly(ethylene terephthalate) in presence of a phase transfer catalyst

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Poly(ethylene terephthalate) (PET) powder was hydrolyzed at atmospheric pressure in 5-10 wt% aqueous NaOH at 95°C for 100 min using some phase transfer catalysts (PTC) with an intention to recover the starting monomers from the waste PET. The intent behind attempting new PTC was to carry out the reaction at milder conditions than those reported in the literature. One of the monomers, terephthalic acid (TPA) was produced in the presence of a PTC during the alkaline hydrolysis of PET. The TPA yield agreed with the degree of hydrolysis of PET. Benzalkonium chloride (BKC) was found to be the most effective catalyst among the ones studied. Operating parameters such as NaOH concentration, catalyst concentration and reaction temperature were optimized.

Keywords: Poly(ethylene terephthalate), Benzalkonium chloride, Phase transfer catalyst

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Poly(ethylene terephthalate), PET is a saturated polyester of terephthalic acid and ethylene glycol. The growing interest in PET recycling is due to the widespread use of packaging made of this polymer mainly as bottles. The pertinent feature of PET, namely, it does not have major side effects on human-beings, is responsible for its wide applications as packaging material for food items¹. PET does not pose a direct hazard to the environment, but due to its substantial volume fraction in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material². Ecological as well as economic considerations advocate the large scale recycling of PET, similar to the recycling of traditional materials such as glass, paper, or metals.

Paszun and Spychaj³ have extensively reviewed the chemical recycling, i.e., depolymerization of PET. Glycolysis⁴⁻⁶, and hydrolysis (acidic^{7,8}, alkaline⁹⁻¹¹, and neutral^{12,13}) are the most studied methods of PET depolymerization. The experimental conditions in some of these studies are quite severe, e.g., Mishra *et al.*¹² report maximum conversion at 250°C and 800 psi. Industrial processes involving techniques such as hydrolysis, methanolysis, etc. have been reported by host of workers, e.g., Mandoki¹⁴, Marathe¹⁵, Dupont

and Gupta¹⁶, Fujita *et al.*¹⁷, Pusztaszeri¹⁸ and Ostrowski¹⁹.

Recently Naik and Doraiswamy²⁰ have proposed the use of phase transfer catalysts (PTC) to carry out reactions at mild operating conditions, i.e., at atmospheric pressure and temperatures below 100°C. Yields of terephthalic acid (TPA) as high as 93%, has been reported in case of PET depolymerization in the presence of the PTC. Kosmidis *et al.*¹ have described the mechanism of this reaction.

The present study was undertaken with the aim to depolymerize PET at milder conditions than those reported earlier. Different PTC were chosen to catalyse depolymerization of PET under alkaline conditions. PTC affording best yields of PTA monomer was studied in detail. Effects of various operating parameters on the performance of the chosen PTC were also studied.

Experimental Procedure

Materials

Pellets and fines of the as-manufactured PET were obtained from the local supplier and the benzalkonium chloride (1-benzyl-1-hexadecyl ammonium chloride, BKC) used was in the form of 80 wt%

aqueous solution purchased from Galaxy Surfactants Ltd., Mumbai. Other chemicals used were of reagent grade.

Depolymerization of PET in alkaline solution

In the alkaline hydrolysis of PET two different approaches were followed, namely, (1) non-catalyzed reaction at high temperatures and autogeneous pressures, and (2) catalyzed reactions, using different tetra alkyl ammonium halides at temperatures less than 100°C. The depolymerization reaction was carried out in a three-neck, 100 mL round-bottom glass reactor equipped with a reflux condenser, a mechanical agitator and an electric heating mantle. Aqueous sodium hydroxide was used as the reaction medium. PET pellets and the catalyst (if used) were then added to it maintaining a molar ratio of NaOH: PET repeating unit = 2.5:1 to 5:1 mol/mol; Catalyst: PET repeating unit = 0:1 to 0.27:1 mol/mol. Reaction was carried out at 95°C.

The reaction time was 100 min. At the end of the reaction, the reaction mass was neutralized to pH 7 with H₂SO₄ and filtered. The TPA in the mixture was precipitated by bringing the pH to 2.5-3 by addition of H₂SO₄. So obtained TPA was dried at 120°C under vacuum. The ethylene glycol formed remained in the filtrate and removal of the catalyst from it is presently being studied. The experimental conditions for some of the reactions are given in Table 1.

Analyses of results

The TPA yield was calculated using the formula:

$$\text{TPA Yield (\%)} = \frac{N_{\text{TPA}}}{N_{\text{TPA},0}} \times 100$$

where, N_{TPA} and $N_{\text{TPA},0}$ refer to the number of moles of precipitated and the theoretical number of TPA moles that would be produced on complete decomposition of PET, respectively.

The percent degradation of PET was calculated using the following equation:

$$\text{PET Degradation (\%)} = \frac{W_{\text{PET},0} - W_{\text{PET},f}}{W_{\text{PET},0}} \times 100$$

where, $W_{\text{PET},0}$ and $W_{\text{PET},f}$ refer to the initial and final weight of PET, respectively.

The purity of the TPA produced was determined following the standard method, namely, titration with KOH. About 0.1 g of TPA was weighed and taken into a 250 mL conical flask. This TPA was dissolved in 25 mL of analytical grade pyridine under reflux. The reflux condenser was washed by about 5 mL of pure pyridine through the top and the content of the flask was titrated with approximately 0.2 N KOH solution. This technique confirms the presence of dicarboxylic monomer formed in the product. Clarity of the samples was checked with the help of UV-spectrophotometer.

Results and Discussion

Reaction process

PET was first hydrolyzed in sodium hydroxide to yield the disodium salt, TPA-Na₂ and ethylene glycol, according to the chemical reaction shown in Scheme 1. The TPA-Na₂ salt was then acidified with 98% sulphuric acid to precipitate out the TPA. Similar study had been reported by Yoshioka¹¹, where 100% yield of TPA was obtained. However, due to the

Table 1—Experimental conditions for PET depolymerization in alkaline solution

PET particle size (mm)	BKC/PET (mol/mol)	PET weight in feed (g)	NaOH (wt%)	Temperature (°C)	PET degradation (wt%)
~2	0	10	10	95	3.43
<0.60	0	10	10	95	69
~2	0.1	10	10	95	58.3
<0.60	0.1	10	10	95	100
<0.60	0.1/3	10	10	95	100
<0.60	0.1/9	10	10	95	100
<0.60	0.1/27	10	10	95	97
<0.60	0.1/9	10	7	95	96.4
<0.60	0.1/9	10	6	95	93.6
<0.60	0.1/9	10	5	95	87.2
<0.60	0.1/9	10	2	95	46.2
<0.60	0.1/9	20	10	95	85.6
<0.60	0.1/9	10	5	120(2.5 bar a)	94
<0.60	0.1/9	10	5	150 (5 bar a)	100

presence of oxygen, ethylene glycol oxidized and its yield was approximately 60%.

Role of phase transfer catalyst

Initially the reaction mixture consists of the solid organic phase of PET and the aqueous alkaline solution (NaOH). The phase transfer catalyst benzalkonium chloride, BKC, fulfilled the requirements of having enough organic character in order to be lipophilic, while small enough in order to avoid steric hindrance. The cationic part of the catalyst does not carry the hydroxide anion into the organic phase (extraction mechanism) but on its surface (interfacial mechanism). In this way the PET macromolecules on the surface of the particles can be easily attacked by the OH^- and then depolymerized. The terephthalate anion produced returns to the aqueous phase and forms the disodium terephthalate salt with Na^+ . The reaction proceeds until complete depolymerization of PET to TPA- Na_2 and ethylene glycol occurs, while the catalyst remains in the aqueous phase.

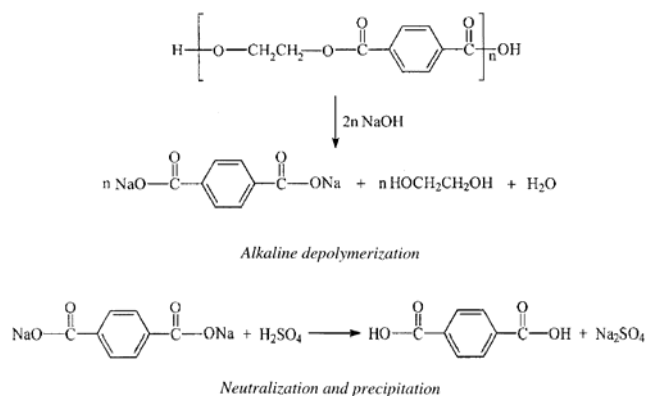
Catalyst screening

PET fed as pellets (~2 mm) = 10 g. 10 wt% NaOH solution in 100 mL DM water. Time taken to reach final temperature = 15 min Final temperature = 95°C. Reaction time = 100 min Cooling time = 15 min. The results on the effect of the catalyst type on PET conversion are shown in Fig. 1.

Very low conversions were observed with lower quaternary ammonium salts (C_0 , ammonium; C_1 , tetramethyl; C_2 , tetraethyl; C_3 , tetrapropyl). Then, long chain phase transfer catalysts (e.g., CTACl, 1-Hexadecyl-1, 1, 1-trimethyl ammonium chloride; CTABr) were attempted. As a result of this exercise, BKC was found to afford the best results. It is thought that the longer carbon chain of BKC is responsible for increased transfer of terephthalate ions from solid phase to aqueous medium. Thus it affords higher PET conversion.

Effect of particle size

Smaller particles can be expected to exhibit higher rate of reaction, or consequently higher conversions for a given volume of reaction mass, due to increased external surface area available. This, in fact, is the case with present study, as is evident from Fig. 2. The pellets used were of diameter 2.00 mm and the fines had particle size <0.60 mm. These size ranges are different from that employed by Kosmidis *et al.*¹, in which case trioctylmethylammonium bromide



Scheme 1—Chemical reactions involved in the process

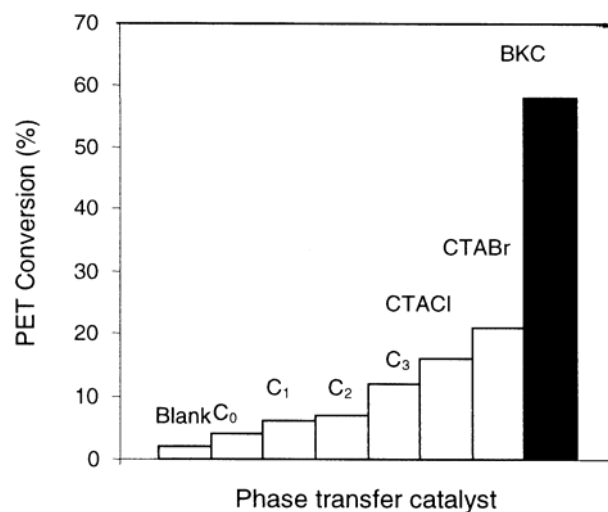


Fig. 1—Screening of phase transfer catalyst. C_0 ammonium bromide; C_1 tetramethyl ammonium bromide; C_2 tetraethyl ammonium bromide; C_3 tetrapropyl ammonium bromide; CTACl cetyl ammonium chloride; CTABr cetyl ammonium bromide; BKC benzalkonium chloride

(TOMAB) was used as the catalyst and the PET used was in the form of flakes. Increased rate of reaction with smaller PET particles had also been reported in the literature⁸.

Effect of catalyst to PET ratio

These experiments were carried out to determine the amount of catalyst to be added to the reaction mixture. The initial catalyst (BKC) to PET weight ratio of 0.27 to 1 (or, 0.1 mol of BKC/mol of PET repeating unit) was brought down by a factor of three to 0.01 g/g (or, 0.1/27 mol/mol). Complete conversion was obtained for a value of 0.03 for the weight ratio of BKC to PET and this value was taken as standard for further experimentation. By optimizing the amount of catalyst fed to the reactor, it can be

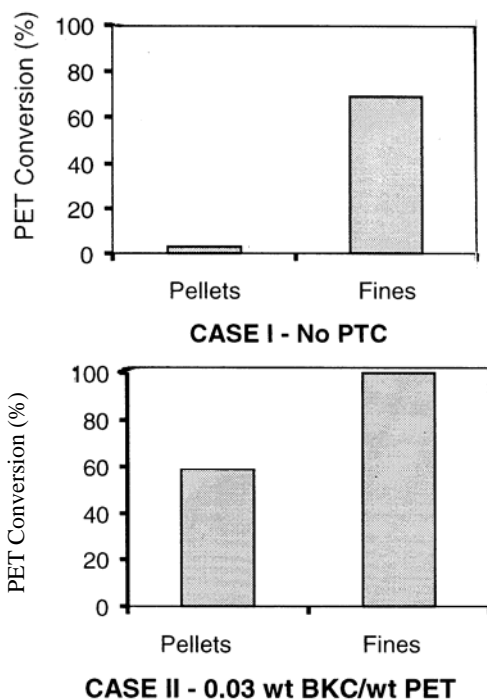


Fig. 2—Effect of particle size. Reaction temp., 95°C, reaction time, 100 min, and reaction medium, 10 wt% NaOH solution in 100 mL demineralized water

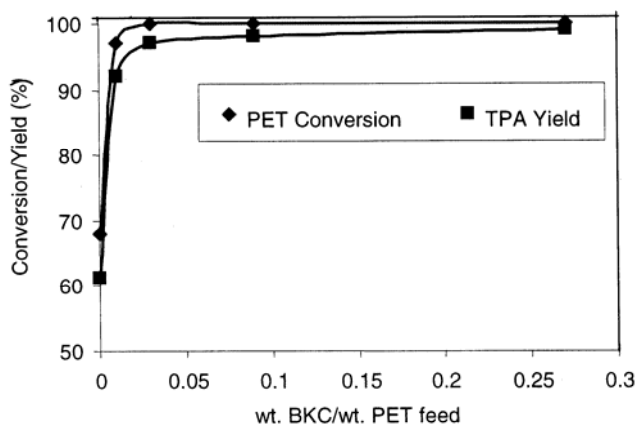


Fig. 3—Effect of catalyst to PET ratio. Reaction temp., 95°C, reaction time, 100 min, and reaction medium, 10 wt% NaOH solution in 100 mL demineralized water

minimized as an impurity in the final product. BKC in product TPA can be removed by washing filter residue with DM water. The yield of TPA (based on theoretical yield of TPA for complete PET conversion) was higher than 90% for low concentrations of BKC, as seen in Fig. 3. In a similar study²¹, optimum catalyst (zinc acetate) to PET weight ratio was found to be 1%, much higher than the present study.

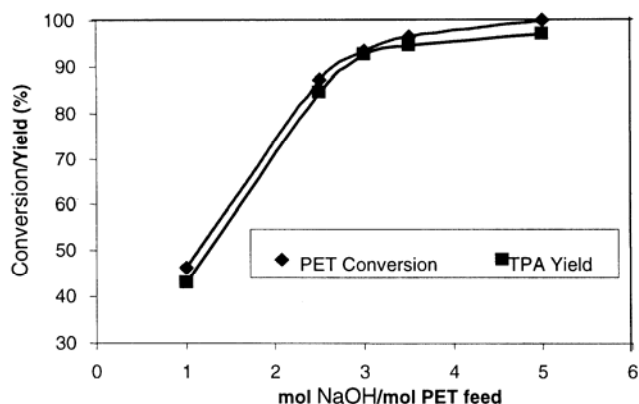


Fig. 4—Effect of NaOH concentration. Reaction temp., 95°C, reaction time, 100 min, and catalyst fed, 0.03 g BKC/g PET

Effect of NaOH concentration

These experiments were performed with an intention of carrying out the reaction at lowest possible alkali concentrations. Reducing the NaOH quantity would finally result in reduced consumption of sulphuric acid at the end of the reaction, which would in effect reduce the amount of washing required to obtain pure product. From Fig. 4 it is evident that decreased proportion of NaOH leads to the reduced PET conversion and TPA yield. The optimum NaOH/PET repeating unit molar ratio was found to be 2.5.

Effect of temperature

After having optimized the alkali and catalyst concentrations of 2.5 mol of NaOH as 5 wt% aqueous solution per mol of PET repeating unit and 0.01 mol of BKC/mol of PET repeating unit, respectively, for PET fine particles, effect of temperature on conversion was studied. For this set of reactions, the experiments were carried out in a high-pressure autoclave operating under autogenous pressure. The temperatures were 120°C at 2.5 bar and 150°C at 5 bar. Complete conversion of PET was observed at 150°C. As can be seen in Fig. 5, the yield of TPA was also higher than 90% for higher temperatures. This temperatures are much less than reported in the literature^{8,13,21}.

Effect of quantity of water

The effect of quantity of water was estimated by doubling all quantities, e.g., alkali concentration, PET feed, and catalyst concentration for same amount of water, reactor volume, temperature and reaction time. No change in extent of conversion was observed.

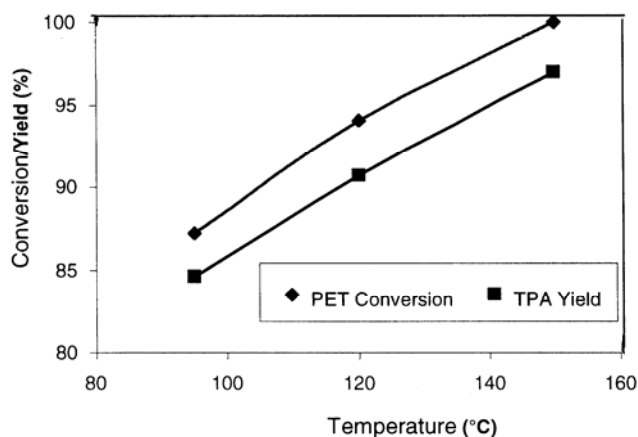


Fig. 5—Effect of temperature. Reaction time, 100 min, catalyst fed, 0.03 g BKC/g PET and reaction medium, 10 wt% NaOH solution in 100 mL demineralized water

Conclusions

The PET depolymerization reaction in alkaline medium was conducted in a batch mode with a homologous series of tetra alkyl ammonium salts, in an attempt to identify catalytic behaviour, if any. Among the catalysts tested BKC was found to be the most effective catalyst. Complete conversion of PET with considerably low catalyst concentration, alkali concentration and temperature could be achieved. The product formed was found to be reasonably pure, though it would demand further purification to be recycled for polymerization. The reaction conditions were very mild as compared to some of the reported literature.

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