

Zeolite Catalyzed Glycolysis of Poly(ethylene terephthalate) Bottle Waste

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ABSTRACT: Polyethylene terephthalate (PET) bottle waste was depolymerized using excess of ethylene glycol (EG) in the presence of zeolites, β -zeolite and γ -zeolite as transesterification catalyst. The glycolysis reaction was carried out under reflux in excess of ethylene glycol up to 8 h. The product of glycolysis was mainly the virtual monomer, bis(2-hydroxyethyl) terephthalate (BHET) admixed with dimer as residue. The BHET was obtained in pure crystalline form. Influence of the reaction time, PET : EG ratio, type, and concentration of catalyst on the yield of the glycolysis products was investigated. The characteriza-

tion of the purified monomer was carried out by elemental analysis, melting point, IR spectroscopy, DSC, and NMR. The yield of BHET monomer was more than 60%, which is comparable with the conventionally used heavy metal catalysts such as zinc acetate and lead acetate. This process of glycolysis of PET is economically viable and the catalysts are environment friendly. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 501–506, 2008

Key words: polyester; recycling; monomers; oligomers; zeolites

INTRODUCTION

Much of the humanity's progress has been marked by dramatic improvements in the materials that the chemists have developed right from the "Stone Age" to the present "Polymer Age." The development of polymers is perhaps the biggest achievement that chemistry has ever met with significant impact on the every day life. Polymers are replacing wood, glass, and metals in a wide variety of applications in almost all fields.

As a result, a huge quantity of nonbiodegradable polymer waste products is introduced into the environment every year. This has given rise to demand for nonbiodegradable polymers mainly for applications related to food packaging. Although polyethylene terephthalate (PET) is not a hazardous polymer, accumulation of this nonbiodegradable polymer into the environment needs serious attention for recycling.¹

Recovery of recyclable polyester is done from two sources: manufacturing waste and the post consumer waste, that is, the PET articles that have been used up and discarded.² There are three distinct

approaches to the recycling of postconsumer polyester waste. It may be reused directly through physical reprocessing of grinding, melting, and reforming or may be subjected to chemical treatment whereby its basic reactants are isolated and reprocessed for use in manufacture. The EPA has adopted a new nomenclature that refers to physical reprocessing as secondary recycling 2° and chemical processing as tertiary recycling 3°. The primary recycling 1° refers to use of pre consumer industrial scrap and salvage to form new packaging, a common occurrence in industry. The EPA considers "recycling" to be the processing of waste to make new articles. Although the EPA does not consider reuse to be a recycling process, using the 1°, 2°, and 3° conventions mentioned earlier, it could be considered "zero order" recycling.³

In particular, PET finds large use in making of disposable soft drink bottles and there is substantial rise in their daily consumption worldwide because of its excellent thermal and mechanical properties, crystal clear transparency, and nontoxic nature.⁴ Chemical recycling of PET through solvolysis has been the subject of keen interest leading to different types of end products. PET is a polyester and solvolytic chain cleavage is possible by reagents, such as water (hydrolysis), alcohols (alcoholysis), amines (aminolysis), acids (acidolysis), leading to a large variety of valuable products.^{5,6} Methanolysis⁷ and hydrolysis^{8–12} of PET were the first to be invented, whereas glycolysis was

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claimed in mid 1960^s.¹³ Glycolysis of PET finds its use in the preparation of unsaturated polyester resins.¹⁴ Glycolysis rate of PET waste using different glycols in the presence of zinc acetate has been studied under different conditions and it is found to be of second order with respect to ethylene glycol concentration.^{15,16} The glycolysis products consisted mainly of bis (2-hydroxyethyl) terephthalate (BHET) monomer and the reaction rate was dependant on pressure, temperature, and concentration of ethylene glycol (EG) as well as type and concentration of the catalyst. Some of these processes are not easy to operate in practice due to severe reaction conditions, pollution problems, and also tedious and costly procedures of separation. The most desirable approach is that the recycling process be effective with respect to processing expenses and energy.

Glycolysis of polyester is carried out conventionally in boiling EG under atmospheric pressure using different types of metal catalysts, zinc acetate, and lead acetate being most common.¹⁷ Zinc and lead both are heavy metal cations that cause pollution because of their nonbiodegradable and toxic nature. The toxicity caused by the heavy metal cations is slow and long lasting. The heavy metals possess a tendency to accumulate in the living organisms over a period of time. High exposure levels to lead induce anemia. It also affects the central nervous system. Although zinc is an essential element in the living organisms at trace levels, its large doses cause gastrointestinal problems. The permissible limits of Pb and Zn cations in the effluent discharged to the surface water are 0.1 and 5 ppm, respectively.¹⁸

In earlier studies, we have used different chemicals namely glacial acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate for the glycolysis reaction of PET waste and observed that the yields of the degradation product BHET are comparable to those obtained by the heavy metal acetate catalysts.¹⁹

Zeolites are naturally occurring crystalline aluminosilicates wherein Si^{4+} and Al^{3+} atoms are tetra coordinated, shared with oxide ions. This feature develops a negative charge on the aluminum atom and demands the existence of counter-ion to reach neutrality of crystalline structure outside the framework when protons (H^+) are used, these materials act as Bronstead acids. Such zwitter ionic character is responsible for the unique chemistry of these materials. Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. Zeolites find major uses in petroleum cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents.²⁰⁻²² They are often referred to as molecular sieves.

Zeolites contribute to a cleaner, safer environment in a number of ways. In fact, nearly every application of zeolites has been driven by environmental concerns, or plays a significant role in reducing toxic impact of conventional catalysts on the environment.

The present article reports the results on glycolysis of PET waste bottle using natural zeolites as catalyst. The reaction conditions of depolymerization have been optimized to get maximum possible yield of pure BHET.

EXPERIMENTAL

Materials

Waste PET bottles were obtained from a local market. These bottles were cut into small pieces of approximate size $5 \times 5 \text{ mm}^2$ after separating from the non-PET components such as labels and caps.

Chemicals

Zeolites were obtained from Sud-Chemie India, Ltd (India). Two zeolites, namely, β -Zeolite Na form ($\text{SiO}_2/\text{AlO}_2$ ratio = 1 : 5) powder and Y-Zeolite H form ($\text{SiO}_2/\text{AlO}_2$ ratio = 4 : 5) were used. Ethylene glycol (EG) (Sd Fine Chemicals, India) was of Laboratory reagent (LR) grade. Lentol FBOL (ICI Uniqema, Mumbai, India) was used as a nonionic detergent for cleaning of polyester waste materials.

Cleaning of polyester waste

PET bottle pieces were boiled with a solution containing 2 g/L of nonionic detergent for 1 h to remove any surface finish and dirt present. It was then washed thoroughly with water and dried in an oven at 80°C.

Glycolysis of polyester waste

Ethylene glycol was used for the glycolysis of PET waste in the molar ratio 1 : 6 (PET : EG) at 196°C under reflux in the presence of catalysts for time period varying upto 8 h. The catalysts, namely, β -zeolite and Y-zeolite were used in concentrations ranging between 0.25 and 1.5% by weight of polymer. After completion of the reaction, excess of distilled water was added to the reaction mixture with vigorous agitation leading to precipitation of the residue as the glycolyzed product. The mixture was then filtered to obtain glycolyzed product as a residue and the filtrate containing unreacted EG, catalyst, BHET and some water soluble oligomers. The filtrate was concentrated by boiling and then chilled to precipitate out white crystals of BHET. The glycolyzed residue was then boiled with water to extract any BHET left. BHET was further purified by

repeated crystallization from hot water, to obtain as a white crystalline solid, and dried in an oven at 70°C for 5 h. Different techniques of analysis were used for its characterization.

Characterization

Melting point of the purified monomer, BHET was determined in an open capillary.

Elemental analysis was carried out by using Heraeus Combustion Apparatus.

For Nuclear Magnetic Resonance (NMR), the glycolyzed residue was dissolved in solvent CDCl_3 . Trimethyl silane (TMS) was used as an internal standard and the spectrograph was recorded on JEOL, FT-NMR (60 MHz).

Infrared spectrum was recorded using KBr disc technique on Shimadzu IR Spectrophotometer (Model 8400S).

The thermal characteristic of the glycolyzed residue was determined by differential scanning calorimetry (DSC) (Shimadzu 60). All runs were carried out with sample consisting of ~ 2 –6 mg of compound. They were carefully put into an aluminum pan while another empty aluminum pan was used as reference. Scans were performed at the heating rate of 10°C/min from 20 to 200°C in nitrogen atmosphere.

Powder X-ray diffraction (XRD) patterns of zeolite samples were analyzed on D/MAX-3B X-ray diffractometer operated at 2θ range from 9 to 40° using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$).

The glycolyzed product obtained was subjected to thin layer chromatography (TLC) analysis with chloroform : ethanol (9 : 1) mixture as an eluent.

RESULTS AND DISCUSSION

In chemical recycling, a variety of depolymerization techniques are available leading to various end products such terephthalic acid, its ester and BHET. The terephthalic acid as well as its ester is conventionally recycled for repolymerization. Bis(2-hydroxyethyl) terephthalate (BHET) shows the potential of further chemical reactions, which has been explored at our laboratory and a few useful textile wet process related chemicals have been synthesized. These experiments form part of further communication. The mechanism of the transesterification of polyesters in presence of aluminum and silicon metal ions involves the coordination of ester through acyl oxygen as an intermediate followed by intermolecular nucleophilic attack of the glycol, which in turn undergoes elimination to give the corresponding BHET and EG as transesterification products.

Earlier, we have reported the efficiencies of different catalysts from the categories of acid, alkali and

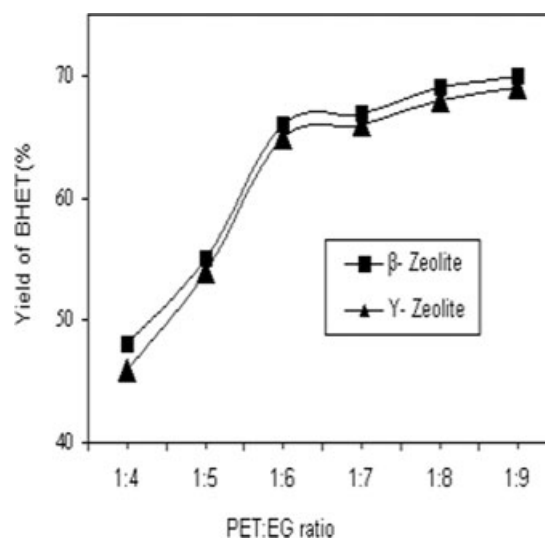


Figure 1 Effect of PET : EG ratio on BHET yield.

metal salts for the depolymerization of PET into BHET^{19,23} using PET : EG ratio (1 : 6) and 196°C as reflux temperature for 8 h. These catalysts were glacial acetic acid, lithium hydroxide, sodium sulfate, potassium sulfate, sodium carbonate, sodium bicarbonate, zinc acetate, and lead acetate. It was reported that the yield of BHET using conventional catalyst zinc acetate was the maximum (67.63%), although few of our reported catalysts followed this value closely. In spite of somewhat low amount of BHET obtained, the process has been claimed to be economical and environmentfriendly due to simple, cheap and less or nonhazardous catalysts. The natural zeolites used in the present work are widely used as the ecofriendly catalysts.

Initially, the reaction mixture is biphasic, one solid phase (PET) and a liquid phase (EG). When the chemical structure of polyesters (molecular weight and compositions) allows their solubilization, they pass into solution with increase of the UV absorbance due to the presence of terephthalic moieties and lowering the EG concentration, due to the introduction of polyesters. The solubilization of polyesters is maximum at 196°C. The PET weight (%) loss was higher at higher temperatures.

The effect of weight ratio of EG to PET on the depolymerization reaction at atmospheric pressure for 8 h and under reflux at 196°C has been indicated in Figure 1. The increase in PET : EG ratio from 1 : 4 to 1 : 9 causes increase in the yield of the monomer BHET from 48 to 70% for β -zeolite and from 47 to 69% for Y-zeolite. The PET : EG ratio 1 : 6 was considered to be optimum since, beyond this ratio, the yield of BHET increased only marginally. Glycolysis occurs predominantly in single liquid phase. It was observed that with increase in the PET : EG

TABLE I
Effect of Concentration of Catalysts on the Yield of BHET

Catalyst concentration % (w/w)	BHET yield ^a in the presence of	
	β -Zeolite	Y-Zeolite
0.25	56	54
0.50	60	58
0.75	61	62
1.00	66	65
1.25	62	63
1.50	58	59

^a Reaction Condition: PET : EG ratio 1 : 6, temp: 196°C, time: 8 h.

ratio at constant catalyst concentration and time, the dissolution of PET occurred at an earlier stage, thereby providing the single liquid phase necessary for glycolysis in less time. Kinetics has shown that glycolysis of PET attains an equilibrium, the reverse reaction being the well-known polycondensation.²⁴ Initial rate of PET glycolysis is proportional to square of EG concentration. In the initial stages of depolymerization, the polycondensation reaction has insignificantly low rate and can be ignored. Glycolysis consists of the transesterification of PET and the degradation of its polymer chain, resulting in the decrease in molecular weight. Thus, with higher PET : EG ratio, the depolymerization reaction is favored upto a certain stage (1 : 6 ratio) leading to maximum amount of the virtual monomer BHET and thereafter the polycondensation reaction does not allow enhancement in glycolysis.

To study the influence of the amount of catalyst on the product yield, experiments were carried out with the reaction time of 8 h, the molar ratio (PET : EG) of 1 : 6 and the weight ratio (catalyst to PET) varying from 0.25 to 1.5%. The monomer yield increases with the amount of catalyst, eventually approaching a steady conversion when the amount of catalyst is increased up to 1% and decreases on increasing the catalyst loading thereafter. This may be because of favoring of transesterification reaction instead of depolymerization of PET. The results are summarized in Table I.

Zeolites as catalyst were found to give predominantly dimer and BHET as was observed from TLC. The R_f values for BHET and the dimer were observed at 0.69 and 0.76, respectively, matching with the reported values.²⁵ Out of the two zeolites, Y-zeolite is the active and the most important component in FCC catalysts. Y-zeolites have high Si/Al ratio and large mesopore surface since it has high hydrothermal stability and suitable acidic and porous properties for catalytic reactions.²⁶ This directly affects the ion exchange equilibrium providing major

TABLE II
Effect of Glycolysis Time on the Yield of BHET Using Zeolite Catalyst

Time (h)	BHET yield ^a %	
	β -Zeolite	Y-Zeolite
2	—	58
3	—	59
4	—	61
5	—	62
6	—	64
7	65	65
8	66	65

^a 1% (w/w) catalyst and 1 : 6 PET : EG ratio.

part of the surface area and the active sites.^{27,28} The number and strength of active sites present in Y-zeolite are the crucial parameters for solubilization of PET and thus it helps in depolymerization of PET in a shorter time. On the other hand, β -zeolite has lower Si/Al ratio and less active sites, hence it cannot solubilize PET as fast as Y-zeolite. The data given in Table II, clearly indicates that even at the very initial stage (2 h), glycolysis proceeds at a high rate for the Y-zeolite giving 58% yield of BHET, whereas in the case of β -zeolite, the yield of BHET even after 7 h is 65% using 1% (w/w) concentration of β -zeolite and 1 : 6 PET : EG ratio.

XRD pattern of β -zeolite given in Figure 2 shows a very strong peak at $2\theta = 22.38^\circ$ due to (310) plane. Other two peaks were also identified with respective 2θ and Miller indices at 3.5° (101) and 3.3° (201). This observation indicates that the sample is of high crystallinity and pure phase. The spectra of β -zeolite shows some sharper peaks than those of Y-zeolite

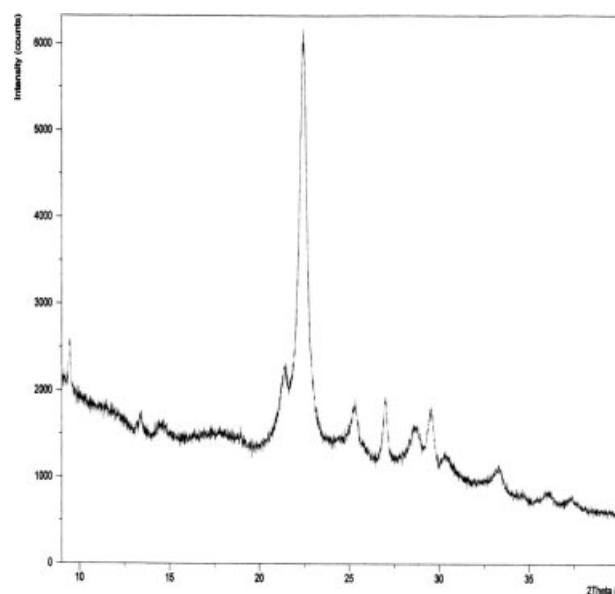


Figure 2 XRD spectrum of β -Zeolite.

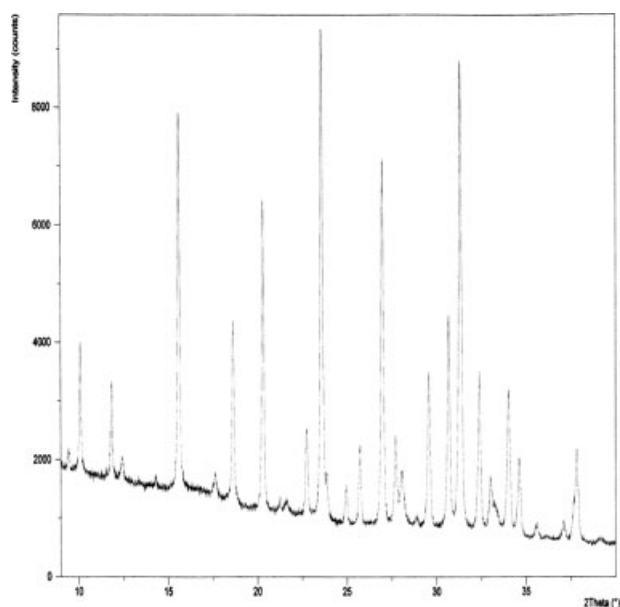


Figure 3 XRD spectrum of Y-Zeolite.

(Fig. 3), which may be caused by the larger particle size. XRD pattern of Y-zeolite exhibits the most intense diffraction peak at $2\theta = 2^\circ\text{--}24^\circ$, thus confirming its good crystalline nature in good agreement with standard.²⁹

According to Choi,³⁰ mostly dimer is produced in the presence of excess glycol, during glycolysis of PET and the BHET concentration reaches a steady state. Baliga and Wang³¹ observed that equilibrium is attained between the dimer and BHET after a long time of reaction. The same observations were confirmed in the present study.

The purified BHET was characterized by elemental analysis and melting point. These results, given in Table III, confirm that the product of glycolytic depolymerization of PET is BHET.

The IR spectrograph of the purified product contains --OH band at 3448 and 1134 cm^{-1} , C=O stretching at 1714 cm^{-1} , alkyl C--H at 2879 and 2964 cm^{-1} and aromatic C--H at $1379\text{--}1504\text{ cm}^{-1}$. These observations on glycolytic depolymerization of PET bottle waste are similar to those reported in our earlier communication.¹⁹

TABLE III
Characterization of BHET

Formula:	$\text{C}_{12}\text{H}_{14}\text{O}_6$
Mol. wt.	254 gm/mol
Melting point:	$109\text{--}112^\circ\text{C}$
Elemental analysis (%)	
C	55.6
H	5.5
O	38.9

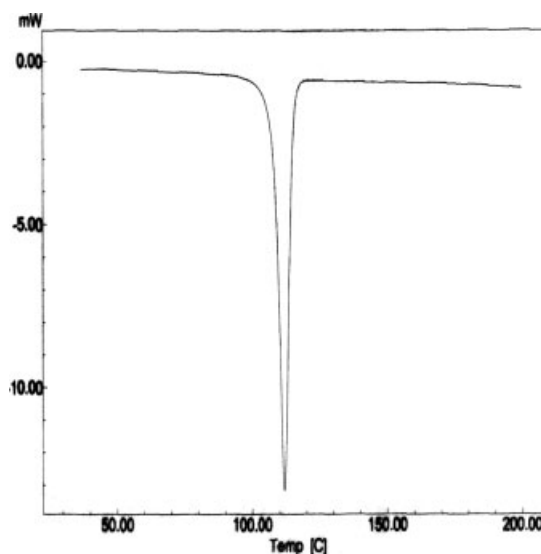


Figure 4 DSC thermogram of BHET.

The ^1H NMR spectrum also confirmed that the compound is pure BHET as in earlier communication.¹⁹ Thus, the signal at δ 8.1 ppm indicates the presence of the four aromatic ring protons. The peak at δ 1.9 corresponds to --OH groups, δ 3.95 corresponds to aliphatic (--CH_2) proton and δ 4.51 to aliphatic (--CH_2) proton.

The DSC scan of the purified fraction (Fig. 4) shows reasonably sharp endothermic peak at 109°C , which agrees well with the known melting point of BHET reported in the literature.^{32,33} The DSC scan of the linear dimer (Fig. 5) consists of endothermic peak at about 172°C confirming its presence as reported in the literature.³⁴ From all these observations it was concluded that the structure of the purified monomer is that of BHET.

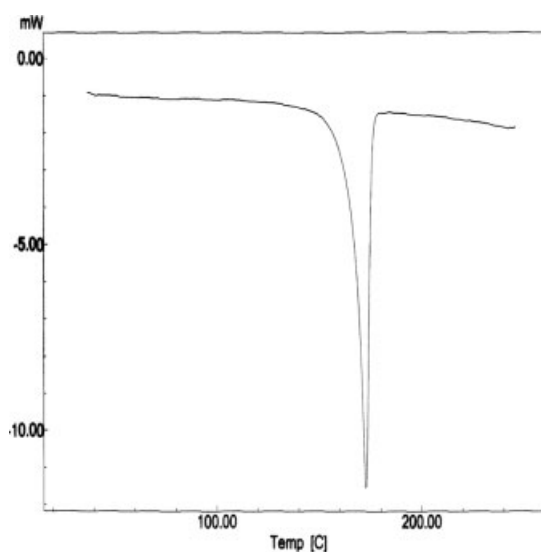


Figure 5 DSC thermogram of dimer.

CONCLUSION

The glycolysis of PET bottle waste was carried out under atmospheric pressure in excess amount of EG. Optimization of the parameters of glycolysis gives the yield of pure BHET of about 65%. Dimer also can be obtained in crystal pure form. The natural and environmentally safe large-pore aluminosilicates having considerably large void spaces such as β -zeolite and Y-zeolite can be used for the effective depolymerization of PET bottle waste with yield comparable to the conventional heavy metal catalysts like zinc acetate and lead acetate. The results lead to environmentally safe process of PET waste depolymerization into pure BHET, which can be further used in synthesis of certain useful chemicals.

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