

Depolymerization of Poly(ethylene terephthalate) Waste

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ABSTRACT: Poly(ethylene terephthalate) waste was depolymerized with ethylene glycol in the presence of different catalysts, two conventional metal catalysts (zinc acetate and lead acetate) and two alkalies (sodium carbonate and sodium bicarbonate). The resulting monomer bis(2-hydroxy ethylene terephthalate) was characterized by thin layer chromatography, melting point, IR spectroscopy, differential scanning calorimetry, and elemental analysis. The results show that the qualitative and quantitative yields of the monomer obtained with alkalies as catalysts were most comparable with the conventional heavy metal catalysts, thus providing a further advantage for the recycling of polyester waste for the cause of environmental pollution abatement. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1765–1770, 2002

Key words: catalysts; polyesters; recycling; waste

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester widely used in the manufacture of high-strength fibers, photographic films, and soft drink bottles.¹ It has been traditionally employed in the production of textile fibers ever since the mid 1940s. In the 1980s, PET began to be used popularly for the production of bottles, so much so that in 1987, more than 700 million pounds of PET were consumed for the production of more than 3 billion bottles. Over the past few years, the uses of PET have been further extended to other sectors such as thermoformed trays, containers for cosmetics, detergents, pharmaceutical products, and so on.²

Growth in synthetic fiber production has resulted in a major shift in production areas from North America and Europe to Asia. The Asian share of synthetic fiber production was 56% in

1998. This compares with a North American and Western European combined share of 61% in 1978, which was down to 37% in 1998.

In 1998, the global production in million metric tons, for the key fiber types, was 16.0 polyester, 4.9 olefin, 3.9 nylon, and 2.7 acrylic. Over the past 20 years, polyester has maintained a substantial lead in volume. Its production share has moved from 34% in 1978 to 54% in 1998. The global production of manufactured PET fiber was 29.9 million metric tons in 1998, an increase of 109% from the 14.3 million tons produced in 1978.

Some of the reactions of the manufacture of synthetic polymer are equilibrium reactions that do not go to completion, leading to unreacted monomer and oligomers that are waste. Deviations from well-defined process parameters in a synthetic polymer manufacturing plant occur due to the fault of an operator, machine, or raw material, leading to production of inferior quality. Problems such as equipment breakdown and power failure occur occasionally, and until normal parameters are restored, all the production is waste. A certain amount of waste is also gener-

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ated during the prespinning and postspinning operations of synthetic fibers.³

PET finds its utilization as fibers, films, coating, and so on. The fiber waste from the textile industry consists of broken filaments, which are contaminated with dyes, pigments, and binders, as well as other fibers. Other products made from PET that generate postconsumer waste include magnetic recording tapes, graphic art materials, electrical insulations, and so on.⁴

Under the pressure of maintaining a clean environment, the industry is facing a monumental challenge: what to do with the nonhazardous, nonbiodegradable solid waste of used polyester. Although recycling is not a new concept to the industry, it is now a necessity brought on by increased fees at landfills and decreased availability of landfill space. Recycling is more than simply a trend or a new marketing campaign designed to make a profit—it is an economic necessity.⁴

It is necessary to utilize this waste by converting it back into raw materials, intermediate products, or into any other nonfibrous useful products. Such processes of waste utilization will also be helpful in minimizing water and air pollution.⁵

The chemical depolymerization of polyester waste can be carried out by the processes of methanolysis,^{6–12} glycolysis,^{13–18} or hydrolysis.^{19,20}

During methanolysis, PET waste is treated with methanol under pressure to recover dimethyl terephthalate and ethylene glycol. A number of catalysts are reported, of which zinc acetate is the most commonly used.

Glycolysis dissolves polyester in boiling ethylene glycol under atmospheric pressure or more rapidly when heated under pressure, and it is catalyzed by transesterification catalysts. On the cooling of the solution, oligomers of ethylene terephthalate are obtained.

Hydrolysis may be carried out with water, acid, or alkali under pressure. The ultimate products are terephthalic acid and ethylene glycol.

EXPERIMENTAL

Materials

PET fiber waste was obtained as a random mixture of staple fibers (1.44 d) of varied staple lengths from Reliance Co. Ltd. (Mumbai, India). Cationic dyeable polyethylene terephthalate (CD-PET) fiber waste (1.38 d) of varied staple lengths was obtained from Nirlon Co. Pvt. Ltd. (Mumbai,

India). Both the varieties were in undyed form. Polyester soft drink bottles were procured from a local market.

Chemicals

All the chemicals used were analytical reagent grade. Auxipon nonylphenol (Auxichem Ltd.; Mumbai, India) was used as a nonionic detergent.

Cleaning of Polyester Waste Material

Polyester fiber waste and CDPET fiber waste were scoured with 2 g/L nonionic detergent solution at a boil for 1 h to remove any surface finish present on the fibers, washed thoroughly, and air dried.

The soft drink bottles free from polyethylene bases, cups, and polypropylene labels were washed with detergent, rinsed with hot water, and dried at 80°C for 4 h. It was then cut into small pieces of about 0.5 × 0.5 mm.

Glycolysis of Polyester Waste

We treated accurately weighed polyester fibers with ethylene glycol by keeping the molar ratio (polyester:glycol 1:6) in the presence of a catalyst. Four different catalysts, namely, zinc acetate, lead acetate, sodium carbonate, and sodium bicarbonate, were used in two concentrations, 0.5 and 1.0% (w/w). The reaction was carried out at 190°C for 8 h. After the completion of the reaction, distilled water was added to the reaction mixture, followed by vigorous agitation. We then filtered the mixture to obtain glycolized product as a residue and the filtrate containing unreacted ethylene glycol, catalyst, bis(2-hydroxy ethylene terephthalate) (BHET), and some water-soluble oligomers.

The filtrate was concentrated via boiling and then chilled to precipitate out white crystals of BHET. The residue was mixed with water and boiled to extract any BHET left, which was further purified by repeated crystallization from water. The metal acetate catalysts present in the filtrate were deactivated by the addition of phosphoric acid. Ethylene glycol was recovered from this deactivated filtrate by distillation. BHET obtained as a white crystalline solid was dried in an oven at 70°C for 4 h to remove traces of ethylene glycol and subjected to analysis by different techniques.

Similar glycolysis experiments were performed with polyester soft drink bottles and CDPET with

Table I Effect of Catalysts on the Glycolysis of Polyester Waste

| Catalyst | Catalyst Concentration (%) | BHET Yield (%) | | |
|--------------------|----------------------------|------------------------|------------------------|-------------------|
| | | PET Staple Fiber Waste | PET Soft Drink Bottles | CDPET Fiber Waste |
| Zinc acetate | 0.5 | 67.63 | 62.51 | 53.20 |
| | 1.0 | 61.32 | — | — |
| Lead acetate | 0.5 | 65.91 | 61.65 | 52.46 |
| | 1.0 | 62.18 | — | — |
| Sodium bicarbonate | 0.5 | 66.22 | 61.50 | 50.32 |
| | 1.0 | 63.78 | — | — |
| Sodium carbonate | 0.5 | 65.43 | 61.94 | 51.23 |
| | 1.0 | 62.18 | — | — |

At 1% (w/w) catalyst, the BHET yields decreased and, hence, were not considered for the PET soft drink bottles and CDPET fiber waste.

a 0.5% catalyst concentration and a substrate: glycol ratio of 1:6.

Analysis of BHET

The melting point of BHET was determined in an open capillary. IR spectra were recorded with the KBr disc technique on a PerkinElmer IR spectrophotometer (Buck Scientific, model 500). Elemental analysis was carried out with a Heraeus combustion apparatus. Differential scanning calorimetry (DSC) was performed with a DSC 2100 (TA instruments) with a 30–200°C scanning window at 10°C under a nitrogen atmosphere.

Analysis of Glycolyzed Product

The residue obtained, called the glycolyzed product, was analyzed by thin layer chromatography. Chloroform–ethanol (9:1) was used as an eluent, and a thin layer chromatography (TLC) plate was visualized in an iodine chamber.

RESULTS AND DISCUSSION

Polyesterification is a step growth reaction that produces BHET. The molecular weight of the polymer increases at a relatively slow rate. The reaction mixture at any instance consists of various sized diols, diacids, and hydroxy acid molecules. Polycondensation of BHET produces PET and, as a by-product in this reversible reaction, ethylene glycol.

The reverse reaction can be utilized to produce BHET from PET with an excess of ethylene glycol

and a *trans*-esterification catalyst. The ratio of glycol to polyester waste in this case may vary between 1 and 10, whereas the amount of catalyst used is 0.1 to 1.0% by weight.

Vaidya and Nadkarni²¹ obtained low-molecular-weight diols from the glycolysis of PET waste with different glycols in the presence of a zinc acetate catalyst. The glycolysis rate was found to be second order with respect to ethylene glycol concentration.²²

During the hydrolytic depolymerization of PET, the catalytic activity of zinc compounds was attributed to the electrolytic destabilization of the water–PET interface. A similar effect was observed by Campanelli et al.²³ during glycolysis below 245°C, wherein the extent of reaction increased in the presence of zinc compounds due to the reaction occurring between two phases, namely, liquid ethylene glycol and solid PET. Above 245°C, due to absence of a heterogeneous system, there was no effect.

Because BHET is supposed to be a true monomer of polyester, glycolysis was selected as the route of depolymerization for PET and CDPET waste in this work. We selected two metal acetate catalysts and two alkali catalysts to estimate their effectiveness in glycolysis.

Table I gives the effect of these catalysts on the amount of BHET obtained by the depolymerization of different types of PET. The data indicates that for all the waste samples, PET staple fibers, PET bottles, and CDPET fibers, the glycolysis catalyzed by zinc acetate gave the maximum yield of BHET. This is in agreement with the earlier results. Kao²⁴ investigated catalytic glycolysis of

PET by DSC using acetates of zinc, cobalt, cupric, manganese, and sodium. The efficiency of glycolysis, as measured from the peak temperature associated with the reaction endotherm, was at a maximum with zinc acetate. Baliga and Wong¹ found that the relative effectiveness of metal acetates in glycolysis was in the order $\text{Zn}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+}$.

Interestingly, the other catalysts used in this work also showed nearly the same efficiency of depolymerization. Thus, at 0.5% (w/w) concentration, zinc acetate gave a 67.63% yield of BHET, whereas the lowest yield obtained was 65.43% with sodium carbonate.

The data in Table I further indicate that the yields of BHET were at a maximum for PET staple fiber waste, followed by PET bottle waste with a small margin, and then CDPET fiber waste, which was considerably low. This may be attributed to the different nature of the waste materials. Petrov and Aizenshtein²⁵⁻²⁷ showed that the rate of glycolysis depends on the fine structure of the starting material. They used PET spinneret face waste and stretched monofilaments for their study.

Molecular weight and the molecular weight distribution requirements for film- or fiber-forming PET materials are different from those used for blow-molding PET bottles. For fiber grade PET, a medium molecular weight with a narrow molecular weight distribution is required, whereas bottle-grade PET requires a high molecular weight and a wider molecular weight distribution so the material can retain a high melt viscosity during the blow-molding process.^{28,29} To achieve this, PET is often modified with comonomers such as multifunctional hydroxy and carboxylic acid compounds as branching agents and some monofunctional chain-terminating agents.³⁰⁻³² In the case of CDPET, the structural variations are additionally caused by the incorporation of comonomers containing sulfonic acid groups to impart the fiber cationic dyeability.

Table II gives the data on the characterization of the BHET obtained. The observed percentages of the elements C, H, and O for the BHET analysis closely related to the theoretical values. Also, all the peaks related to BHET structure were appropriately indicated by the IR spectrograph, confirming that the depolymerized product through the glycolysis route was BHET of a high purity.

The DSC scan of BHET is shown in Figure 1. It indicates that the melting onset temperature was

Table II Characterization of BHET

| Formula | $\text{C}_{12}\text{H}_{14}\text{O}_6$ | |
|--|--|-------------|
| Molecular weight | 254 | |
| Melting point | 109–112°C | |
| Elemental Analysis (%) | Calcd | Found |
| C | 56.6 | 55.9 |
| H | 5.9 | 5.4 |
| O | 37.5 | 38.7 |
| Assigned peaks of IR spectrograph (cm^{-1}) | | |
| | 3450 | (O—H) |
| | 3045 | (ArC—H) |
| | 2900 | (Alkyl C—H) |
| | 1700 | (C=O) |
| | 1600 | (ArC—C) |
| | 1150 | (C—OH) |

107.89°C and the peak temperature was 110.65°C. This was in close agreement with the melting of BHET as reported by Tomita.³³

The glycolyzed product residues obtained with different catalysts were subjected to TLC analysis with a chloroform–ethanol (9:1) mixture as an eluent. The R_f values obtained for the different oligomers present in the residues are reported in Table III. With all the catalysts, dimer was predominantly obtained in the residue on glycolysis. The presence of other oligomers in the different residues was dependent on the catalyst selected for glycolysis. Similar R_f values for the oligomers were observed in our earlier work on the characterization of oligomers obtained from PET samples by extraction and dissolution routes.³⁴

Thus, this work indicates that it is possible to use mild alkalies such as sodium carbonate and sodium bicarbonate as depolymerization catalysts in polyester glycolysis.

The acetates of zinc and lead both belong to the category of heavy metals, and much evidence is available on the ill effects of these metal ions on the environment in general.

Heavy metal ions are known to be among the most dangerous polluting agents because they are nonbiodegradable. Further, they have a unique property of accumulation along the food chain, and very high levels can be accumulated over a period of time in organisms from very low concentrations in water and sediment. The toxicity caused by metal pollution is slow and long lasting due to the nondegradability of metals.

The effects of lead on health are manifest. It may induce anemia at high levels of exposure.

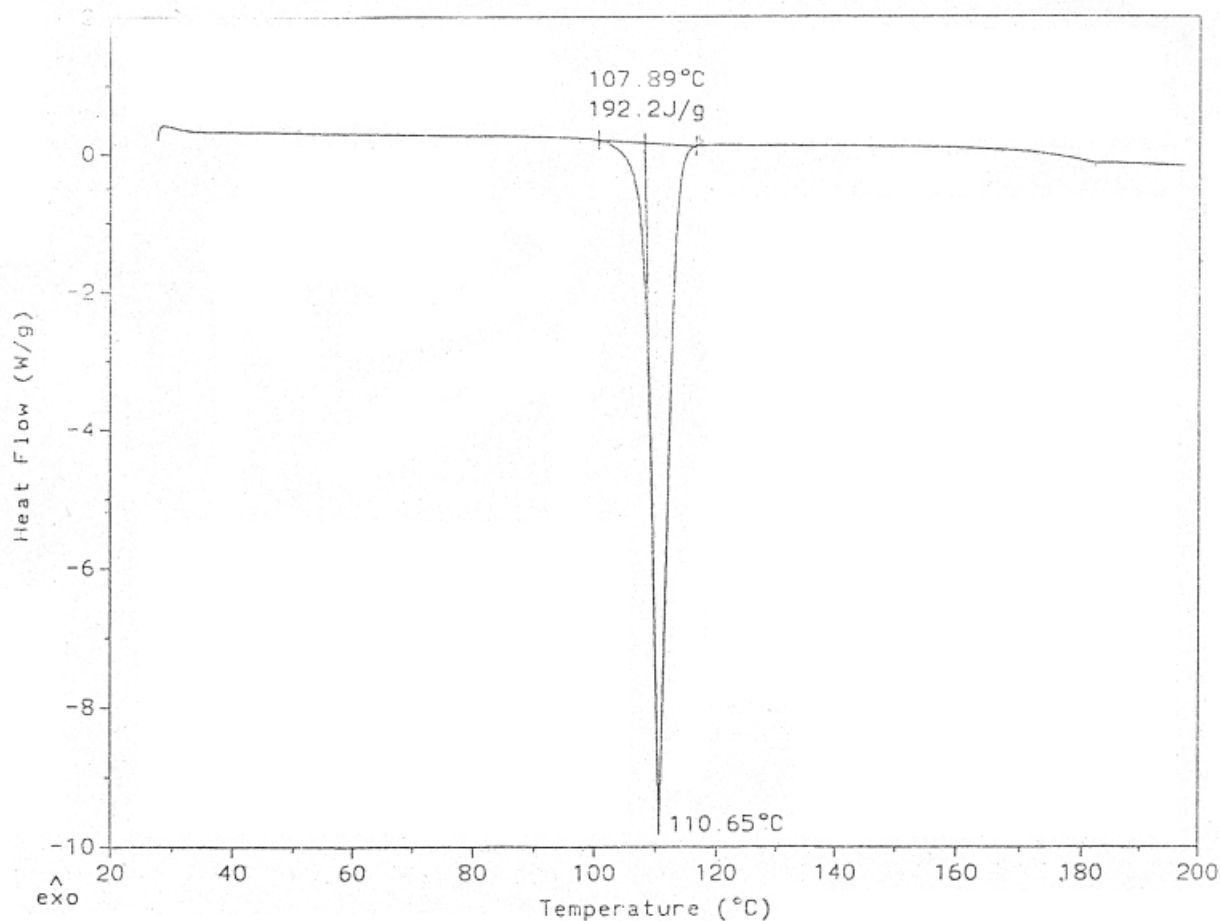


Figure 1 DSC scan of BHET.

Acute effects of lead on the central nervous system are generally seen in children exposed from pica. Zinc is essential for the proper functioning of plants and animals in a very little amount. It is only second to iron as a trace element in human beings. However, large doses of zinc may cause gastrointestinal problems. Permissible levels in the effluent discharged to surface waters are 0.1 ppm for lead and 5.0 ppm for zinc.

Table III R_f Values of Glycolyzed Residue Product

| R_f | Description |
|-------|--------------------------|
| 0.43 | Cyclic pentamer |
| 0.47 | Cyclic pentamer with DEG |
| 0.63 | Trimer |
| 0.75 | Dimer |

DEG, diethylene glycol.

Earlier, work was carried out in our laboratories on the removal and recovery of a number of heavy metal ions from the effluents by their adsorption on cheap cellulosic substrates.^{35,36}

In this work, the heavy metal acetates of zinc and lead were left into the filtrate-cum-effluent after BHET crystallized out and ethylene glycol was recovered by distillation, thus causing pollution of the discharged water.

Oku, Hu, and Yamada³⁷ carried out glycolysis of PET waste in the presence of sodium hydroxide under atmospheric conditions to obtain ethylene glycol and disodium terephthalate as reaction products. In this case, however, the true monomer of polyester, namely, BHET, was not obtained. Moreover, caustic soda is a strong alkali. Instead, in this work, safe and mild alkalies such as sodium carbonate and sodium bicarbonate were used to obtain good yields of BHET. Also, these alkalies are quite harmless from the point of view

of effluent pollution, except that they add to the total dissolved solids. They are also cheap compared to conventional metal acetates.

It may, therefore, be concluded that mild alkalis such as sodium carbonate and sodium bicarbonate are effective for the production of a good yield of BHET from the depolymerization of PET through glycolysis. Further, they are environmentally friendly.

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