

Studies of Glycolysis of Poly(ethylene terephthalate) Recycled from Postconsumer Soft-Drink Bottles. I. Influences of Glycolysis Conditions

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ABSTRACT: The glycolysis of recycled poly(ethylene terephthalate) flakes by ethylene glycol (EG) is investigated. Bis-2-hydroxyethyl terephthalate (BHET) and oligomers are predominately glycolysis products. The influences of glycolysis temperature, glycolysis time, and the amount of catalyst (cobalt acetate) are illustrated. The BHET, dimer, and oligomers are predominately glycolysis products. The optimum glycolysis temperature is found to be 190°C. If a 190°C glycolysis temperature, 1.5-h glycolysis time, and 0.002 mol glycolysis catalyst (cobalt acetate) are used, the glycolysis conversion is almost 100%. The glycolysis conversion rate increases significantly with the glycolysis temperature, glycolysis time, and the amount of cobalt acetate. Thermal analyses of glycolysis products are examined by differential scanning calorimetry. In addition, the chemical structures of glycolysis products are also determined by a Fourier transform IR spectrophotometer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 943–948, 2001

Key words: glycolysis; poly(ethylene terephthalate); ethylene glycol; postconsumer soft-drink bottles; cobalt acetate; bis-2-hydroxyethyl terephthalate

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester. PET products have the characteristics of high strength, transparency, and safety. Currently, PET is widely used in the manufacture of soft-drink bottles for replacing poly(vinyl chloride) and glass bottles. However, because it is difficult to dispose of PET bottles in nature, the disposal of a large number of PET bottles has caused serious environmental problems.^{1,2} Since the green revolution movement beginning in the 1980s, researchers have begun to focus on recycling and management of plastic

wastes.^{3,4} Today, PET bottles have become one of the most valuable and successfully recyclable materials.

There are various possibilities for dealing with recycled PET bottles. These methods involve hydrolysis with acids or bases in aqueous solution,^{5,6} noncatalytic hydrolysis or alcoholysis in supercritical media,^{7,8} and alcoholysis or glycolysis by catalytic reactions.^{9–11} Campanelli et al.⁷ studied the reaction of PET melts with ethylene glycol (EG) in a pressure reactor at temperatures above 245°C. They concluded that the reaction rate was dependent on the temperature, the concentrations of EG, and the ethylene diester groups in the polymer. Chen et al.⁸ illustrated the kinetics of the glycolytic depolymerization of PET in a pressure reactor at temperatures between 190 and 240°C. They found that the depolymer-

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ization of PET was dependent on the pressure, temperature, and EG/PET ratio. They also demonstrated that the glycolysis rate was second order with respect to the EG concentration. The behavior of EG acting as both the reactant and catalyst in the glycolysis reaction was mentioned in this report. Baliga and Wong¹¹ found that zinc acetate had the best result of four metal acetates (lead, zinc, cobalt, and manganese) tested; zinc acetate was the best, yielding the highest amount of bis-2-hydroxyethyl terephthalate (BHET) monomer.

Glycolysis of recycled PET bottles can lead to the production of BHET monomer. BHET has been widely used in the production of unsaturated polyesters and rigid or flexible polyurethanes.⁹ A simple glycolysis system that could obtain almost 100% glycolysis conversion in 1.5 h was set up in the present study. Moreover, we studied the influences of glycolysis conditions (temperature, time, and amount of catalyst) on the glycolysis conversion of recycled PET flakes. The thermal properties and chemical structure analyses of glycolysis products were also discussed.

EXPERIMENTAL

Materials

Commercially clear PET soft-drink bottles were recycled, washed, and cut into 0.4×0.4 cm flakes. These recycled PET flakes were dried for glycolysis experiments. These recycled PET flakes were blow-molding grade (IV = 0.85 in 60% phenol/40% tetrachloroethane). The EG and cobalt acetate were purchased from Katayama Chemical. All reagents were used without further purification.

Glycolysis Experiment

A 1000-mL four-necked flat-bottom reactor was used for all glycolysis experiments. In order to ensure that the water content in the reactor was as low as possible, we heated the reactor to 110°C and held that temperature for at least 2 min. The reactor was equipped with a thermometer and a reflux condenser. A stirrer was put in the reactor to ensure proper mixing. The ratio of EG:PET used in the glycolysis experiments was 2:1 (w/w). The weights of EG and recycled PET flakes were 160 and 80 g, respectively. In order to ensure the limited water content in the reactor, it was heated

to 110°C and held at this temperature for at least 2 min.

In order to realize the influences of glycolysis temperature, glycolysis time, and amount of catalyst on the depolymerization of recycled PET flakes, three groups of glycolysis experiments were designed. In the first group the glycolysis temperature was set at 190°C and 0.002 mol metal acetate (catalyst) was used. The glycolysis time was varied (0, 0.5, 1.0, 1.5, and 2 h) from 0 to 2 h at 0.5-h intervals. In the second group the glycolysis temperature was set at 190°C and the glycolysis time was 1.0 h. The molar amounts of metal acetate were 0, 0.001, 0.002, 0.003, 0.004, 0.005, and 0.006 mol. In the third group a glycolysis time of 1.0 h and 0.002 mol metal acetate were used. The glycolysis temperature was varied from 110 to 190°C at 20°C intervals.

After the specified glycolysis experiment was finished the reactor was removed from the hot plate, and 200 mL of boiling water was slowly added into the reactor. Then the whole product mixture was quickly filtered using a copper screen with a 0.05×0.05 cm pore size. The undepolymerized PET flakes were collected, dried, weighed, and labeled as the PET fraction. The conversion for the glycolysis of the recycled PET flakes was defined as

$$\% \text{ conversion} = \frac{A - B}{A} \times 100\%$$

where A represents 80 g of recycled PET flakes and B represents the weight of undepolymerized PET flakes (PET fraction). The residual product mixture was filtered by using a suction filter funnel with filter paper. The filter cake was collected, dried, and labeled as the X fraction. The filtrate was collected and stored in a refrigerator for 24 h. The white crystalline flakes of BHET were formed in the filtrate and filtered. The BHET flakes were also washed with 600 mL of cooled distilled water in order to remove the metal acetate, collected, dried, and labeled as the BHET fraction.

Analyses

The hydroxyl values of the BHET fraction and X fraction were analyzed according to ASTM D2849 Method A.^{8,11} White BHET crystalline flakes were prepared by grinding powdery samples with KBr powder and then pressing the mixtures into a thin tablet. A Fourier transform IR spectroscopy (FTIR) spectrophotometer (BioRad FTS155) was used to identify the chemical structure of the

BHET fraction. Differential scanning calorimetry (DSC; Perkin–Elmer DSC 7) was used for thermal analyses of the BHET fraction, X fraction, and PET fraction. These samples were heated from room temperature to a preset temperature with a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The results of the elemental analysis of the BHET fraction was 56.73% C, 5.41% H, and 37.86% O. This experimental result was similar to the theoretical result (56.74% C, 5.5% H, and 37.76% O). The oxygen content in the elemental analysis result was a little bit higher than that in the theoretical result. This might have been due to the presence of moisture. The theoretical hydroxyl values of pure BHET monomer and its dimer were 441.5 and 251.3 mg KOH/g, respectively.¹¹ In this study, the hydroxyl values of the BHET fraction and X fraction were analyzed according to ASTM D2849 Method A.¹¹ The hydroxyl numbers of the BHET and X fractions were 438.5 and 340.5 mg KOH/g, respectively. The hydroxyl values of the X fraction were higher those of the dimer. This implies that the X fraction was a mixture of BHET, dimer, and other oligomers.

The relationship between the glycolysis conversion of the recycled PET flakes and glycolysis time is shown in Table I and Figure 1. The glycolysis temperature was set at 190°C, and the amount of cobalt acetate was 0.002 mol. Generally speaking, the glycolysis conversion increased with glycolysis time, eventually approached steady conversion when the glycolysis time was longer than 1.5 h. In Figure 1, the glycolysis conversion is only 23% when the glycolysis time is set at 0.5-h glycolysis time, and the glycolysis conversion is almost proportional to the first order of glycolysis

Table I Influence of Glycolysis Time on Glycolysis Conversion of Recycled PET Flakes

Time (h)	Conversion (%)
0	0
0.5	23.4
1.0	85.7
1.5	98.8
2.0	98.9
2.5	98.9

The glycolysis temperature was 190°C, and the amount of cobalt acetate was 0.002 mol.

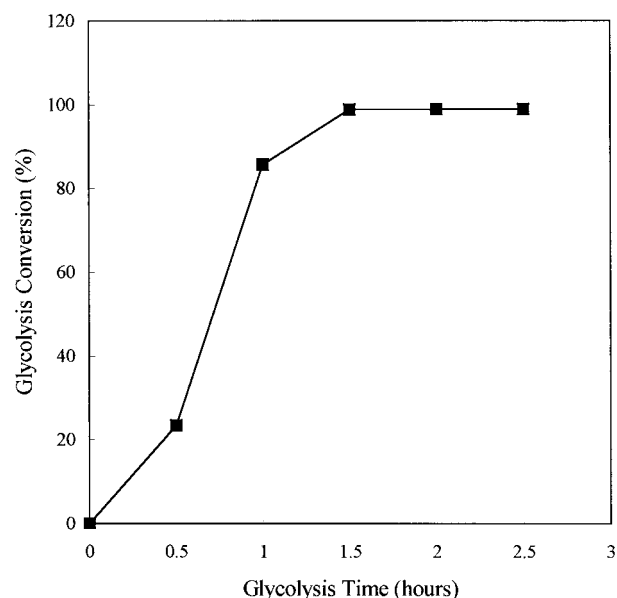


Figure 1 The relationship between the glycolysis time and glycolysis conversion of recycled PET flakes with a glycolysis temperature of 190°C and 0.002 mol cobalt acetate.

time during a period of 0–0.5 h. However, if the glycolysis time is set at 1.0 h, the glycolysis conversion increases dramatically (up to 86%) and the glycolysis conversion is almost proportional to the second order of glycolysis time during a period of 0.5–1.0 h. If the glycolysis time is extended to 1.5 h or longer, the glycolysis conversion is almost 100%.

Figure 2 and Table II display the relationship between the glycolysis conversion of recycled PET flakes and the amount of cobalt acetate. The glycolysis temperature was set at 190°C and the glycolysis time was set at 1.0 h. In Figure 2 the glycolysis conversion increases with the amount of cobalt acetate and eventually approaches a steady conversion when the amount of cobalt acetate is more than 0.002 mol. Figure 2 also illustrates that the glycolysis conversion is about 55% if 0.001 mol cobalt acetate is used, and the glycolysis conversion is almost proportional to the first order of the amount of cobalt acetate. Moreover, if 0.002 mol cobalt acetate is used, the glycolysis conversion increases to 86% and it is almost proportional to the 0.7 order of the amount of cobalt acetate from 0.001 to 0.002 mol. If the amount of cobalt acetate is higher than 0.002 mol, the glycolysis conversion is almost a constant (approximately 87%).

Figure 3 and Table III show the relationship between the glycolysis conversion of recycled PET

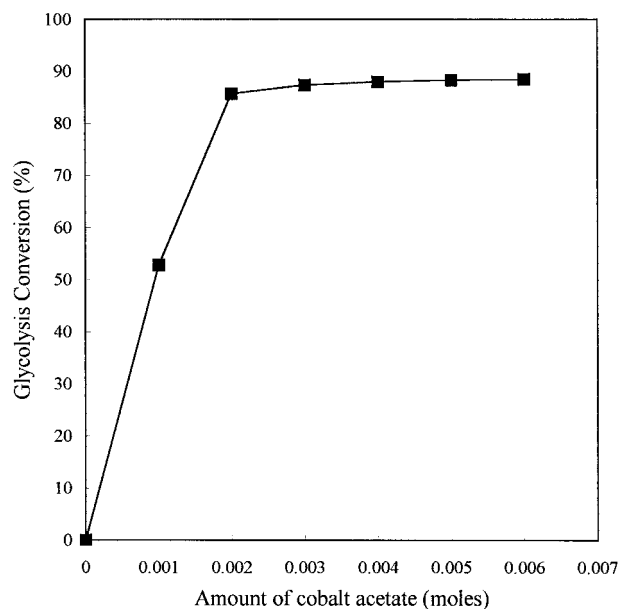


Figure 2 The relationship between the amount of cobalt acetate and the glycolysis conversion of recycled PET flakes with a glycolysis temperature of 190°C and a glycolysis time of 1.0 h.

flakes and the glycolysis temperature. The figure shows a glycolysis time of 1.0 h and 0.002 mol cobalt acetate conditions. The glycolysis conversion is very low if the glycolysis temperature is set below 150°C. However, if the glycolysis temperature is higher than 150°C, then the glycolysis conversion apparently increases with the glycolysis temperature. When the glycolysis temperature is set at 170°C, the glycolysis conversion begins to reach 12%. Eventually, when the glycolysis temperature is set at 190°C, the glycolysis conversion increases dramatically from 12 to 86%. Therefore, the glycolysis temperature is a very critical factor for glycolysis conversion.

Table II Influence of Amount of Cobalt Acetate on Glycolysis Conversion of Recycled PET Flakes

Cobalt Acetate (mol)	Glycolysis Conversion (%)
0	0
0.001	52.8
0.002	85.7
0.003	87.4
0.004	88.0
0.005	88.5
0.006	88.6

The glycolysis temperature was 190°C, and the glycolysis time was 1.0 h.

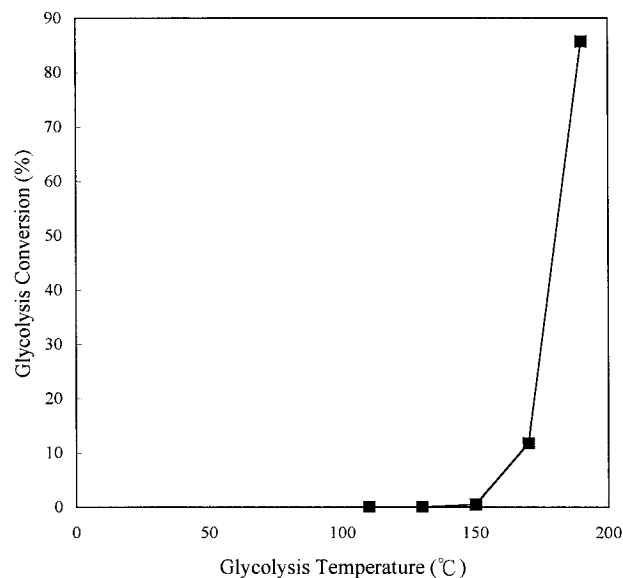


Figure 3 The relationship between the glycolysis conversion and the glycolysis temperature of recycled PET flakes with a glycolysis time of 1.0 h and 0.002 mol cobalt acetate.

There are two DSC thermal analysis curves in Figure 4. The DSC thermal analysis of the BHET fraction is illustrated in Figure 4 as curve a. The melting onset temperature and the peak temperature of the BHET fraction shown in curve a are 107 and 110°C, respectively. Curve b in Figure 4 displays the DSC thermal analysis of the X fraction. There are two endothermic peaks in curve b of Figure 4. One peak is around 105°C; therefore, it can be reasonably associated with the melting temperature of BHET. However, the other peak, centered at around 143°C, is quite broad and hence is not readily considered as the melting of the dimer. According to the reports of Chen et al.⁸ and Baliga and Wong,¹¹ the known melting temperatures of BHET and dimer are around 110 and

Table III Influence of Glycolysis Temperature on Glycolysis Conversion of Recycled PET Flakes

Temperature (°C)	Conversion (%)
110	0
130	0
150	0.5
170	11.8
190	85.7

The glycolysis time was 1.0 h, and the amount of cobalt acetate was 0.002 mol.

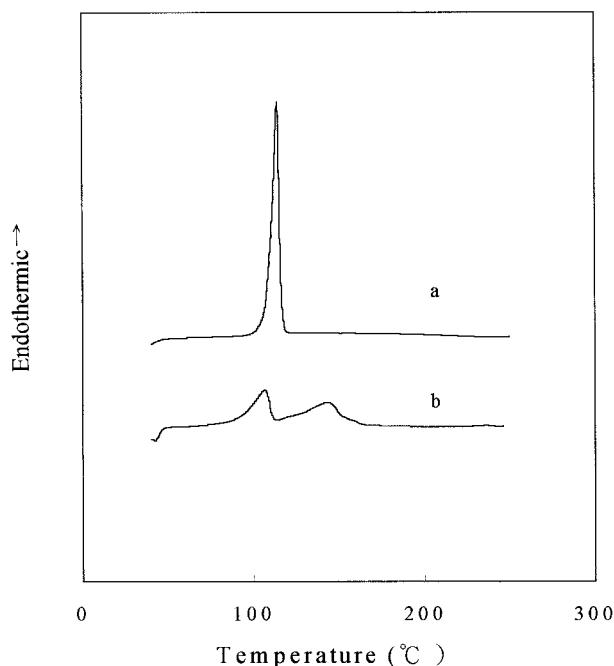


Figure 4 DSC thermal analysis curves of the BHET fraction (curve a) and X fraction (curve b) at a heating rate of 20°C/min.

170°C, respectively. Therefore, the X fraction can be assumed to consist mainly of BHET and dimer. Moreover, the research results from this DSC thermal analysis seem to suggest that there are some interactions between the monomer and dimer at elevated temperature.¹¹ This agrees very well with the results reported by Baliga and Wong¹¹ and Tomita.¹²

Curve a in Figure 5 shows the FTIR spectroscopy of the BHET fraction. The absorptions at 3000–3500, 2850–3000, 1720, 1503, and 1100 cm^{-1} are due to the —OH, —CH₂, C=O, aromatic group, and C—O stretching, respectively, of the BHET fraction. There is a broad peak between 3000 and 3500 cm^{-1} . It may result from strong hydrogen bonding among the BHET molecules. Meanwhile, curve b in Figure 5 shows the FTIR spectroscopy of the X fraction, which is a mixture of BHET, dimer, and a little oligomer. The absorption peaks at 3000–3500, 2850–3000, 1720, 1503, and 1100 cm^{-1} are due to —OH, —CH₂, C=O, aromatic group, and C—O stretching, respectively, of the mixture's chemical structure.

Although the absorption peaks in curve a of Figure 5 are almost similar to those in curve b, there are some differences between 3000 and 3500 cm^{-1} . First, in curve b of Figure 5 the absorption peak between 3000 and 3500 cm^{-1} is much sharper than that in curve a. Moreover, this

absorption peak in curve b is close to 3500 cm^{-1} . Another interesting observation is that a shoulder exists between 3000 and 3500 cm^{-1} in curve b but not in curve a. This indicates that the energy of hydrogen bonding is lower among molecules in the X fraction than that among BHET molecules in the BHET fraction. The higher hydroxyl number may result in stronger hydrogen bonding. This result proves the same tendency that the BHET fraction has higher hydroxyl numbers than the X fraction.

CONCLUSIONS

The influences of glycolysis temperature, glycolysis time, and the amount of catalyst (cobalt acetate) were illustrated. The optimum glycolysis temperature was observed to be 190°C. The results showed that if the glycolysis temperature was 190°C, the glycolysis time was 1.5 h, and the amount of catalyst (cobalt acetate) was 0.002 mol, then the glycolysis conversion was almost 100%. Moreover, the glycolysis conversion rate increased significantly with the glycolysis temperature, glycolysis time, and the amount of cobalt acetate (glycolysis catalyst). Almost no glycolysis conversion occurred without adding catalyst or at a glycolysis temperature set below 150°C. The DSC and FTIR results indi-

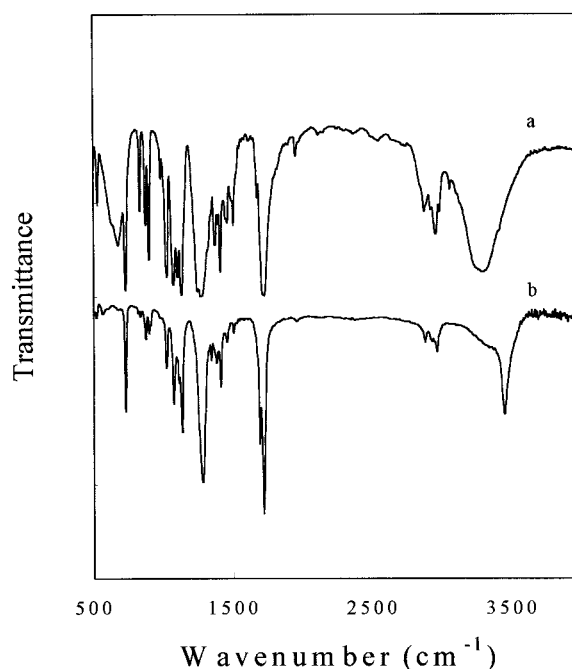


Figure 5 The FTIR spectroscopy of the BHET fraction (curve a) and X fraction (curve b).

cated that the BHET, dimer, and other oligomers were predominately glycolysis products. The hydroxyl numbers of the BHET fraction and *X* fraction were 438.5 and 340.5 mg KOH/g, respectively. The higher hydroxyl number may result in stronger hydrogen bonding.

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