CHAPTER 2

GLYCOLYSIS OF POLYETHYLENE TEREPHTHALATE (PET)

Contents

2.1 INTRODUCTION

Glycolysis of PET wastes from soft drink PET bottles in excess diol has been studied for many years and most frequently using ethylene glycol [1-3], diethylene glycol [4, 5], triethylene glycol [6] and propylene glycol [7, 8]. The process is conducted in a wide range of temperatures from (180-250) °C [1-8] and various reaction times from 0.5 to 8 hours. Generally, catalyst of 0.5% based on weight of PET is added and the most frequently used is zinc acetate [2, 6, 7]. Utilization of the product obtained has been the main target for most of the research study. For example, PET glycolysates find applications in the manufacture of polyurethane foams [9] and unsaturated polyester resins [7, 10].

In this work, PET has been glycolysed in excess of triol. As previous study, the most preferred catalyst, zinc acetate, is used and the reaction was done under specific reaction conditions. Common soft-drink PET bottles were glycolysed by glycerol in the presence of zinc acetate as a catalyst. Three sets of experiments were designed to study the influences of glycolysis temperature, time, and ratio of PET to glycerol on the glycolysis conversion of recycled PET flakes. The optimum conditions determined and were used as a guide to design a series of glycolysed PET with different hydroxyl value and other characteristics of glycolysed PET. The glycolysed PET in the form of polyester polyol, was then characterised.

2.2 EXPERIMENTAL

2.2.1 Materials and reagents

The poly(ethylene terephthalate) (PET) used in the glycolysis process was from soft drink clear PET bottles. These bottles were cleaned and washed with detergent, dried at room temperature before shredded into flakes by a rapid granulator. The size of PET flakes is about 0.6 x 0.6 cm. PET flakes, as shown in appendix Figure A2-1 were then dried in an oven at 150 °C for 3 hours and kept in the desiccators prior to use in the glycolysis process.

Technical grade of glycerol (R&M Chemicals) was used as degrading agent. Zinc acetate (R&M Chemicals), pyridine (MERCK), ethanol, toluene and phthalate anhydride used were of analytical grade supplied by Systerm Chemicals and use as-received.

2.2.2 Glycolysis conversion of recycled PET flakes

Glycolysis reaction was carried out in a 500 ml round bottom flask as reactor, which was equipped with a thermometer, mechanical stirrer and reflux condenser. While heating mantle with variable power control was used for heating. Appendix Figure A2-2 shows the reaction set-up.

To study the influences of glycolysis temperature, time, and ratio of PET to glycerol, on the glycolysis conversion of recycled PET flakes, 3 sets of experiment were designed. In the first set, glycolysis temperature was set at 210 ˚C in 2 hours, and the equivalent weight ratio of PET:Glycerol was varied from 1:3 to 1:12 as shown in Table 2.1. Zinc acetate, 0.5% w/w based on weight of PET, was added as transesterification catalyst.

Table 2.1 Ratio variation of glycolysis conversion

Glycolysed PET	Equivalent weight ratio of PET: Glycerol
C-0	1:3
C-3	1:6
C-4	1:8
C-5	1:10
C-6	1:12

After the specified reaction time, flask reactor was removed from the heating mantle and hot water was slowly added into the reactor followed by vigorously agitation. Then the whole product was quickly filtered using the strainer with a 1.0 x 1.0 mm pore size. Those PET flakes which were not degraded were collected, dried and weighed.

The conversion for the glycolysis of the recycled PET flakes was determined as;

$$\% \text{ Conversion} = [(PET_{initial} - UF)/ PET_{initial}] \times 100$$

Where $PET_{initial}$ refers to weight of PET flakes before reaction and UF represents the weight of unreacted flakes.

The above experimental procedure was repeated for the second and third set of experiment excluding the temperature and reaction time. In the second set, the glycolysis time of 2.0 hours and 1:6 ratio of PET:Glycerol were fixed while glycolysis temperature were varied from 150 ˚C to 210 ˚C at 20 ˚C intervals, i.e. (150, 170, 190, 210) ˚C. Same as in the first set, zinc acetate, 0.5% w/w based on weight of PET was added as transesterification catalyst.

Glycolysis in the third set was carried out at 210 ˚C and the ratio of PET:Glycerol was 1:6, whereas manipulated variable which is the glycolysis time was varied from 0.5 to 4 hours. (0.5, 1.0, 2.0, 3.0, 4.0 hours). Zinc acetate catalyst (0.5% w/w based on weight of PET) was added. The influences of glycolysis ratio of PET to glycerol, temperature and reaction time on the conversion of recycled PET flakes were discussed in section 2.3.

2.2.3 Polyester polyol from recycled PET flakes

Basically, the experimental arrangement and procedures to prepare polyester polyol from recycled PET flakes were almost similar to glycolysis process which had been described in the previous section. The main difference was that after the reaction time and temperature were maintained in the required range, glycolysed product was then left to cool to room temperature before collected for further analysis. Glycolysis reactions were also carried out in longer period with a minimum of 6 hours to ensure all PET flakes were glycolysed completely since the amount of PET flakes used was larger. All of the glycolysed PET (GP) was analysed for hydroxyl value, acid number, moisture content and other test as discussed further in the next section. Table 2.2 summarised the variation of reaction parameters in this experiment.

Table 2.2 Variation in parameters used in the PET glycolysis

Parameter	PET:Glycerol	Time (h)	Temp. (˚C)	Product Code
Ratio	**1:3**	6	200	GP-0
	1:4	6	200	GP-1B
	1:5	6	200	GP-2A
	1:6	6	200	GP-3B.r
Time	1:6	**6**	200	GP-3B.i
	1:6	**9**	200	GP-6
	1:6	**12**	200	GP-7
Temperature	1:6	6	**180**	GP-4
	1:6	6	**200**	GP-3B
	1:6	6	**220**	GP-5

PET is a large molecule with only two terminals. One side is hydroxyl group and the other side is carboxylic group. Thus it does not contribute to hydroxyl value of the glycolysed PET. However, when certain amount of glycerol is add in, the glycerol will be the one who is responsible for introducing the hydroxyl group. Example calculation in the preparation of glycolysed PET is shown in appendix Table Ap2-1.

Expected hydroxyl value, OHv from the calculation is then used as a guide in the determination of hydroxyl value by titration method.

2.2.4 Procedure and Characterisation

2.2.4.1 Determination of Hydroxyl Value (OHv)

The hydroxyl value (OHv) of a polyol, sometimes called the hydroxyl number, is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of the sample. The hydroxyl value is determined via esterification of the hydroxyl groups with an excess of anhydride pyridine mixture. After conversion the surplus anhydride is titrated with aqueous sodium hydroxide. In this study, hydroxyl value determination is based on ASTM D4274-94 (Standard Test Method for Testing Polyurethanes Raw Materials: Determination of Hydroxyl Numbers of Polyols) as a correction to the theoretical calculated OHv.

The procedure is described further in appendix-Chapter2_2.2.4.

2.2.4.2 Determination of molecular weight

The average molecular weights of glycolysed PET products were determined by gel permeation chromatography, GPC (Waters model). Samples were dissolved in THF at a constant concentration of 0.2 wt% and all GPC scans were carried out up to 55 minutes.

2.2.4.3 Determination of moisture content

This determination is based on a titration in accordance with the Karl Fischer method which corresponds to the reaction equation:

Equation: $SO_2 + I_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$

Sulphur dioxide is oxidised to sulphuric by iodine acid in the presence of water. The bases added have an effect that the balance of the reaction is shifted to the right hand side. The titration end point is potentiometrically determined.

Water content of the sample was determined by Karl Fisher titrator, DL 31, with electrode DM 143-SC from Mettler Toledo as shown in appendix Figure A2-3. Weight of sample used was in range of 0.4 to 1.4 g and was ensured to be homogenized before the test.

2.2.4.4 Determination of acid value

Acid value (Av) of glycolysed PET, sometimes called the acid number, was determined based on Standard Test Methods for Polyurethane Raw Materials: Determination of Acid and Alkalinity Numbers of Polyols (ASTM D 4662-93). Acid number is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of glycolysed products. The purpose of this test was to estimate the degree of conversion of PET. All the reagents and chemicals used were of analytical grades and details procedures are described further in appendix.

2.2.4.5 FTIR and ^{1}H NMR spectroscopy

FTIR analysis was performed on the flake of PET bottle and its glycolysed product. The IR spectrum of glycolysed product was analyzed from a thin film of sample on a sodium chloride cell using a Perkin-Elmer FTIR Spectrum RX-1. Samples were scanned at wave numbers from 4000 - 400 cm^{-1} at a resolution of 4 cm^{-1}.

For polyurethane foam, IR analysis was done with Spotlight 400 Perkin Elmer Spectrometer, from 4000 - 400 cm^{-1} at resolution of 4 cm^{-1} and 15 scanning numbers using attenuated total reflectance (ATR) method.

^{1}H NMR was obtained using DMSO as solvent for the identification of chemical structures of the glycolysed PET products.

2.2.4.6 Thermogravimetric analysis (TGA)

Thermogravimetric measurement was carried out on Perkin Elmer 4000, as shown in appendix Figure A2-4. Thermogram obtained was used to analyse the composition of multi –component in glycolysed product as well as the thermal decomposition behavior of the glycolysed product and polyurethane foam.

About 5-10 mg of sample was placed into the crucible cup that was positioned in the furnace of the equipment. The test was carried out in the temperature range of 50 °C to 900 °C at heating rate of 20 °C/min and under the purge nitrogen gas flow of 20 mL/min.

2.3 RESULTS AND DISCUSSION

2.3.1 Glycolysis of PET flakes

The conversion of the glycolysis is shown to be influenced by equivalent weight ratio of PET to glycerol, the duration of glycolysis as well as the reaction temperature.

2.3.1.1 Influence of equivalent weight ratio

In this series of experiment, amount of PET flakes was fixed while amount of glycerol used was varied based on their equivalent weights as in table below:

Table 2.3 Influence of equivalent weight ratio of PET:Gly on conversion of recycled PET flakes at 210 °C and glycolysis of 2 hours.

PET:Gly	Glycolysis conversion (%)
1:3	98
1:6	99
1:8	95
1:10	99
1:12	93

The glycolysis temperature was set at 210 ˚C and glycolysis time was set at 2 hours. Figure 2.1 displays the relationship between the equivalent weight ratio of PET:Gly and conversion of recycled PET flakes.

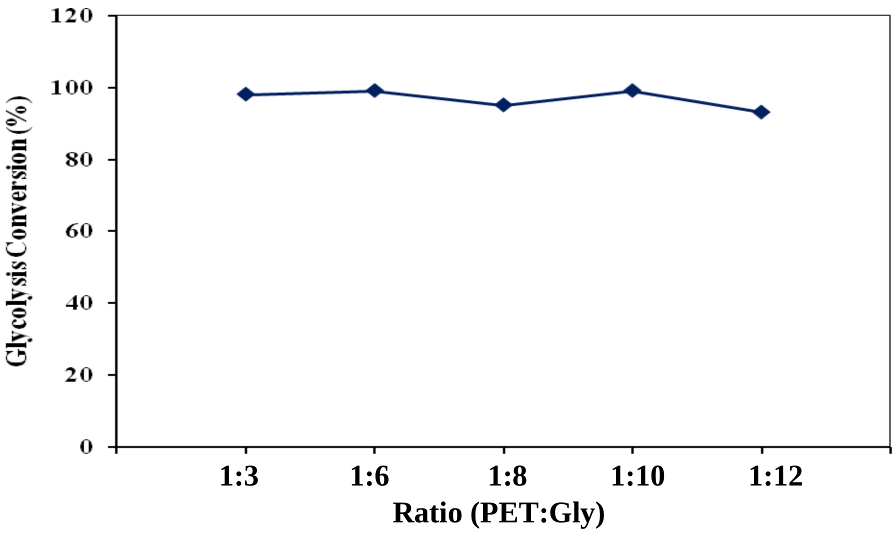


Figure 2.1 The relationship between the equivalent weight ratio of PET:Gly and glycolysis conversion (%) of recycled PET flakes at 210 ˚C and glycolysis time of 2.0 hours

The percentage of glycolysis conversion is 98% when the equivalent weight ratio of PET:Gly is 1:3. Almost all of the PET flakes have successfully converted in this lowest ratio used. The conversion percentage was steady in the range of (93-99) % even when the equivalent weight ratio of PET to glycerol was changed with higher amount of glycerol used.

2.3.1.2 Influence of glycolysis temperature

Table 2.4 and Figure 2.2 illustrates the relationship between the glycolysis conversion and glycolysis temperature of recycled PET flakes when the glycolysis time is 2.0 hours and ratio of PET to glycerol is 1:6.

The glycolysis conversion is very low when the glycolysis temperature is lower than 170 ˚C. In spite of this, if the temperature is higher than 170 ˚C, the glycolysis conversion obviously increases with the glycolysis temperature. When the glycolysis temperature is set at 190 ˚C, the glycolysis conversion increases sharply from 0.8 to

95% and become steady at 99% conversion when the temperature is set at 200 ˚C and up to

210 ˚C. Hence the glycolysis temperature is a very critical factor for glycolysis conversion.

Table 2.4 Influence of glycolysis temperature on conversion of recycled PET flakes

Glycolysis Temp. (˚C)	Glycolysis conversion (%)	1/T	ln k
150	0.3	0.0067	-1.2040
170	0.8	0.0059	-0.2231
190	95	0.0053	4.5539
200	99	0.0050	4.5951
210	99	0.0048	4.5951
220	99	0.0045	4.5951

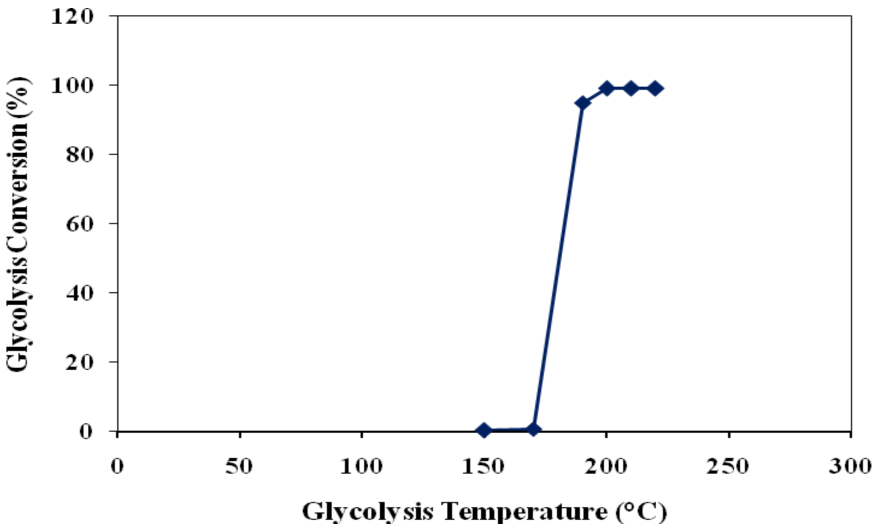


Figure 2.2 The relationship between the glycolysis temperature and glycolysis conversion of recycled PET flakes with a glycolysis time of 2.0 hours and 1:6 ratio of PET:Gly

Chemical intuitions suggest that the higher the temperature, the faster a chemical reaction will proceed. Quantitatively this relationship between the rate of reaction proceeds and its temperature is determined by the Arrhenius Equation. Theoretically at higher temperatures, higher collision rate will result in a higher kinetic energy, which has an effect on the activation energy of the reaction. The activation energy, Ea based on the empirical expression, $k = A^{-Ea/RT}$, can be determined from the slope of a graph of ln k versus 1/T. (Value of ln k and 1/T are as shown in Table 2.4).

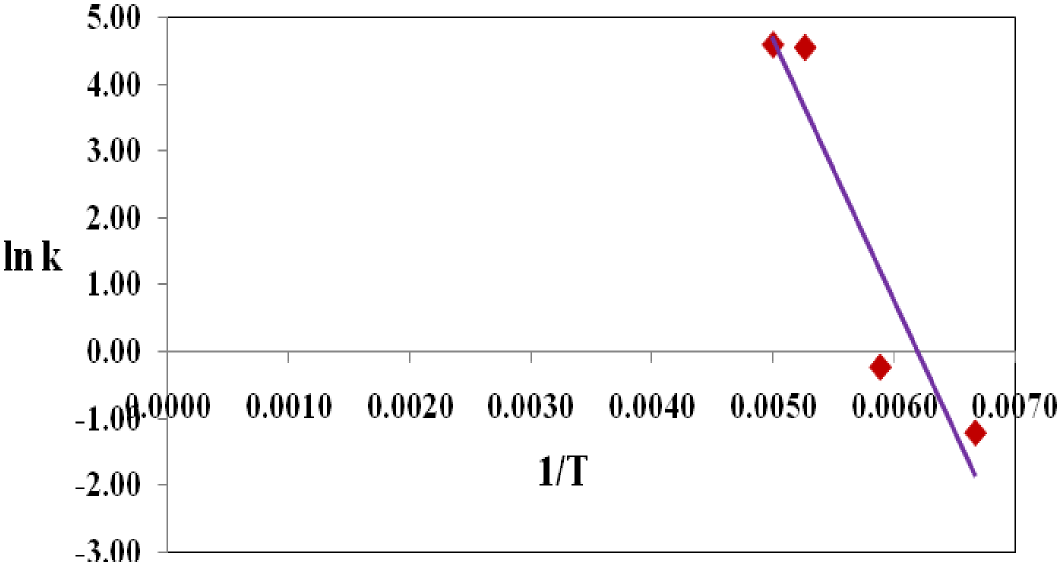


Figure 2.3 ln k versus 1/T

From the graph in Figure 2.3, the Ea is 32.4 kJ/mol. [$-Ea = -3902\ (8.314 \times 10^{-3}$ kJ/mol/K)] Sample calculation is shown in appendix Figure A2-6.

Several studies on the kinetic of glycolysis of PET under various conditions have been reported. Chen and friends (2012) carried out glycolysis with excess ethylene glycol in the presence of zinc acetate under microwave irradiation and reported that the activation energy as evaluated using the Arrhenius equation was found to be 36.5 kJ/mol [11]. An even lower values of activation energy of 26.3 kJ/mol and 24.2 kJ/mol have been reported by Mishra S. (2003) [12] and Goje,A.(2004) [13] respectively. The former value was obtained from alkaline depolymerisation of waste PET while the latter from hydrolysis of PET waste with nonaqueous potassium hydroxide solution.

2.3.1.3 Influence of glycolysis time

The relationship between glycolysis time and the conversion of recycled PET flakes is presented in Table 2.5 and Figure 2.4. The glycolysis temperature was set at 210 ˚C and the ratio of PET to glycerol was 1:6. As shown in Figure 2.4, generally the glycolysis conversion increases with the time of glycolysis and reaches a steady conversion when the time is longer than 2.0 h.

Table 2.5 Influence of glycolysis time on conversion of recycled PET flakes

Glycolysis time (hour)	Glycolysis conversion (%)
0.5	0.9
1	92
2	99
3	99
4	99

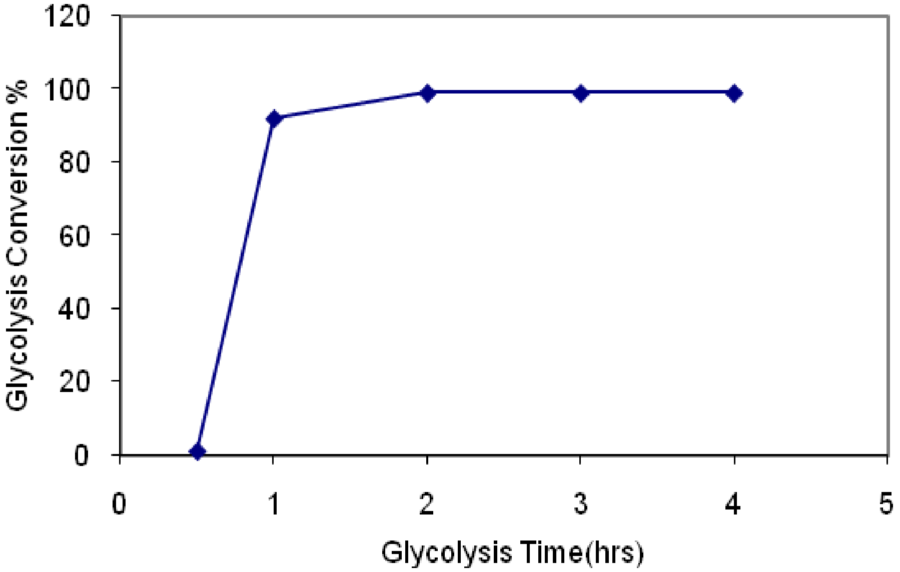


Figure 2.4 The relationship between the glycolysis time and glycolysis conversion of recycled PET flakes with a glycolysis temperature at 210 ˚C and ratio of PET:Gly of 1:6

The conversion is very low and almost zero percent for the initial half hour of glycolysis before increases drastically within 0.5 to 1.0 h and slowly increases during the next 1.0 to 2.0 hours before reaching 99% after 2.0 h or longer.

2.3.2 Characteristics of glycolysed PET

Based on the optimum glycolysis condition of recycled PET flakes, a series of glycolysed products have been produced. Glycolysed PET obtained is a brownish thin liquid at temperature above 60 °C as shown in appendix Figure A2-5. However it became viscous liquid when it was cooled to room temperature at 25 °C. Other characteristics (hydroxyl value (OHv), acid value (Av), water content and molecular weight, M_w of glycolysed PET) were also studied. Following the same procedure as in section 2.2.2, PET flakes and glycerol were charged into the reactor. Zinc acetate, 0.5% w/w based on weight of PET was added as transesterification catalyst. Due to high ratio of solids to liquid in the flask, the stirrer was not turned on until the PET flakes start dissolving and change from solid phase to liquid phase. In this series, reaction conditions were varied as shown in Table 2.2. Variations in these conditions were done with the aim of investigating the effects of a number of parameters on the properties of glycolysed products and the final product of polyurethane foams. These include effect of different molar ratios of PET to glycerol and effect of different reaction temperatures. The OHv, water content, IR spectrum and acid value of the glycolysed PET are shown in Table 2.6.

Table 2.6 Hydroxyl value (OHv), acid value (Av), water content and number average molecular weight,(M_W) of the glycolysed PET

Product code	PET:Gly	Time (h)	Temperature (°C)	OHv (mg KOH/g)	Av (mg KOH/g)	Water content (%)	MW (Daltons)
GP-0	**1:3**	6	200	527	-	0.85	-
GP-1B	**1:4**	6	200	646	8.55	1.47	-
GP-2A	**1:5**	6	200	710	7.72	0.81	889
GP-3B	**1:6**	6	200	805	3.91	0.84	1247
GP-3B	1:6	**6**	200	805	3.91	0.84	-
GP-6	1:6	**9**	200	774	8.52	1.30	935
GP-7	1:6	**12**	200	726	8.74	1.91	1170
GP-4	1:6	6	**180**	815	3.60	0.80	-
GP-3B	1:6	6	**200**	805	3.91	0.84	-
GP-5	1:6	6	**220**	796	10.78	1.91	-

It is found that glycolysed products have low acid value (Av) in the range of 3.0 – 10 mg KOH/g, although the glycolysis of PET should yield oligomers with hydroxyl end groups. This low acid value indicates that insignificant hydrolysis may be occurring during glycolysis reaction [6] due to the presence of water as impurity or formed by side reactions.

The results indicate that the OHv of the olygomeric triols increases with the amount of glycerol used in the glycolysis. This shows that the extent of depolymerization increases with the amount of glycerol. This is in agreement to the previous reported study on glycolysis of PET using ethylene glycol. The hydroxyl values are comparable to that of *bis*(hydroxyethyl) terephthalate implying that the extent of depolymerization is quite significant. However OHv decreases with increasing reaction time. This may probably be due to the conversion of hydroxyl group to water since the moisture content increases with time. All the glycolysed products have water content of 2.0 % and below as shown in Table 2.6. Average molecular weights, $M_{w,}$ of the selected glycolysed products as determined from GPC are in the range of 889 to 1247.

FTIR and H^1 NMR spectrum

IR spectrum of PET film is expected to show strong features with ester functionality (1718, 1252, and a doublet at 1126 and 1099 cm^{-1}) and aromatic ring (3054, 1615, 1578, 1505, 1021 and 728 cm^{-1}). Bands assigned to the “ethylene” CH_2 group of –O-(CH_2CH_2)-O- moiety are also observed at 1134 and 848 cm^{-1} [14]. This is comparable to the PET flakes taken from soft-drink PET bottles from this research materials where absorptions at 1714, 1242, and 1096 cm^{-1} were observed as well as 1505 and 723 cm^{-1} for aromatic ring.

Previous study on glycolysis of PET bottles had also reported that the IR spectra for glycolysed product have absorptions at 3000-3500, 2850-3000, 1720, 1503 and 1100 cm^{-1} attributed to -OH, $-CH_2$, C=O, aromatic group and C-O stretching respectively [15]. This is close to the IR spectrum of the glycolysed product obtained as shown in Figure 2.5 (B) where the presence of absorptions at 3352 cm^{-1} is for –OH, 2882-2948 cm^{-1} for $–CH_2$, 1711 cm^{-1} for the carbonyl group (C=O), 1505 cm^{-1} represents the aromatic group and 1102 cm^{-1} for C-O stretching .

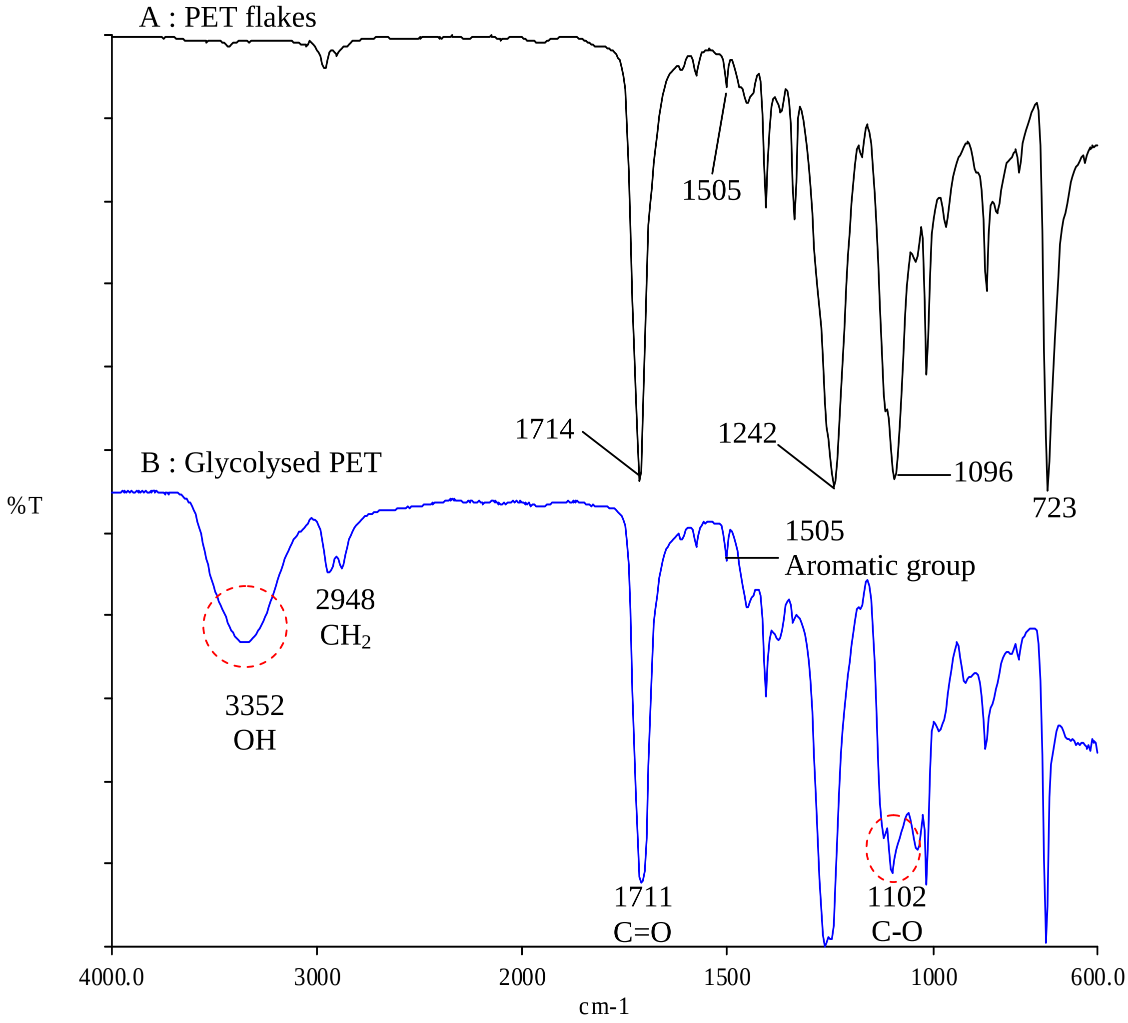


Figure 2.5 FTIR spectra for PET flakes before (A) and after (B) glycolysis

Although the absorption bands in spectrum B are almost similar to those in spectrum A, there is an obvious band between 3000 and 3500 cm^{-1} in spectrum B compared to spectrum A. This may result from strong hydrogen bonding in the glycolysed product. The broad band is observed in all the glycolysed products which is not obtained in PET spectrum. Another absorption band is observed in the range of 1000-1200 cm^{-1} due to C-O of C-OH group stretching but it may overlap with the terephthalate group which also has the same absorption range.

Figure 2.6 shows a ^{1}H NMR spectrum of a typical glycolysed PET (GP3B).

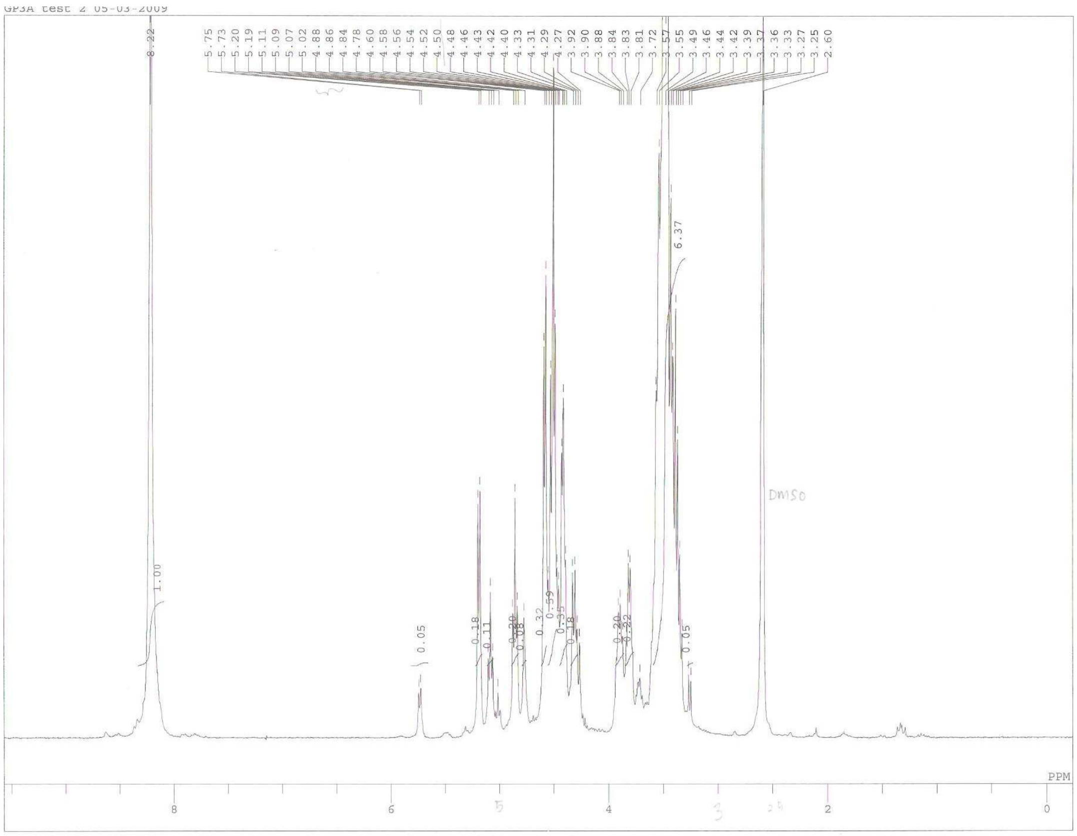


Figure 2.6 NMR spectrum of the glycolysed product, GP3B

The peak at 8.22 ppm can be assigned to benzene ring (P) as shown in Figure 2.7. Multiplets at 4.4 ppm and 4.6 ppm are characteristic of the secondary (Q) and primary OH (R) groups. The other signals at 3.5-3.9 ppm correspond to protons of S, T and U. Based on the IR and ^{1}H NMR spectra, there is strong evidence that glycolysed product has a chemical structure as shown in Figure 2.7(a) though the glycolysed product actually mainly consists of oligomers.

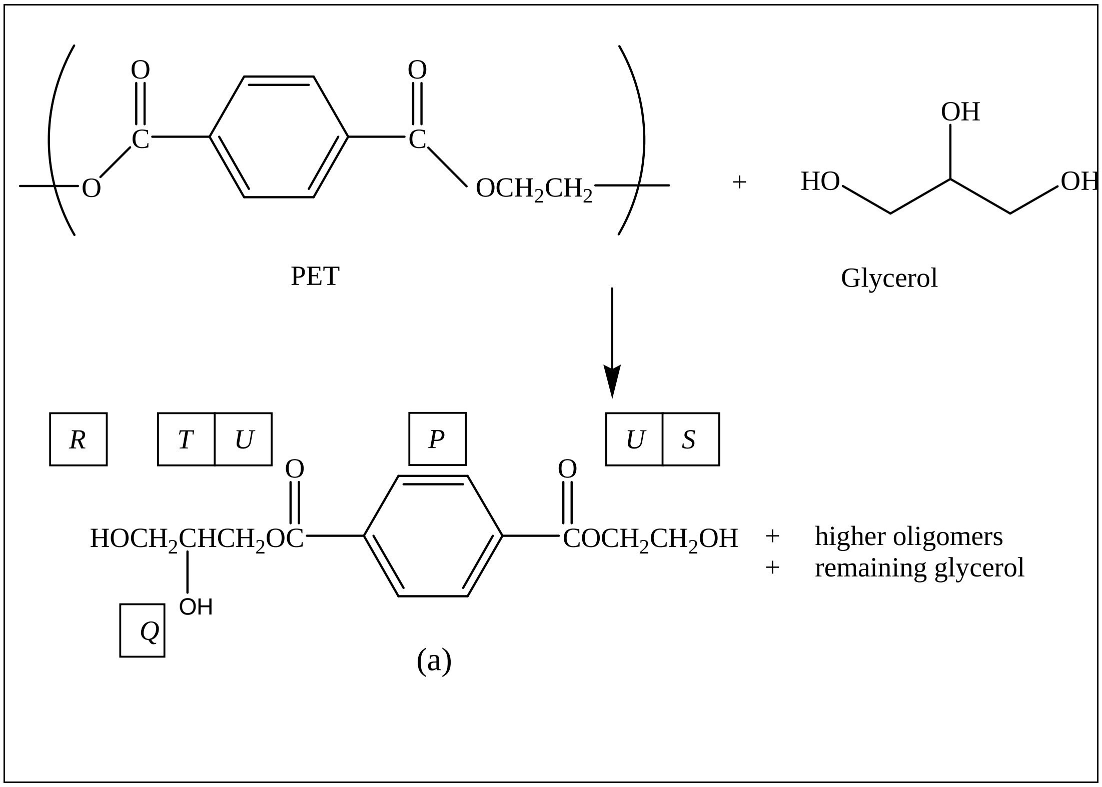


Figure 2.7 Possible structure for the glycolysed product obtained in the glycolysis reaction of PET and glycerol

Thermogravimetric analysis

Figure 2.8 in next page shows the thermogram of the glycolysed product. A clear two-step degradation process under nitrogen atmosphere is observed. The first step illustrates that the glycolysed product undergoes thermal degradation at 220 °C. The weight loss decomposes slowly with a total mass loss of 38 %. Meanwhile the second step degradation process demonstrates that the glycolysed product undergoes thermal degradation at about 415 °C. However at this step, glycolysed product decomposes rapidly with a total mass loss of 50%.

While Figure 2.9 in the following page displays the TGA thermogram of glycerol and PET flakes used in glycolysis experiments. The thermogram shows the glycerol thermal degradation begins at 221 °C while the PET flakes red thermogram,(b) at 421 °C. Both these temperatures are close to the first and second steps of thermal degradation of glycolysed PET. As shown in Figure 2.8, thermal degradation of first step is about 220 °C almost similar to glycerol whereas second step is around 415 °C which is considered to be PET flakes.

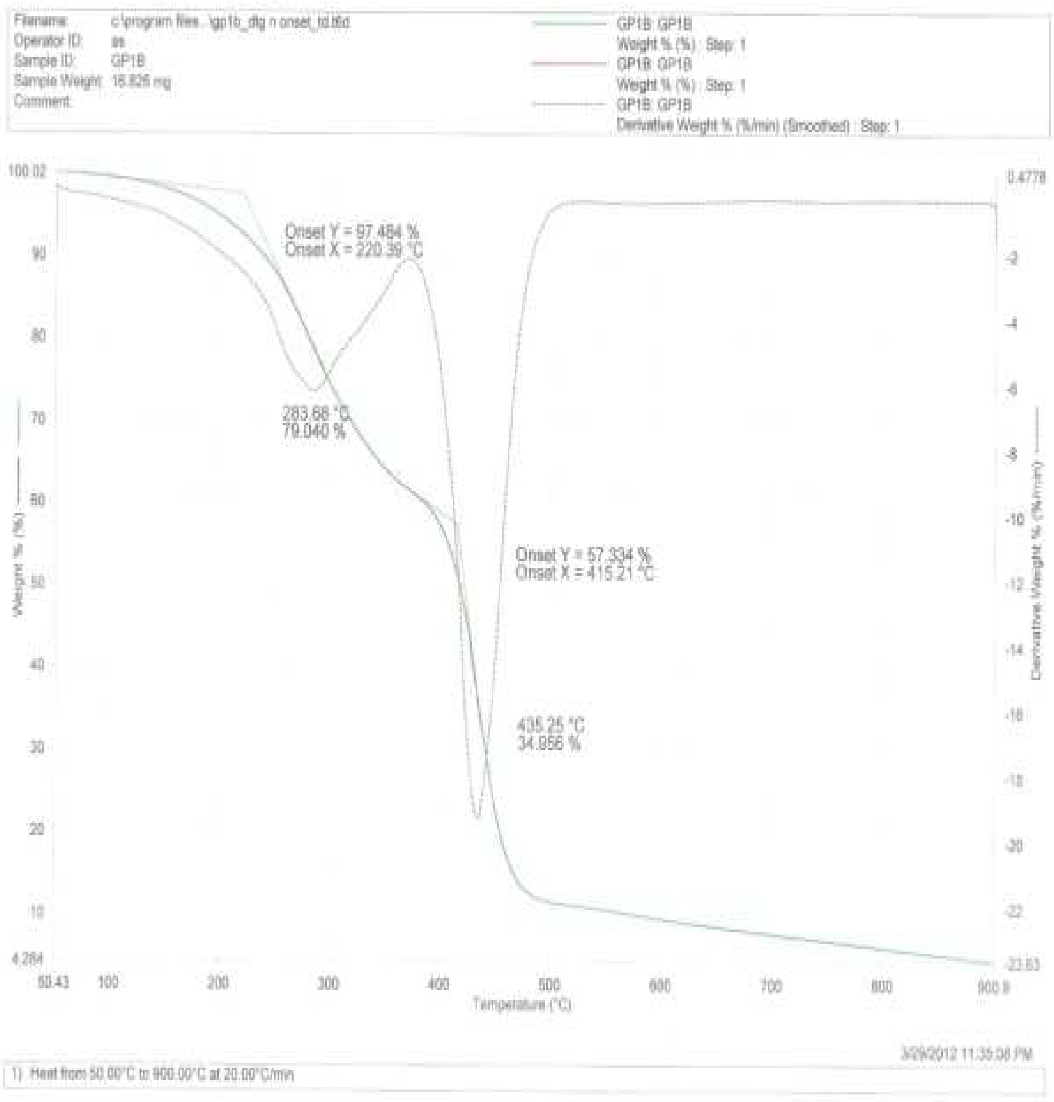
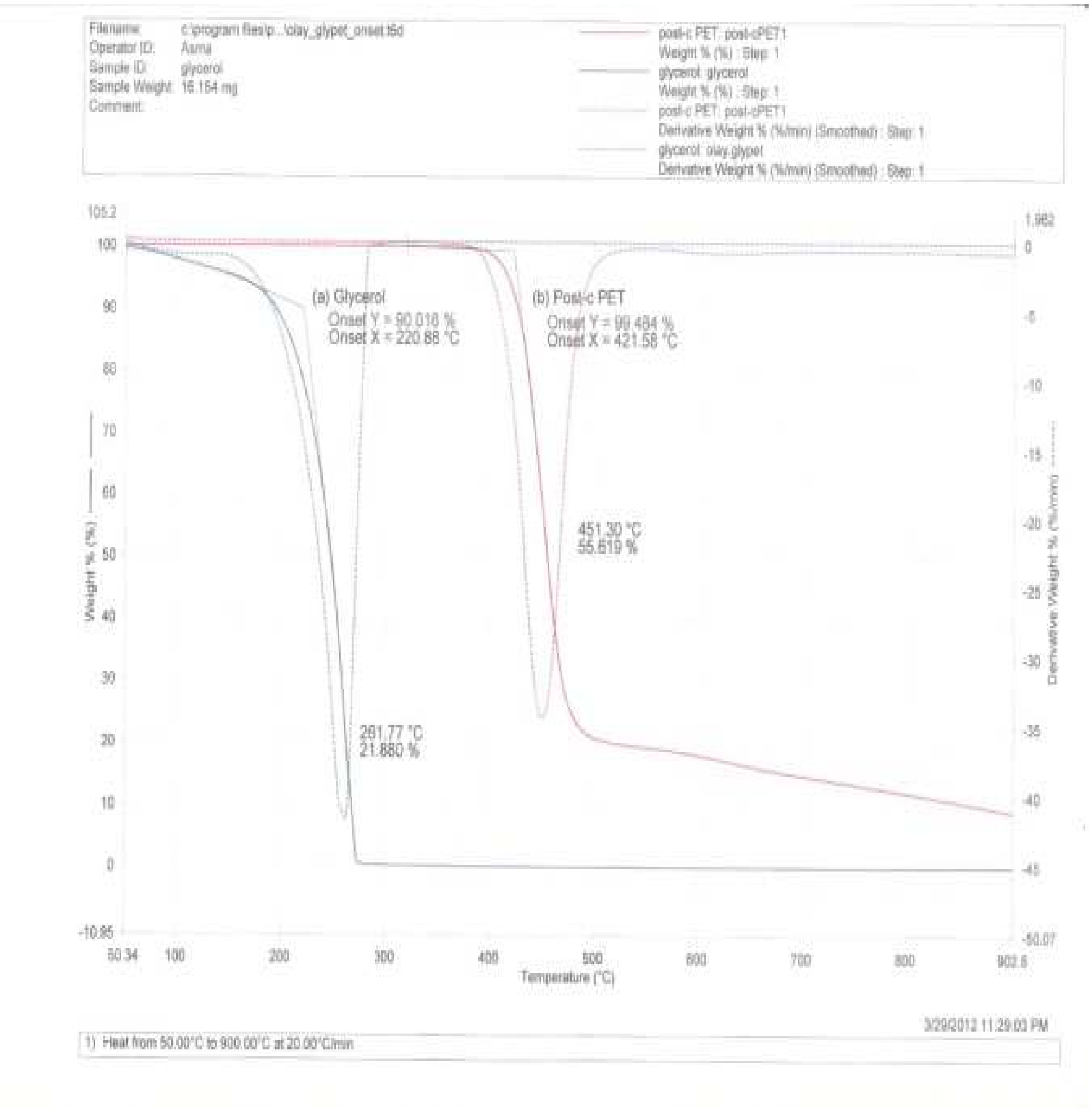


Figure 2.8 TGA thermogram of the glycolysed product, GP1B



Filename: c:\program files\p...\olay_glypet_onset.t5d
Operator ID: Asma
Sample ID: glycerol
Sample Weight: 16.154 mg
Comment:

1) Heat from 50.00°C to 900.00°C at 20.00°C/min

3/29/2012 11:29:03 PM

Figure 2.9 Thermogram of (a) glycerol-blue curve and (b) PET flakes-red curve

2.4 CONCLUSION

Post-consumer PET waste bottles can be glycolysed using glycerol. The influences of glycolysis time, glycolysis temperature and the equivalent weight ratio of PET to glycerol (amount of glycerol) were presented. Highest yield of 98 % of glycolysed PET was obtained at glycolysis temperature of 200 ˚C, glycolysis time of 2 hours and glycolysis ratio of 1:6 with the glycolysis conversion of almost 100 %. The rate constants for glycolysis were calculated for four different temperatures, yielding activation energy of 32.4 kJ/mol. The FTIR and NMR results confirmed structure of the glycolysed PET while GPC shows presence of oligomers. The hydroxyl number is found to be in the range of 527-815 mg KOH/g depending on their ratio of equivalent weight ratio of PET to glycerol.

2.5 REFERENCES

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