

Unsaturated Polyester from Glycolized PET Recycled from Post-consumer Soft-drink Bottles

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ABSTRACT

Glycolysis of recycled polyethylene terephthalate (PET) from post-consumer soft-drink bottles was carried out with ethylene glycol (EG) at different weight ratios of PET to EG using zinc acetate as catalyst at the boiling point of EG under nitrogen atmosphere for a constant time of 8 h. The results showed that in excess of EG (at mole ratio of PET/EG = 0.12) the glycolized products contained predominantly bis(hydroxyethyl) terephthalate (BHET). Kinetics of polyesterification of glycolized product, BHET, made from a mole ratio of 0.12 of PET/EG with maleic anhydride was also studied without using acid catalyst. The polyesterification was carried out at different temperatures (135, 160, 200 and 210 °C) comparable to the industrial process scheme. It was observed that the acid value of the reaction mixture decreased and the extent of reaction increased sharply with increasing temperature or time of the reaction. At 135 °C the kinetic plots, using third-order kinetics, were non-linear at initial times.

Key Words: PET, depolymerization, recycling, unsaturated polyester, PET waste

INTRODUCTION

Poly(ethylene terephthalate), PET, is a semi-crystalline thermoplastic polyester most extensively used in the manufacture of high strength fibers, films, soft-drink bottles and food containers. The volume of PET consumed in the beverage industry alone is progressively increasing, and the disposal of a large number of PET bottles has become one of the most valuable recyclable materials. As the consumption of polymers grows, the necessity of plastics recycling becomes

one of the major problems, which must be solved due to the foreseen shortage in petroleum resources. The chemical recycling of waste polymers has been gaining greater attention in recent years as a means of obtaining valuable products from waste plastics [1]. In addition to mechanical methods of reusing plastics, PET can be reclaimed through chemical means. The various possibilities for utilizing PET product waste have been studied for many years and are revealed in few patents [2, 3]. One promising route is the depolymerization of recycled PET into its monomer

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and higher oligomers, which can then be used as building blocks to synthesize other oligomers. A condensation polymer, such as PET, has been treated by hydrolysis [4-7], under supercritical conditions of water [8], and glycolysis [1, 9, 10]. Depolymerization of PET by glycolysis in a diol such as ethylene glycol, propylene glycol, and diethylene glycol has also been studied [11, 12]. Hydrolysis and ethylene glycolysis are of particular interests because they can afford dimethyl terephthalate and di(hydroxyethyl) terephthalate, respectively, which can be used as the starting monomers of polymerization [9, 10, 12, 13]. The extent of depolymerization of PET by glycolysis in excess of ethylene glycol is also dependent on the type of catalyst, such as zinc, lead, cobalt and manganese acetates, which are known to be effective in transesterification reactions [14]. The rate of decomposition of PET is significantly accelerated by the addition of ethereal solvents to ethylene glycol, such as dioxane, THF, and dimethoxy ethane [15].

In this paper, results of the glycolysis of PET recycled from post-consumer soft-drink bottles are presented. The PET waste was glycolized with ethylene glycol at different weight ratios. The glycolized product, bis(hydroxyethyl) terephthalate (BHET), was then reacted with maleic anhydride to prepare unsaturated polyester. The kinetics of polyesterification of glycolized PET product with maleic anhydride is reported. The prepared unsaturated polyester from PET waste can be used in applications such as glass-reinforced plastics.

EXPERIMENTAL

Materials and Instruments

The PET used in these experiments was obtained from consumed soft drink bottles as described in the next section. Phenol, ethylene glycol and tetrachloroethane from Fluka, used without further purification.

Pye Unicam SP-1100 infrared spectrometer was used for recording IR spectra.

Glycolysis of PET Waste

PET Flakes were prepared as follows: Soft-drink

bottles were washed, dried and cut into small pieces in order to create maximum surface area. No attempt was made to assess the level of contamination in the flakes that if there is any, and so they were used directly. The PET flakes were dissolved in the mixture of solvents of phenol and 1,1,2,2-tetrachloroethane with a weight ratio of 40 to 60, respectively. IR Spectrum of PET film made from this solution is shown in Figure 1. In all glycolysis experiments, a constant weight of 20 g of PET flakes equivalent to 0.1 mol of repeating unit (molecular weight: 192) in the PET chain was added to different amounts of ethylene glycol (EG) (molecular weight: 62), such that the mole ratios of PET repeating unit to EG were: 0.24, 0.22, 0.20, 0.16, 0.14, and 0.12. 0.5 % w/w zinc acetate, based on weight of PET, was used as catalyst. The mixture was charged into a four-necked reaction vessel fitted with a stirrer, reflux condenser, nitrogen inlet and thermometer. The solution was then refluxed at the boiling point of EG (198 °C) under nitrogen atmosphere for a constant time of 8 h. At the end, the contents of the reaction vessel were allowed to cool to room temperature and 500 mL of distilled water was added while stirring vigorously. The water would dissolve any unreacted EG and the catalyst. After filtration, the residual was transferred to a beaker containing 500 mL of distilled water and the suspension was boiled with stirring. This was intended to extract the BHET, which is known to be quite soluble in boiling water [12]. After prolonged boiling, while still hot, it was quickly filtered. Upon immersing the filtrate in an ice bath, the crystalline needles were precipitated and its melting point,

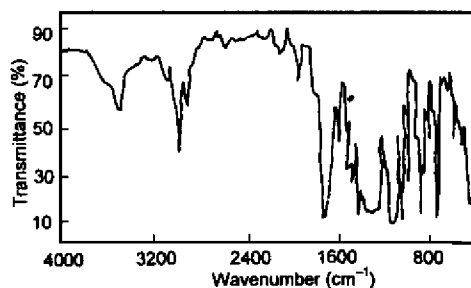


Figure 1. IR Spectrum of recycled PET film.

Table 1. Polyesterification data obtained at 135 °C for different times. 0.5 N KOH was used for the titration of 0.5 g polymer sample in acetone solution.

Time (min)	30	60	90	120	150	210	300
Acid number	3.7	3.3	3.1	3.0	2.61	2.24	1.73
Hydroxyl number	8.7	7.9	7.3	6.8	6.4	5.8	5.2
N($\times 10^{-4}$)	4.42	3.99	3.71	3.40	3.21	2.87	2.47
Extent of reaction	0.17	0.26	0.31	0.33	0.42	0.5	0.61
Average molecular weight	2262	2506	2702	2941	3112	3485	4045

after filtration and drying in a vacuum oven, was in the range of 108–110 °C.

Synthesis of Unsaturated Polyester

Poly[bis(ethyl) terephthalate]maleate

Unsaturated polyester was prepared by the reaction of BHET with maleic anhydride, which is the commonly used unsaturated diacid in the manufacture of this resin. Polyesterification was carried out in a 500 mL round-bottom flask having a distillation condenser and connected to a water-jet vacuum. Equivalent molar concentration (0.1 molar) of maleic anhydride (9.8 g) and BHET (25.4 g) were added to the flask. The flask was heated from room temperature to 135 °C, above the melting point of BHET (~110 °C), and it was held at this temperature for 300 min while stirring continued. To study the effect of time on the extent of polyesterification, samples were taken out of the reaction mixture every 30 min. To study the effect of temperature on the extent of polyesterification, in a second experiment, the reaction mixture was heated to 135 °C and held for 2 h to make sure oligomers were formed, it was then increased to 160, 200, and 210 °C, respectively.

Samples were taken from the reaction mixture at each temperature after a period of 30 min. The acid value of these samples, Tables 1 and 2, were determined by titrating the solution of accurately weighed of 0.5 g sample against 0.5 N KOH standard solution [16]. Hydroxyl number of the samples was determined using a standard procedure [17], of ASTM D2849.

IR Spectrum of the polyesterification product was obtained using solution of a small amount of polymer sample in chloroform. The unsaturated polyester was a viscous liquid and soluble in acetone and chloroform.

The polyesterification reaction was carried out about 25 °C above the melting point of BHET, which is at 135 °C and was held at this temperature for 2 h before increasing the temperature. The reason for this was to prevent ethylene glycol from vaporization, which can take place at higher temperatures and reduce its concentration in the reaction mixture. The unsaturated polyester obtained at higher temperatures was very viscous and hard to be handled.

RESULTS AND DISCUSSION

PET flakes were depolymerized in the presence of excess EG using zinc acetate as catalyst. The solid product obtained from the glycolysis of PET was bis(hydroxyethyl terephthalate), BHET, with melting point at 108–110 °C and IR spectrum given in Figure 2. The absorptions at 3400, 3000–2800, 1750 and 1300 1/cm are due to OH, C–H, C=O and C–O stretching, respectively. From our experimental data, the glycolized products consisted of monomer BHET and higher oligomers. BHET is a white solid which dissolves in boiling water, and was separated from the rest of oligomers. A sharp peak just below 800 1/cm

Table 2. Polyesterification data at different temperatures*.

Temperature (°C)	160	200	210
Acid number	2.2	1	0.9
Hydroxyl number	5.8	4.2	3.8
Average molecular weight	3508	5405	5968
Extent of reaction	0.51	0.77	0.8

(*) For analysis, samples were taken from reaction mixture after 30 min at each particular temperature.

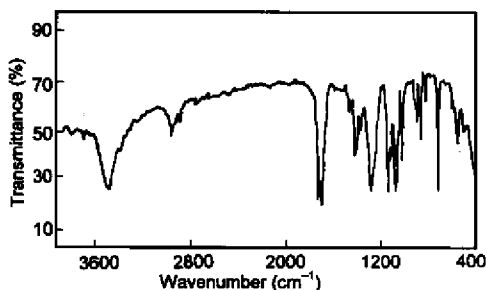
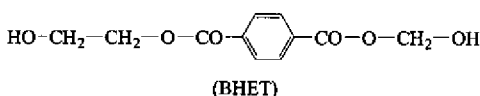
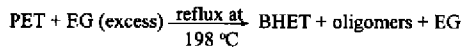


Figure 2. IR Spectrum of BHET.

in IR spectrum is related to the *para* substituted aromatic ring. The chemical structure of BHET is shown in Scheme 1.

According to our study, as shown in Figure 3, the rate of depolymerization reaction under constant temperature and pressure, depends on the mole ratio of PET/EG. The rate of depolymerization is expressed here as percent yield of BHET product. The depolymerization rate was very slow at low molar concentration of EG, and this may be due to the surface reactivity of solid PET, which constitutes the major rate-determining stage. The maximum yield of 92 % BHET was obtained at a mole ratio of PET/EG= 0.123. The amount of BHET increased with increasing the mole ratio of EG/PET. Therefore, in a low PET/EG mole ratio, e.g. at 0.222, the glycolized products consisted of oligomers having higher molecular weights. This implies that the degree of depolymerization products can be regulated easily by EG/PET ratio used in glycolysis. In other words a sufficient amount of EG was needed to depolymerize PET long chains to short chain lengths. These results showed that in excess EG (0.12 mole ratio of



Scheme 1. Chemical structure of BHET.

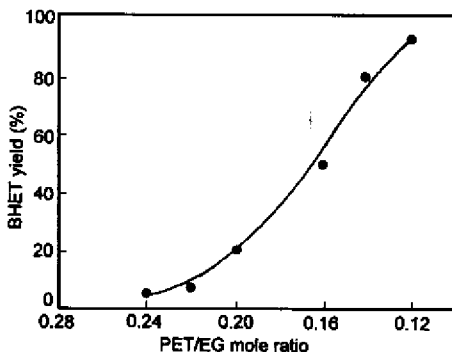
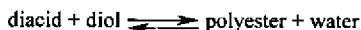


Figure 3. Change in the rate of depolymerization of PET with mole ratio of PET/EG.

PET/EG), the glycolized products contained predominantly BHET. As the extent of depolymerization increased with the amount of glycol, this meant that the amount of EG taken for glycolysis increased. The experimental data are summarized in Table 3.

Polyesterification is a step growth reaction. The molecular weight of polymer increases at a relatively slow rate, particularly in the absence of catalyst. At any instance, the reaction mixture consists of various sizes of hydroxy acid oligomers. Any carboxyl group can react with any hydroxyl group, regardless of the size of oligomers. In theory the kinetics of such a system could be very complicated but in practice it is greatly simplified by the assumption that the reactivity of a functional group is unaffected by the length of polymer chain to which it is attached. Polyesterification is a reversible reaction:



In order to shift the equilibrium of the reaction towards the product side, water of the reaction was removed continuously. The rate of reaction was defined as the rate of consumption of acid groups which is of course also equal to the rate of consumption of hydroxyl groups, because every COOH group reacts with one OH group. In the case in which no catalyst is added it was found experimentally [18] that acid groups in the reaction mixture act as self-

Table 3. Experimental data on glycolyzed PET.

Sample no.	PET weight (g)	EG Volume (mL)	EG Weight (g)	Mole ratio PET/EG	BHET Weight (g)	Oligomers weight (g)	Efficiency (%)
1	20	25.0	28.68	0.25	1	19	5
2	20	26.2	29.06	0.22	1.5	18.5	7.5
3	20	29.1	32.30	0.20	4	16	20
4	20	35.0	38.75	0.16	10	10	50
5	20	45.0	50.00	0.14	16	4	80
6	20	51.6	57.35	0.12	18.5	1.5	92.5

catalyst, then the rate equation can be expressed as:

$$-d[\text{COOH}]/dt = k[\text{COOH}]^2[\text{OH}] \quad (1)$$

where k is the rate constant for the reaction. Since equal numbers of functional groups were employed then: $[\text{COOH}] = [\text{OH}] = C$ and eqn (1) becomes:

$$-dC/dt = kC^3 \quad (2)$$

After integration at $t=0, C=C_0$, it becomes:

$$\frac{1}{C^2} - \frac{1}{C_0^2} = 2kt \quad (3)$$

Since $C=C_0(1-P)$, where P is the extent of reaction; eqn (3) can be expressed as:

$$\frac{1}{(1-P)^2} = 1 + 2C_0 \times kt \quad (4)$$

Data on KOH consumption in titrating sample solutions and the extent of polyesterification reactions at constant temperature (135 °C) are given in Table 1. The extent of polyesterification reaction was calculated using $C=C_0(1-P)$.

For the polycondensation reaction without addition of catalyst, a plot of $1/(1-P)^2$ versus reaction time, eqn (4), should yield a straight line of slope $2kC_0^2$. This plot is shown in Figure 4. The non-linearity in the initial region of this plot is not a characteristic of the polymerization reaction. The deviation from the third order plot is characteristic of esterifications in general. This type of behaviour was also observed [19] for the esterifications between mono- and dicarboxylic acids with alcohol and glycol.

The non-linearity was observed in the third order plot in the initial stage of the polyesterification reaction at less than 50% conversion, Figure 4. The fitting of the data to the third order plot is reasonably good over a much greater range of the higher conversion region. The region of high conversion is of prime importance since high molecular weight polymer is only obtained at high conversions. From the practical viewpoint, the low conversion region of the kinetic plot is of little significance. One possibility for this non-linearity is that the ability of the reaction starting materials to donate a proton to the carboxyl group is not correctly accounted for in the kinetic expression eqn (4) by the carboxyl concentration. This was also ascribed to be due to the large changes in the polarity of the reaction mixture where the polar carboxylic acid groups are converted to the lesser polar ester linkages [18]. The acid values of the reaction mixtures at different times in a constant temperature (135 °C) are given in Table 1 along with hydroxyl numbers. The average

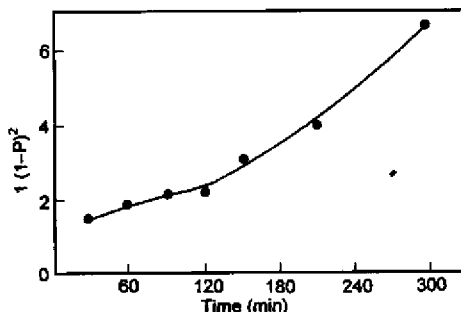


Figure 4. Plot of $1/(1-P)^2$ versus time, for polyesterification of BHET and ethylene glycol at 135 °C.

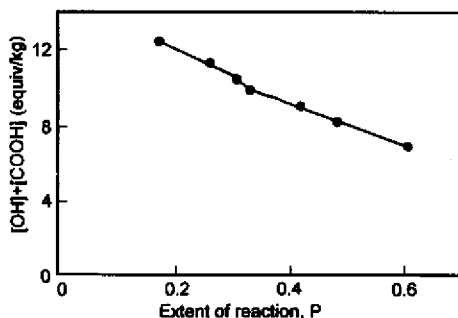


Figure 5. Change in the total concentration of functional groups with extent of reaction at 135 °C.

molecular weight of polyesterification products were obtained using number of moles (N) of polymer molecules in 1 g sample which were calculated by the following equation [16]:

$$N = \frac{(\text{acid number} \times \text{hydroxyl number})^2}{56 \times 1000}$$

where 56 is the molecular weight of KOH, and it is multiplied by 2 since 0.5 g polymer sample used initially for the titration. Figure 5 shows the change in the total concentration of functional groups with the extent of reaction at 135 °C. Figure 6 shows the change in the extent of polyesterification reaction with time at 135 °C. These results show that the extent of polyesterification and the average molecular weight of polymer increase with increasing time of

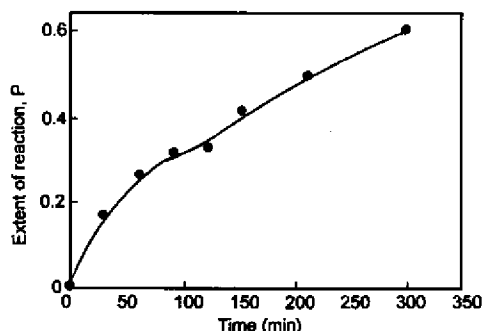


Figure 6. Change in the extent of reaction with time at 135 °C.

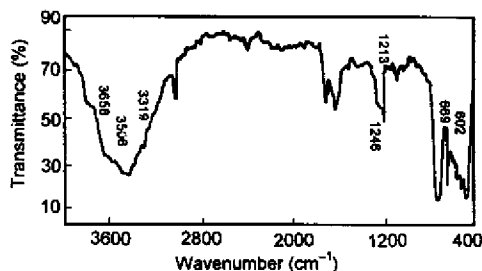


Figure 7. Typical IR spectrum of polyesterification products from BHET and ethylene glycol at 135 °C for 120 min.

reaction. It was also observed that when the temperature of the polyesterification reaction increased from 135 to 160, 200 and finally to 210 °C, the acid value of the reaction mixture decreased sharply and the extent of reaction increased grossly. These results are shown in Table 2. Figure 7 shows the IR spectrum of unsaturated polyester prepared from equal mole ratio of carboxyl and hydroxyl groups at 135 °C for 120 min. Peaks in the regions 3200–3650 1/cm are assigned to the hydroxyl groups at the end of polymer chains, absorption at 800 1/cm shows bending of =C–H in aromatic ring and also its *para* substitution and at 1680 1/cm to the carbonyl groups which is overlapped with the absorption related to the C=C bending of maleic unit in the polymer chains.

CONCLUSION

It is concluded from first part of this project that PET waste can be depolymerized by glycolysis with ethylene glycol. The extent of depolymerization increases with the amount of ethylene glycol, which is consistent with the results obtained by other workers [11]. The intermediate product prepared from PET waste by glycolysis reactions was BHET. The highest yield of BHET (92.5 %) was obtained at temperature 198 °C after 8 h reflux in the presence of zinc acetate catalyst when a mole ratio of 0.123 was used for PET/EG. In the second part of this project, the monomeric product from depolymerization of PET, (BHET), was readily esterified with maleic anhydride

to obtain unsaturated polyester. Kinetic studies of the polyesterification reactions were carried out at 135 °C. The polyesterification reactions follow third-order kinetics at the regions higher than 50% conversion as indicated by plots of $1/(1-P)^2$ versus time in Figure 4.

The experimental data deviate from the third order plot in the initial region, which is characteristic of esterifications in the absence of acid catalyst. The polyesterification reactions between BHET and maleic anhydride were also investigated at higher temperatures such as: 160, 200, and 210 °C. The results show that the extent of polyesterification reactions and also the average molecular weight of the products increase with time and or temperature of the reaction.

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