

## Kinetics of Glycolysis of Poly(ethylene terephthalate) Under Microwave Irradiation

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**ABSTRACT:** The glycolysis of poly(ethylene terephthalate) (PET) was carried out using excess ethylene glycol (EG) in the presence of zinc acetate as catalysts under microwave irradiation. The effects of particle size, microwave power, the weight ratio of EG to PET, the weight ratio of catalyst to PET, reaction temperature and stirring speed on the yield of bis(hydroxyethyl terephthalate)(BHET) were investigated. The experimental results indicated that the glycolysis rate was significantly influenced by stirring speed and initial particle size. The optimal parameters of glycolysis reactions were the weight ratio of catalyst to PET of 1%, the weight ratio of EG to PET of 5, 500 W and 196°C, the yield of BHET reached to 78% at only 35 min. The glycolysis products were analyzed and identified by FTIR, differential scanning calorimetry, and elemental analysis. The kinetics of glycolysis of PET under microwave irradiation could be interpreted by the shrinking core model of the film diffusion control. The apparent activation energy was evaluated using the Arrhenius equation and it was found to be 36.5 KJ/mol, which was lower compared to the same process using conventional heating. The experimental results also showed that the reaction time was significantly decreased under microwave irradiation as compared with it by conventional heating. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** PET; glycolysis; microwave irradiation; shrinking core model

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### INTRODUCTION

Poly(ethylene terephthalate) (PET) is extensively used in the manufacture of high strength fibers, films, soft drink bottles and food containers. PET waste does not create a direct hazard to the environment but due to its high resistance to atmospheric and biological agents, it is considered as a noxious material. So the recycling of PET waste is gaining greater attention nowadays. In recent years, several chemical methods have been proposed for recycling post-consumer PET, such as glycolysis, hydrolysis, methanolysis, aminolysis, and others.<sup>1–3</sup> Among the above recycling techniques, glycolysis reaction can be described as the transesterification process between diols, usually using ethylene glycol(EG),<sup>4–8</sup> and ester groups of PET to obtain the monomer bis(hydroxyethyl terephthalate)(BHET) and oligomers. Guoxi et al.<sup>4</sup> proposed that glycolysis conversion was almost 85.6% at 196°C, reaction time of 3 h, the weight ratio (catalyst to PET) of 1% and the weight ratio (EG to PET) of 5. Ghaemy and Mossaddegh<sup>5</sup> reported that the yield of BHET from glycolysis of PET fibers was 75% under the optimal conditions and purified BHET was separated from products of glycolysis by

changing with temperature. The main advantage of this process is that BHET can be reused as raw material to reproduce to PET by blending with virgin BHET. Moreover, the monomer can be used in the synthesis of unsaturated polyester,<sup>9,10</sup> alkyd resins<sup>11,12</sup> and others.

The first publications concerned with the possibilities of use of microwave irradiation in polymer chemistry at the end of 1960's. Nowadays, there is hardly find any reaction that has not been attempted under microwave due to microwave heating offers increasing in reaction rates. Two mechanisms have been proposed to explain this phenomenon, one of theories proposed that the reduction of the reaction time is the result of instantaneous and uncontrollable temperature growth of the reaction systems under microwave irradiation, which was called "thermal effect."<sup>13</sup> Some authors demonstrated that microwave irradiation could speed up chemical reaction due to "specific microwave effect," it has been argued that the presence of electric field leads to orientation effects of molecules and changes the alteration of pre-exponential factor or activation energy under microwave irradiation.<sup>14</sup> In recent years, Microwave-assisted glycolysis of

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PET has attracted great interest and been studied by some researchers. Krzan<sup>15</sup> studied that the effects of different glycols and zinc acetate as a catalyst on the glycolysis of PET under microwave irradiation 500 W almost complete solubilization of PET was achieved in about 10 min. The glycolysis of PET under microwave radiation, using sodium carbonate, sodium bicarbonate, and barium hydroxide as catalysts and the weight ratio of PET to EG 1 : 4 to 1 : 10 was investigated by Pingale and Shukla,<sup>16</sup> the experimental results revealed the time taken for completion of reaction was reduced drastically from 8 h to 35 min. Similar studies were carried out by Nikje and Nazari<sup>17</sup> using an excess of methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol.<sup>17</sup> More recently, D.S. Achilias et al.<sup>18</sup> carried out the glycolysis reaction of PET in a microwave reactor with diethylene glycol in the presence of manganese acetate as a transesterification catalyst, the activation energy was evaluated by a kinetic model, and complete depolymerization was observed at irradiation powers greater than 150 W for 2 min, or 100 W for 5 min.

The depolymerization of PET is a heterogeneous liquid–solid reaction and reaction proceeds at the liquid–solid interface. Moreover, taking into account that PET is nonporous material and virtually insoluble in the solution. The kinetics of depolymerization of PET can be described by shrinking core model. For example, Toshiaki et al. reported that the kinetics of the hydrolysis of PET in nitric acid and sulfuric acid could be explained by a modified shrinking core model of chemical reaction control.<sup>19,20</sup> More recently, shrinking core model for the alkaline hydrolysis of PET, in the presence of tributylhexadecylphosphonium bromide as phase transfer catalysts, was reported by López-Fonseca et al.<sup>21</sup>

The purpose of this article is to comprehensively study the optimal parameters of the glycolysis process (particle size, microwave power, the weight ratio of EG to PET, the weight ratio of catalyst to PET, reaction temperature, and stirring speed) under microwave irradiation. Furthermore, we describe the kinetics of glycolysis of PET by a simple shrinking core model of the film diffusion control. The main objective is to prove that reaction times will be shorter under microwave irradiation through decreasing the apparent activation energy of glycolysis of PET.

## MATERIALS AND METHODS

### Materials

Consumed PET soft drink bottles were cut into  $0.5 \times 0.5 \text{ mm}^2$ ,  $1.5 \times 1.5 \text{ mm}^2$ , and  $3 \times 3 \text{ mm}^2$  flakes by using self-made manual skiving machine for glycolysis experiments after washing and removing caps, labels and bottom parts, the size of PET flakes are controlled by adjusting distances of blades of skiving machine. PET samples were dissolved in the mixture solution (60 wt % phenol/40 wt % tetrachloroethane), the viscosity average molecular weight of  $2.8 \times 10^4 \text{ g/mol}$  was calculated using an Ubbelohde viscometer at 30°C according to the equation  $M = 3.61 \times 10^4 [\eta]^{1.46}$ .<sup>5</sup> EG and zinc acetate were purchased from Sinopharm Chemical Reagent Factory and used without further purification.

### Glycolysis Reaction

The glycolysis reactions were performed in Microwave Synthesis Workstation (MAS-II, Sineo Microwave Chemistry Technology)

equipped with a magnetic stirrer and a reflux condenser. Three gram of PET particle and EG (the weight ratio of EG to PET of 3, 5, 7) were placed in a round-bottomed flask. The 0%, 0.5%, 1%, 1.5%, 2% w/w zinc acetate, based on weight of PET, was used as catalysts. The flask was heated by microwave irradiation to reach and maintain the desired temperature within  $\pm 3^\circ\text{C}$  under nitrogen atmosphere, and the mixture was stirred at between 300 and 800 rpm for 5–35 min with reflux.

At the end of reactions, boiling water was added to the round-bottomed flask and the mixture was separated into solid and liquid phases by filtration. The solid was washed, dried, and weighted as oligomers and the white crystalline of BHET was obtained from liquid phase by filtering after storing in a refrigerator at 5°C for 24 h, the BHET was also washed with cooled distilled water, then dried in an oven at 50°C, and weighted to estimate the yield of BHET. All the experiments were repeated three times, the arithmetical averages were calculated as the experimental results.

PET is depolymerized under conventional heating according to the procedures described in the literature.<sup>4</sup>

The yield of BHET monomer and conversion percentage of PET were calculated using the following equations:

$$\text{yield of BHET (y\%)} = \frac{\text{weight of BHET monomer}/M_{\text{BHET}}}{\text{weight of initial PET}/M_{\text{PET}}} \times 100 \quad (1)$$

$$\text{conversion percentage of PET (x\%)} = \frac{\text{weight of initial PET} - \text{weight of rest PET}}{\text{weight of initial PET}} \times 100 \quad (2)$$

where  $M_{\text{BHET}}$  and  $M_{\text{PET}}$  refer to the molecular weights of BHET (254 g/mol) and repeating unit of PET (192 g/mol), respectively.

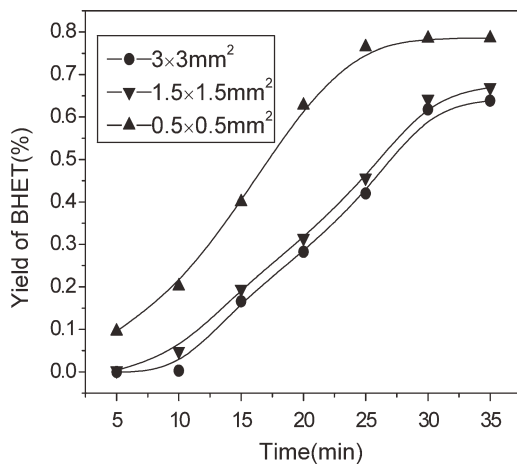
### Analysis of Glycolysis Products

Fourier transform infrared (FTIR) spectroscopy (EQUINOX 55, BRUKER) was used to identify the chemical structure of the products of glycolysis using KBr disc technique. Elemental analysis was performed on Elementer Vario El III apparatus by combustion analysis. In this technique, a sample of the products of glycolysis is burned at 1150°C in an excess of oxygen. Differential scanning calorimeter (DSC) was carried out STA 409 PC Luxx apparatus with the heating rate of 10°C /min from 25 to 250°C under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Effects of Reaction Parameters

The effect of the particle size on the yield of BHET is investigated with the weight ratio (EG to PET) of 5 at 196°C and queating with the weight ratio (catalyst to PET) of 2% under 500 W and the stirring speed of 800 rpm. The results (Figure 1) show that the reaction rates are inversely proportional to the initial particle size. Clearly, the surface area available for the reaction decreases with increasing particle size. However, the yield of BHET is slightly decreased from  $1.5 \times 1.5 \text{ mm}^2$  to  $3 \times 3 \text{ mm}^2$ ; this is because decreasing surface area far

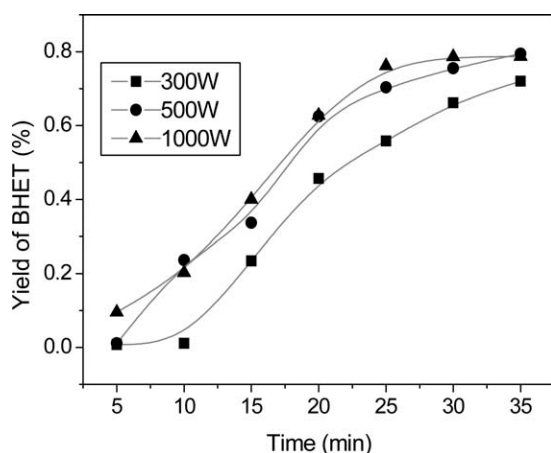


**Figure 1.** The effect of particle size on the yield of BHET (the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%, 196°C, 500 W, 800 rpm).

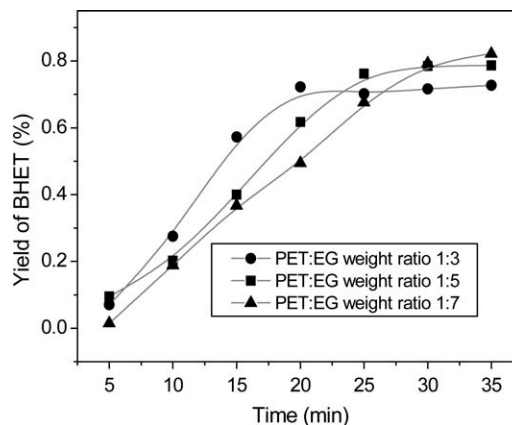
smaller than the intrinsic surface of larger PET flakes.<sup>22</sup>  $0.5 \times 0.5 \text{ mm}^2$  particles are used as material in following experiments.

To study the influence of the microwave power on yield of BHET, the experiments are carried out with the weight ratio (EG to PET) of 5 at 196°C and the weight ratio (catalyst to PET) of 2% under stirring speed of 800 rpm. The results (Figure 2) indicate that the yield of BHET increased with increasing microwave power from 300 to 500 W and then the ascending tendency becomes less distinct from 500 to 1000 W. It implies that 500 W microwave power is an optimal parameter and adopted in following experiments.

To study the influence of the weight ratio of EG to PET on the yield of BHET, the experiments are carried out with the weight ratio (catalyst to PET) of 2% under stirring speed of 800 rpm at 196°C. The same trend can be seen from these curves in Figure 3. Glycolysis of PET possesses high reaction rate at initial



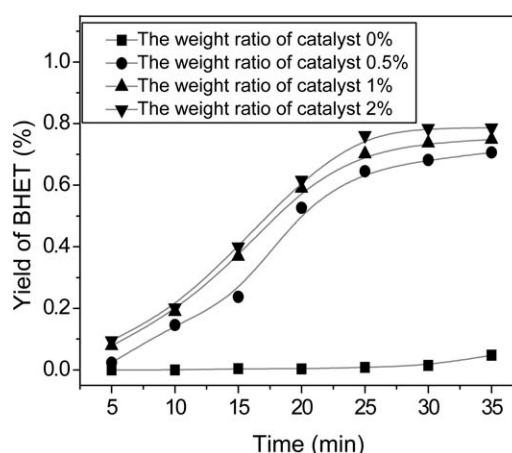
**Figure 2.** The effect of microwave power on the yield of BHET ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%, 196°C, 800 rpm).



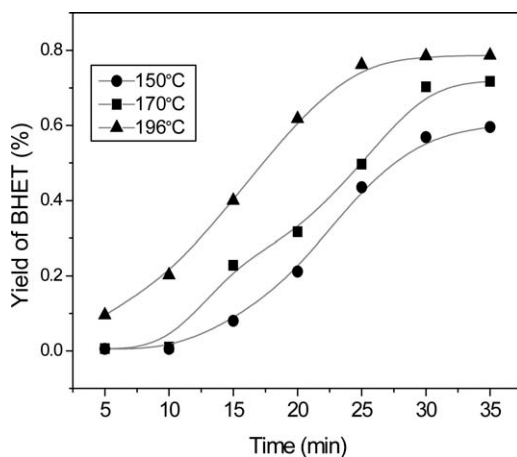
**Figure 3.** The effect of the weight ratio EG to PET on the yield of BHET ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio of catalyst to PET of 2%, 196°C, 500 W, 800 rpm).

stage, then the rate becomes moderate. Interestingly, the reaction time to reach an equilibrium state is shortest under the weight ratio (EG to PET) of 3. These results clearly indicate that glycolysis rate can be accelerated by increasing the concentration catalyst with decreasing the amount of EG, on the other hand, the yield of BHET in an equilibrium state decreases with decreasing the amount of EG.

The effect of the weight ratio of catalyst to PET on the yield of BHET is investigated with the weight ratio (EG to PET) of 5 at 196°C under the stirring speed of 800 rpm. It can be observed (Figure 4) that increase of the weight ratio of catalyst to PET from 0 to 0.5% causes significantly increase of yield of BHET. When the weight ratio of catalyst to PET is 1%, the yield of BHET reaches a higher level and then increases slowly. This is in accordance with the previous results discussed (Figure 3) that rate of glycolysis increases with increasing the concentration of catalyst. The optimal range of the weight ratio of catalyst to PET is from 0.5% to 1%.



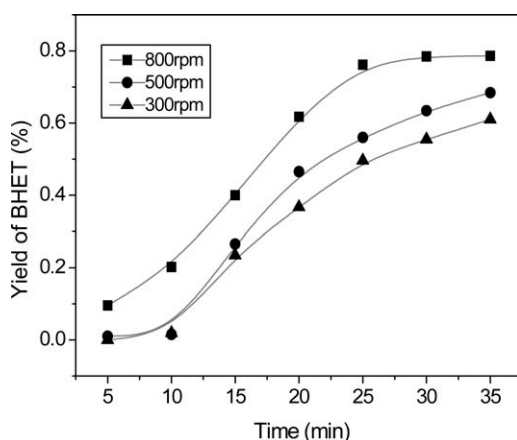
**Figure 4.** The effect of the weight ratio of catalyst to PET on the yield of BHET ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, 196°C, 500 W, 800 rpm).



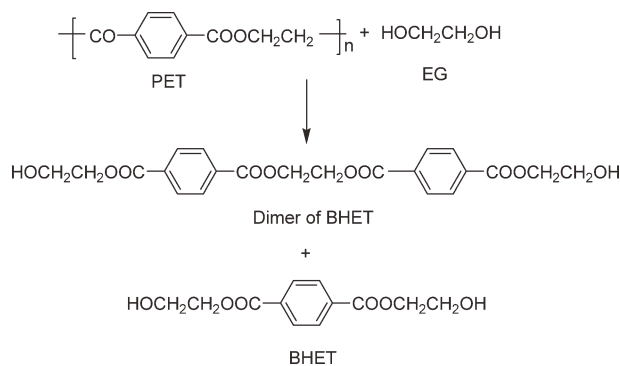
**Figure 5.** The effect of reaction temperature on the yield of BHET ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%, 500 W, 800 rpm).

The effect of reaction temperature on yield of BHET is investigated with the weight ratio (EG to PET) of 5 and the weight ratio (catalyst to PET) of 2% under stirring speed of 800 rpm. The results (Figure 5) show that the yield of BHET increases moderately with increasing temperature as compared with that reported by Toshiaki et al.<sup>19,20</sup> In fact, it is generally accepted that the chemical step is usually much more temperature sensitive than the physical steps. So we may speculate that film diffusion is glycolysis rate determining step.

To study the influence of the stirring speed on yield of BHET, the experiments are carried out with the weight ratio (catalyst to PET) of 2% and the weight ratio (EG to PET) of 5 at 196°C. It can be seen (Figure 6) that a notable enhancement of the yield of BHET is observed with stirring rate from 300 to 800 rpm. So we confirm that mass transfer through the EG film between main body of EG solution and the surface of PET particles is glycolysis rate determining step under this experiment condition.



**Figure 6.** The effect of the stirring speed on the yield of BHET ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%, 196°C, 500 W).

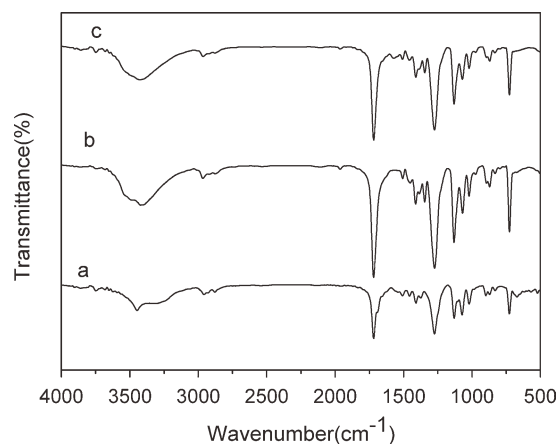


**Scheme 1.** Glycolysis of PET under microwave irradiation.

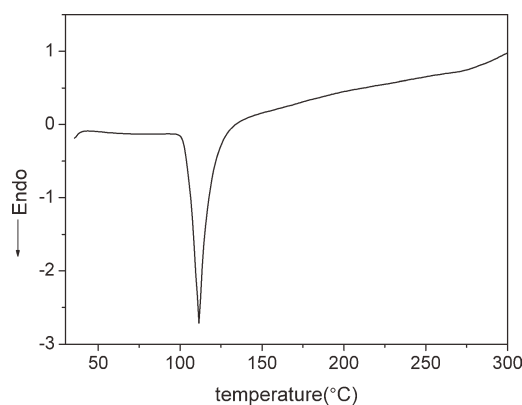
### Analysis of Glycolysis Products

Since dimer of BHET is known to probably soluble in boiling water to some extent, it suggests that glycolysis of products includes at least two components (BHET monomer and dimer). Therefore, the reaction of glycolysis PET under microwave irradiation can be described as follows (Scheme 1):

The characterization of the products of glycolysis is confirmed by FTIR, DSC and elemental analysis. IR spectra of BHET monomer and residual PET are shown in Figure 7, IR spectra of BHET monomer shows that  $\text{—OH}$  band at  $3447 \text{ cm}^{-1}$ , alkyl C-H at  $2885$  and  $2966 \text{ cm}^{-1}$ , C=O stretching at  $1718 \text{ cm}^{-1}$ , the ester C—O peak at  $1131$  and  $1273 \text{ cm}^{-1}$ , benzene ring peak at  $1569 \text{ cm}^{-1}$  as well as at  $728$ ,  $873 \text{ cm}^{-1}$ .<sup>4,16</sup> It can be seen that three spectra are similar, because no new groups are formed during the process of glycolysis.<sup>18</sup> The DSC curve (Figure 8) shows the sharp endothermic peak at  $110^\circ\text{C}$  in agreement with the known melting point of BHET.<sup>4,5</sup> Figure 8 also demonstrates high level of purity (no extra peak other than BHET) of the monomer produced by our process. The result of elemental analysis of products of glycolysis is C = 56.46%, H = 5.44 %, O = 38.1% (by difference), comparatively similar to the theoretical results of the BHET monomer. The results



**Figure 7.** FTIR spectra of BHET and residual PET : (a) BHET monomer; (b) residual PET for 10 min; (c) residual PET for 20 min ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%, 196°C, 500 W, 800 rpm)



**Figure 8.** DSC of BHET( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%,  $196^\circ\text{C}$ , 500 W, 800 rpm, 30 min)

indicate that the BHET monomer is predominately glycolysis products, similar results were obtained in previous research.<sup>4,7</sup>

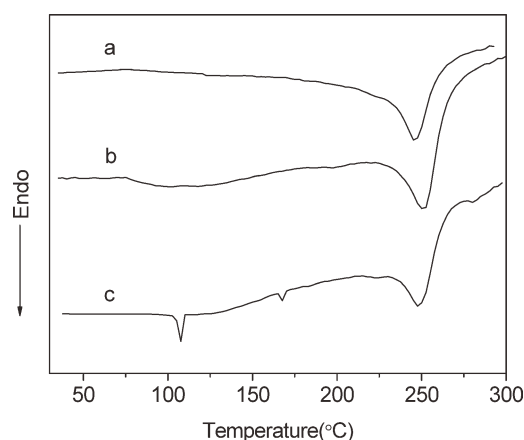
To further reveal evolution of the glycolysis of PET, the fresh PET and residual PET obtained from the filtration step after extractions with boiling water are analyzed by DSC. The DSC profiles are presented in Figure 9. Large endothermic peak is observed in DSC profiles of the residual PET, which is similar to that of PET melting of the fresh PET. The results indicate that most of the residual PET still maintains their original PET structure.<sup>23</sup> However, the other two DSC peaks at about  $110^\circ\text{C}$  and  $169^\circ\text{C}$  in DSC profiles of residual PET for 25 min should correspond to BHET and dimer produced on the surface of PET during glycolysis reactions.<sup>5,24</sup>

### Kinetic Modeling

To describe the kinetics of the glycolysis process of PET, the following assumptions and simplifications are used:

- The particles are spherical and maintained its spherical shape during the glycolysis process;
- The weight of EG is above three times greater than that of PET. Therefore, the amount of EG can be considered as constant in every experiment process;
- The glycolysis of PET was a reversible equilibrium reaction, during the initial stages of depolymerization, polycondensation proceeded at low rate and hence it could be ignored.

The BHET is readily soluble in EG solution at glycolysis reaction temperatures ( $150\text{--}196^\circ\text{C}$ ), so BHET is not deposited on the surface of PET particles. Combined with the previous conclusions, we conclude that the kinetics of glycolysis of PET under microwave irradiation should be interpreted by the sim-



**Figure 9.** DSC thermograms for original residual PET for difference reaction time: (a) original PET; (b) 10 min; (c) 20 min( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%,  $196^\circ\text{C}$ , 500 W, 800 rpm)

ple shrinking core model for the film diffusion control.<sup>25</sup> In other words, this means that the rate of BHET monomer and reactant EG transfer through the EG film surrounding the PET particles is slower than the rate of reaction of glycolysis.

When film diffusion controls, the kinetic model can be represented as the following equation<sup>25</sup>:

$$1 - (1 - X)^{2/3} = \frac{2bC_A D}{\rho R_0^2} t = kt \quad (3)$$

where  $k$  is the apparent rate constants;  $X$  is conversion percentage of PET, these are shown in Table I for all three temperatures;  $\rho$  is the molar density of PET;  $b$  is stoichiometric coefficient;  $R_0$  is initial radius of PET particle;  $D$  is the diffusion coefficient;  $C_A$  is EG concentration.

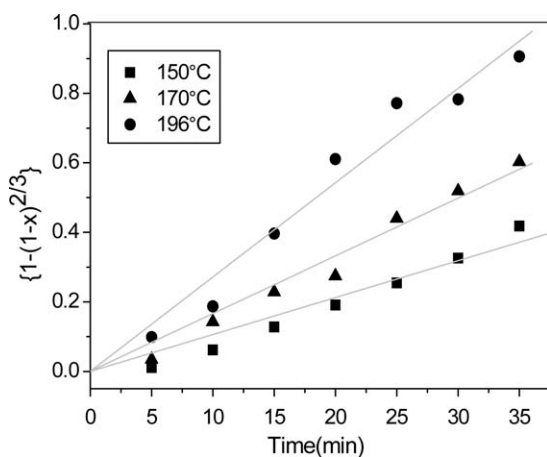
Applying eq.(3), the plots of  $\{1 - (1 - x)^{2/3}\}$  vs. times for PET glycolysis reactions at  $150\text{--}196^\circ\text{C}$  are shown in Figure 10, the results show that the kinetic model provides a good linear relationship ( $r^2 > 0.97$ ). The reaction rate constant  $k$  can be determined from the slope of lines, Arrhenius plots are shown in Figure 11, data fell on straight line with linear correlation factor( $r^2$ ) higher than 0.99. The apparent activation energy for glycolysis reaction under microwave irradiation is found to be 36.5 KJ/mol, and the value of the apparent activation energy confirms the proposed film diffusion control mechanism.

Petrov and Repina reported that the apparent activation energy of glycolysis PET is 100 KJ/mol in temperature range  $160\text{--}180^\circ\text{C}$  and 150 KJ/mol in the range  $180\text{--}197^\circ\text{C}$  without any

**Table I.** Conversion Percentage of PET ( $X$ ) Under Microwave Irradiation at Different Temperatures

	5 min	10 min	15 min	20 min	25 min	30 min	35 min
$150^\circ\text{C}$	1.65%	9.09%	18.51%	27.21%	35.64%	44.64%	55.07%
$170^\circ\text{C}$	5.05%	20.55%	32.24%	38.19%	58.15%	66.62%	75.01%
$196^\circ\text{C}$	14.45%	26.73%	53.14%	75.73%	89.09%	90.39%	97.12%



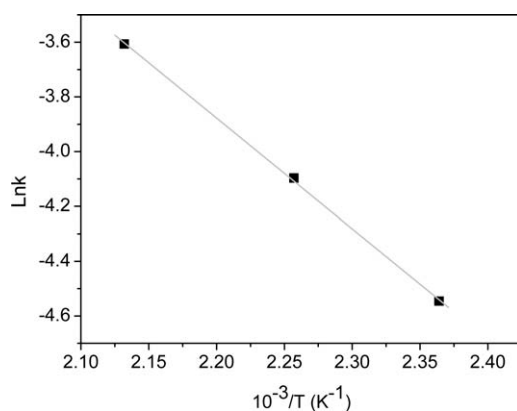


**Figure 10.** Plots of  $\{1 - (1 - x)^{2/3}\}$  vs. times for the effect temperature on glycolysis rate.

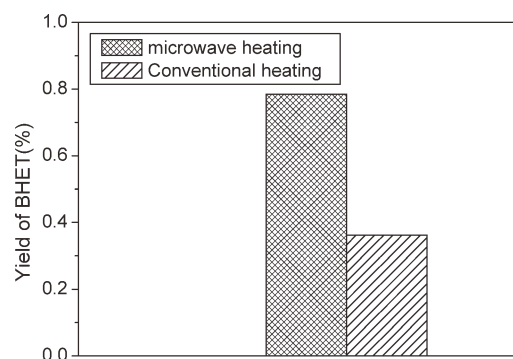
catalyst.<sup>26</sup> Chen et al. reported that the apparent activation energy was 108 KJ/mol without addition of catalyst and decreased to 85 KJ/mol with zinc acetate.<sup>27</sup> The value of 92.175 KJ/mol in the presence of manganese acetate as catalysts was reported by Chen.<sup>28</sup> The apparent activation energy is significantly decreased under microwave irradiation as compared with it by conventional heating. This may be attributed to the fact that the quantum energy of microwave irradiation causes the vibration of molecules and increases the average energy of molecular of PET, which facilitates the destruction of chemical bond and helps to decrease the activation energy. Microwave assisted depolymerization is compared with those achieved by conventional heating at the same experimental condition (Figure 12). The experimental results also show that the microwave irradiation significantly enhances the glycolysis of PET.

## CONCLUSIONS

The effects of operation parameters on glycolysis of PET under microwave irradiation were investigated in this study, the yield of BHET increased with increasing of the weight ratio of EG to PET, the weight ratio of catalyst to PET, temperature and stirring speed until the reaction reached equilibrium condi-



**Figure 11.** Arrhenius plots of the apparent rate constant.



**Figure 12.** Comparative yield of BHET using different heating sources under the same experiment condition. ( $0.5 \times 0.5 \text{ mm}^2$ , the weight ratio EG to PET of 5, the weight ratio of catalyst to PET of 2%,  $196^\circ\text{C}$ , 800 rpm, 35 min).

tions. The experimental data also indicated that the stirring speed and particle size had significant effects on the rate of glycolysis of PET. The maximum yield of BHET was 78% at  $196^\circ\text{C}$ , with the weight ratio of catalyst to PET of 2%, the weight ratio EG to PET of 5 and microwave power of 500 W at only 35 min. A detailed study on the properties of BHET revealed its high purity. The kinetics of glycolysis of PET under microwave irradiation could be explained by simple shrinking core model of the film diffusion control, the apparent activation energy for this glycolysis process is 36.5 KJ/mol, which was found to be lower compared to the same process using conventional heating. On the other hand, the experiment also demonstrated that the use of microwave irradiation on glycolysis of PET results in a significant shortening of the required depolymerization time.

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