Microwave assisted glycolysis of poly(ethylene terephthalate) catalyzed by 1-butyl-3-methylimidazolium bromide ionic liquid

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ABSTRACT: The combination of ionic liquid (IL) associated with microwave energy may have some potential application in the chemical recycling of poly (ethylene terephthalate). In this processes, glycolysis of waste poly (ethylene terephthalate) recovered from bottled water containers were thermally depolymerized with solvent ethylene glycol (EG) in the presence of 1-butyl-3-methyl imidazolium bromide ([bmim]Br) as catalyst (IL) under microwave condition. It was found that the glycolysis products consist of bis (2-hydroxyethyl) terephthalate (BHET) monomer that separated from the catalyst IL in pure crystalline form. The conversion of PET reach up to 100% and the yield of BHET reached 64% (wt %). The optimum performance was achieved by the use of 1-butyl-3-methyl imidazolium bromide as a catalyst, microwave irradiations temperature (170–175°C) and reaction time 1.75–2 h. The main glycolysis products were analyzed by ^{1}H NMR, ^{13}C NMR, LC-MS, FTIR, DSC, and TGA. When compared to conventional heating methods, microwave irradiation during glycolysis of PET resulted in short reaction time and more control over the temperature. This has allowed substantial saving in energy and processing cost. In addition, a more efficient, environmental-friendly, and economically feasible chemical recycling of waste PET was achieved in a significantly reduced reaction time. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41666.

INTRODUCTION

Poly (ethylene terephthalate) (PET) is formed by the reaction of terephthalic acid (TPA) and ethylene glycol (EG) or by the trans-esterification of dimethyl terephthalate and EG.[1] PET is widely used in food packaging, soft drink bottles, X-ray films, audio, and videotapes.[2] Its mechanical and thermal properties, chemical resistance, aesthetic appearance, transparency, low permeability of gases, and ease of processing has led to a number of industries utilizing this material in many diverse applications with high tonnage. The overall world demand for PET mounts to 30 million tons, 65% of which is used for carbonated soft drinks and water bottles, 18% for hot drinks, fruit juice, and alcoholic beverages. The remaining is used to make sheets, food, and nonfood packaging.[3,4] As a result the amount of PET waste is increasing particularly in developing countries and becoming a substantial problem to the world's environment. PET itself is a relatively stable polymer and can stay in the environment for a long time because of its slow degradation rate; it does not pose a direct hazard to the environment. However, due to the substantial volume in the waste stream and resistance to degradation, it was classified

as a noxious material. Ecological and economic consideration urges PET recycling or safe disposal of it.[5]

Both physical and chemical strategies have been utilized to recycle PET. The properties of physically recycled PET are inferior to those of the original; hence decomposition of the PET into reusable chemical products is one of the preferred PET recycling strategies.[6] Several chemical depolymerization processes have been put forward, such as methanolysis, hydrolysis, glycolysis, aminolysis, or amonolysis.[7,8] Out of these processes, glycolysis was given more research attention due to its straightforwardness to degrade polyester. The glycolysis process involves the insertion of EG in to the polymer chain to produce *bis*(2-hydroxylethylene) terephthalate (BHET) that has been widely used to produce polyesters and polyurethanes.[2]

A number of catalysts such as titanium phosphate,[9] metal acetates,[10] solid super acids,[11] and ionic liquids (IL)[2,12] have been reported to facilitate the glycolysis process. Although the titanium phosphate and zinc, lead, cobalt, and manganese salts showed a high yield of BHET, they pose difficulty when separating the

product.[10,13–15] Because of their thermal stability, low flammability, nonvolatility, ILs have been widely used in the extraction, catalysis, and synthesis of various products.[16–18] A number of reports have shown the utilization of ILs as catalysts in the decomposition of PET.[12,19] The ILs have good microwave absorbance capacity[20] and the solid products from the glycolysis process can be easily separated from the IL.

Microwave assisted de-polymerization of PET is a versatile process used to obtain complete conversion of the PET compared to the conventional heating methods. The degradation of PET usually occurs at temperatures above 150°C or under high-pressure conditions. The currently used conventional oil bath heating and high-pressure conditions is associated with a number of disadvantages[21] therefore, microwave heating is the preferred method because of advantages such as accurate temperature control, less energy consumption, and improved reaction time. The microwave irradiation also showed higher heating rate, quick start up and shut down of heating as well as uniform heating, energy saving and a higher yield in faster reaction time.[22]

Microwave heating was utilized to depolymerize PET with zinc acetate, sodium carbonate, and barium hydroxide as catalysts, but separation of the catalyst from the reaction mixture was difficult Hence, the catalysts were not recycled and reused further.[13] Herein we report the combination of microwave heating and IL assisted polymer degradation as a robust method for PET depolymerization. The PET readily converted into BHET after a 2 h reaction time using microwave energy and catalyzed by 1-butyl-3-methylimidazolium bromide IL. The conversion of waste PET with respect to time and temperature using microwave-assisted depolymerization was investigated.

EXPERIMENTAL

Materials

PET drinking water bottles were collected from the local recycling depot, washed, dried, and shredded into small chips approximately ($2 \times 2 \times 2$ mm^3) in size. Anhydrous EG and 1-butyl-3-methyl-imidazolium bromide were obtained from Sigma-Aldrich and were used as supplied. Standard sample of BHET (99.5%) was obtained from Sigma-Aldrich, and used as standard monomer for comparison. For the de-polymerization reaction of waste PET, a 300 W microwave synthesizer (CEM) was utilized. Nitrogen gas was used to purge and perform the reaction in an inert atmosphere (SOC, UAE).

Glycolysis of PET

A 100 mL round bottom single-neck-flask equipped with a reflux condenser and nitrogen inlet was loaded with 5.0 g of PET, 20.0 mL of EG and 2.5 g of 1-butyl-3-methylimidazolium bromide IL. The glycolysis reaction was carried out under microwave irradiation at reaction temperature ranging from 50 to 175°C and 1 atmospheric pressure. The reaction time varied from 0.5 to 2 h (or the reaction studied at different time intervals ranging from 30 to 120 min. After a 2 h reaction time, the solid PET was completely soluble and the reaction mixture became a clear pale yellow color solution. It was left to cool down to room temperature for several minutes, then 200 mL of cold water was added to the reaction mixture with vigorous agitation. The reaction mixture was cooled to 0°C. A white precipitate formed that was filtered carefully with a Buchner funnel. The filtrate contained unreacted EG and monomer *bis*(2-hydroxyethyl) terephthalate (BHET). White crystalline powder of BHET was purified by recrystallization with 3V THF and 3V hexane (3 : 3) combination. The reaction product was then dried in an oven at 60°C for 8 h and weighed. It was then subjected to various characterization techniques, NMR, TGA, DSC, FTIR, and LC-MS.

The glycolysis reaction was carried out under different parameters, such as time and temperature. When each glycolysis reaction was finished, the still polymerized PET pellets were quickly separated from the liquid phase before the products precipitated. An excess amount of cold distilled water was used to wash the polymerized PET pellets, and the water was then mixed with the product fraction. The remaining polymerized
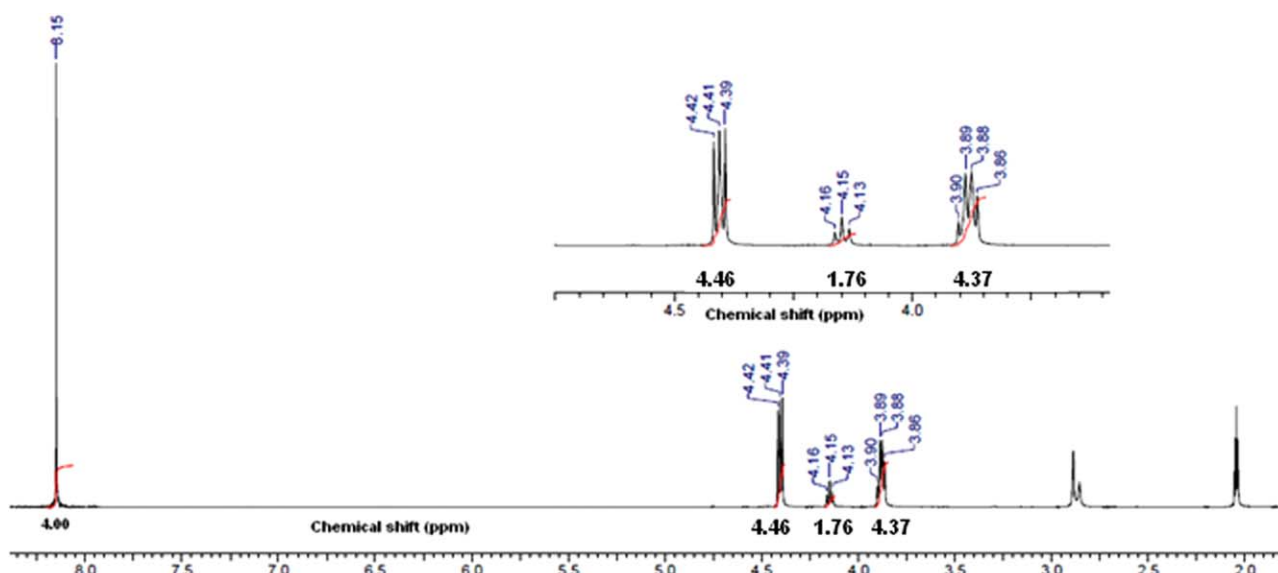

Figure 1. ^{1}H NMR spectrum of BHET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
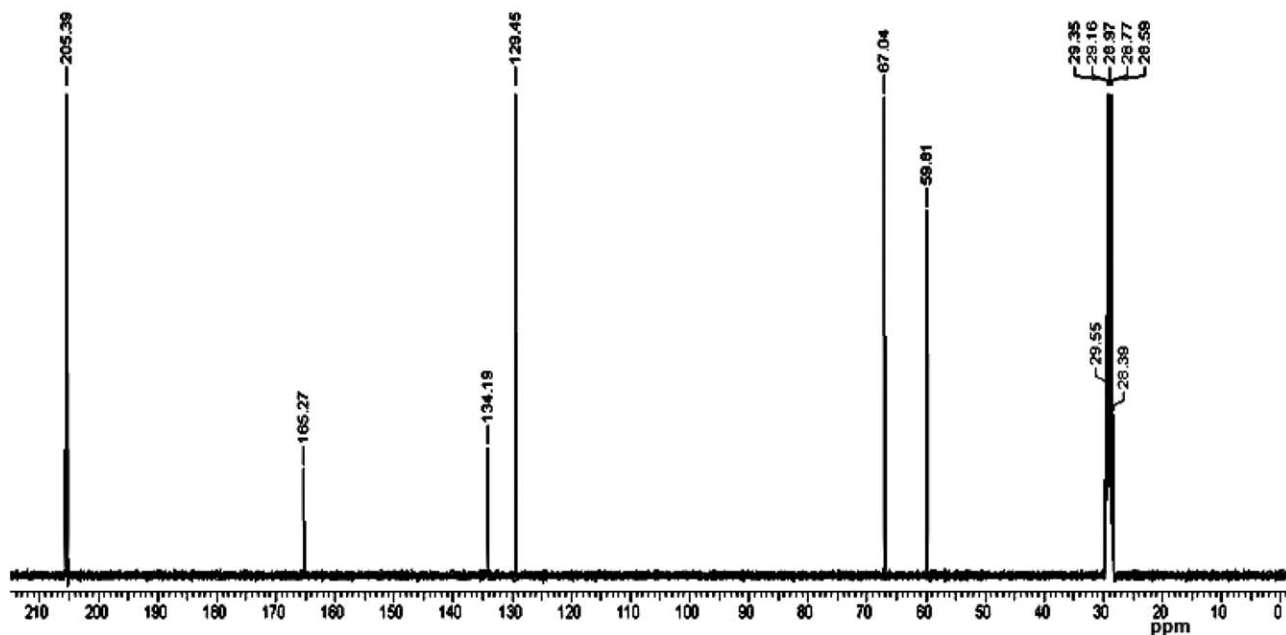
Figure 2. ^{13}C NMR spectrum of BHET.

PET was collected, dried and weighed. The conversion percentage of PET is defined by the following equation.

$$\text{Conversion percentage of PET} = \frac{(W_0 - W_1)}{W_0} \times 100\%$$

where W_0 represents the initial weight of PET and W_1 represents the weight of still polymerized PET.

Characterization of BHET

The structure of BHET produced during the depolymerization reaction was determined by ^{1}H NMR and ^{13}C NMR spectra using Varian 400 NMR operating at 400 MHz. The NMR spectra (^{1}H and ^{13}C) were obtained in d$_6$ –acetone solution. Fourier transform infrared spectroscopy (FTIR) was used to characterize the presence of specific functional groups. The mass spectrum of the fragmented PET performed using LC-MS (ACQuity, Ultra Performance LC) with electrospray ionization. Thermogravimetric analysis of the glycolysed product was carried out in TGA Q50 (TA instrument). BHET (5 mg) was heated at a rate of 10°C/min in a nitrogen atmosphere from 20 to 600°C. DSC scans of the product were obtained using DSC Q200 (TA instrument) by heating from 25 to 180°C at a rate of 10°C/min under nitrogen atmosphere.
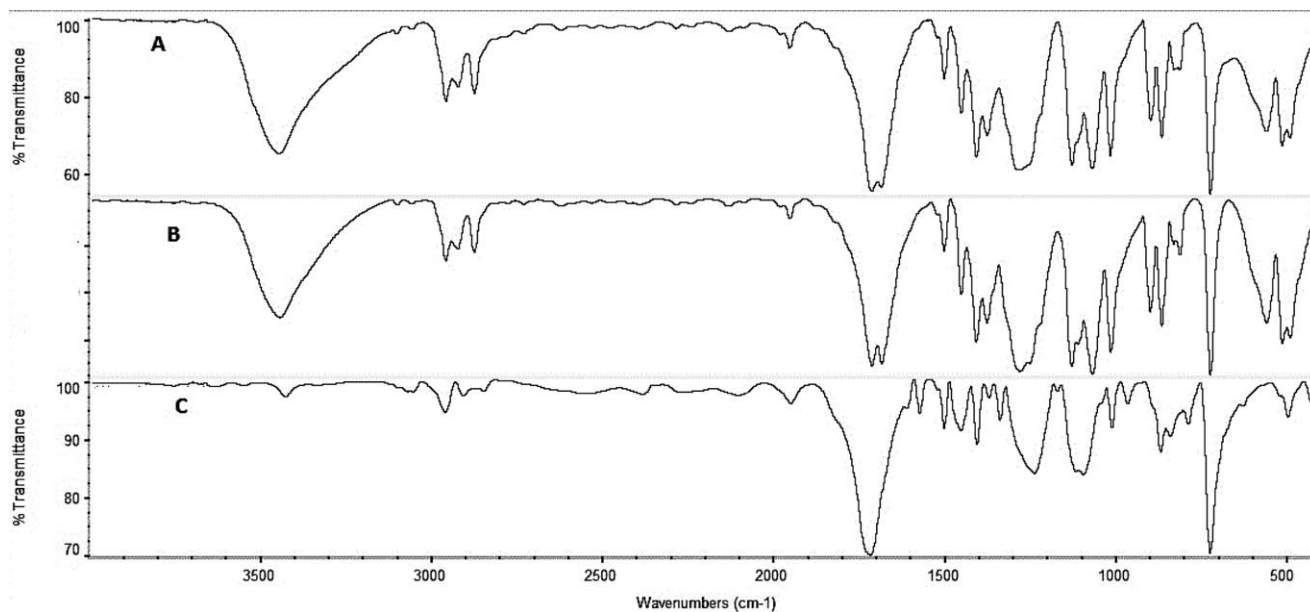

Figure 3. Three FTIR spectra, (A) is for BHET standard, (B) BHET obtained after glycolysis of PET, and (C) PET before glycolysis.
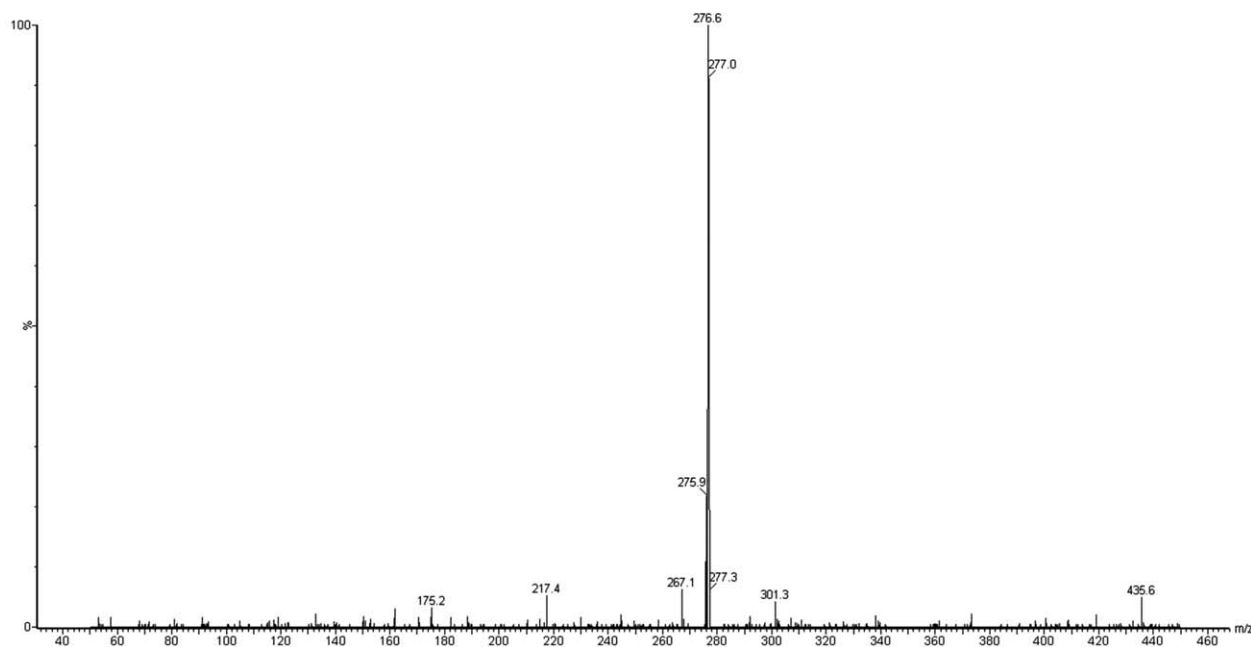
Figure 4. Mass spectrum of BHET.

RESULT AND DISCUSSION

Selection of Catalyst

It has been proven that the depolymerization of PET using ILs gave more advantages as compared to conventional catalysts such as metal acetate.[12] Among these ILs; 1-butyl-3-methyl imidazolium bromide ([bmim]Br), which showed high conversion and low preparation cost.[2]

The catalytic effects of IL during the glycolysis of PET were tested. When the glycolysis with the absence of catalyst, the reaction did not proceed; however, the conversion of PET started after the use of catalyst 1-butyl-3-methyl imidazolium bromide. The affordable price and high catalytic effect of [bmim]Br IL provide a gave good advantage for this processes.

Recycling of the Residual Ionic Liquid and EG

The recycling of the residual IL and EG was adopted by filtering the BHET from the reaction medium. The reaction mixture was concentrated in a rotary evaporator at 55°C for 1.5–2 h using a
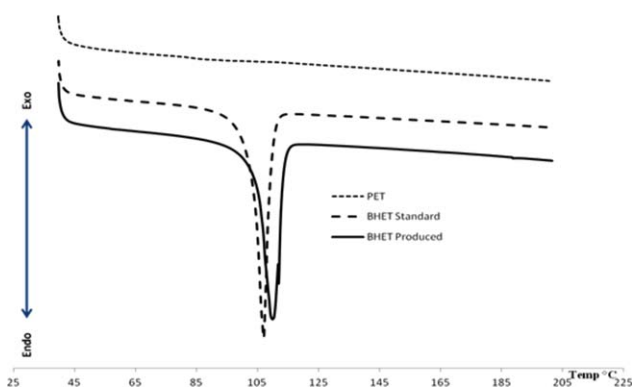

Figure 5. Combined DSC curves for, BHET (Standard and produced by glycolysis) and un-degraded PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vacuum pump. For azeotropic removal of water impurities, the crude residue was treated with 10 mL of toluene and concentrated for another 30 min. This was then kept in a vacuum oven for 7 h at 60°C. The crude residue weight was checked and balanced if found less than the initial weight of fresh catalyst and EG. This recycled IL and EG can be used further for the degradation of PET.[19]

NMR

The structure of the BHET was confirmed by ^{1}H NMR (Figure 1) and ^{13}C NMR (Figure 2), and the spectra of purified samples after glycolysis reaction were performed. In the ^{1}H NMR spectrum, the peak at δ 8.15 ppm shows the presence of four aromatic protons of the benzene ring. The peaks at δ 4.4 and 3.8 ppm are characteristic of the methylene protons of methylene near to carboxyl group and hydroxyl group, respectively. The triplet at δ 4.1 ppm is characteristic of the protons of the hydroxyl group. The peaks at δ 2.05 and δ 2.84 ppm is known for the solvent acetone and water impurities.[23] The ^{13}C NMR spectra (Figure 2) showed clearly the presence of different carbon atom in the purified sample. The signals at δ 165.27 ppm indicate the carboxyl carbon and signal at δ 134.19 is due to the quaternary carbon adjacent to the carboxylate group. The signals at δ 129.45 ppm indicate the unsubstituted aromatic carbon atoms. The two characteristic methylene carbons, which is attach to the carboxyl group are appeared at δ 67.04 and hydroxyl group appeared at δ 59.81, respectively. The signals at δ 28.97 and δ 205.39 ppm are believed to be from solvent impurity (acetone).[23] Consequently, the ^{1}H and ^{13}C NMR spectra reveal the structure of isolated product, which is identical with the structure of BHET and agreed well with those reported in Ref. 10.

FTIR

Fourier Transform Infrared spectroscopy (FTIR) was used to study the nature of chemical bonds during the thermal degradation of PET, which occurred because of changes in the main backbone of

Table I. Data Obtained from the TGA for Three Samples

Type of product	First degradation range of temp. (°C)	% weight loss first stage	Second degradation range of temp. (°C)	% weight loss second stage	Final degradation range of temp. (°C)	Percentage weight loss. final stage, (Residue %)	Temperature at 20% weight loss (°C)	Temperature at 50% weight loss (°C)
Untreated PET	400–475	85	475–600	7	>600	8	426	450
BHET produced	185–325	37	390–475	60	>600	3	230	412
BHET standard	185–297	85	375–465	32	>600	2	250	276

the polymer. When degradation occurs, it will certainly alter the chemical structure during the bond cleavage or formation of new bond. It is a chemical process, which affects both, the chemical composition and the physical. The degradation initiated at the weakest link and propagated throughout the process resulting in the formation of different types of monomers, dimers, while end-groups resulted in substantial modification of the polymer backbone. The ester linkage scission was occurred first resulted in the formation of smaller molecular weight species or through chain ends degradation producing carboxyl end groups. The FTIR spectra were obtained for PET before and after glycolysis and as compared with the standard monomer.

The FTIR analysis was carried out after purification of the degraded product and all three spectrums are given in Figure 3. The only monomer, which was recovered from the degradation process, is BHET. The most intense bands correspond to the ester carbonyl (C═O) stretching was observed at 1716 cm^{-1} and the hydroxyl end group (OH) was observed at 3444 cm^{-1}. The ether linkage band due to carbon-oxygen (C—O—C) bond was observed at 1300 cm^{-1}. The para-substituted benzene ring was observed at 1456 cm^{-1} and the carbon–carbon bond in the aromatic ring was observed at 1504 cm^{-1}. The alkyl (C—H) stretching groups of bands were observed at 2963, 2879, and 879 cm^{-1}. The FTIR spectra of the PET present here (spectra C) exhibit a similar pattern to those of the pristine polymer reported in Ref. 15. The IR spectrum of the standard BHET (spectra A) shows an overall increase in the peak intensities par-
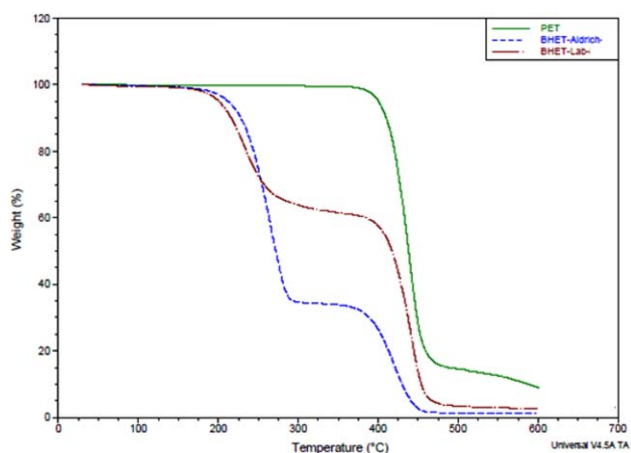
ticularly for the hydroxyl (OH) terminal group, which appears at 3444 cm^{-1}. Peak profile and marginal shifts in the positions of typical bands were also observed. The increase in peak intensities indicated the presence of a terminal hydroxyl group. The broadness of this peak also indicates the presence of large number of hydrogen bonding, which are largely associated, and predominately present in the monomers and dimers to a slighter extend. The above observations drawn from the degraded sample were also observed in the standard sample (spectra B), which provides strong evidence that the material obtained after glycolysis is the monomer of BHET.

Mass Spectrometry (MS)

MS analysis is used to identify the molecular weight of a molecule. Kim and Lee[24] explained the identification and existence of BHET monomer, dimer, trimer, and oligomer in food containers when analyzed using HPLC-ESI-MS. For confirming the molecular weight of isolated product and eliminating the possible presence of dimer, trimer, and oligomer, a sample was subjected for LC/MS. The mass spectrum of isolated product after glycolysis reaction is given in Figure 4. The molecular ion of BHET showed up m/z 255 [M+H]$^+$ and 277 [M+Na]$^+$. In the MS spectra of isolated sample the pseudo molecular ion peak 277 with intensity almost 100% was observed. This peak is related to BHET ionized by Na$^+$ (in electrospray ionization, the fraction could be ionized by H$^+$, Na$^+$, or K$^+$). Hence, the molecular weight of the isolated product was, 254 g/mol, which is the same as the molecular weight of BHET standard bought

Figure 6. TGA curves for PET, and BHET produced during glycolysis and BHET standard. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
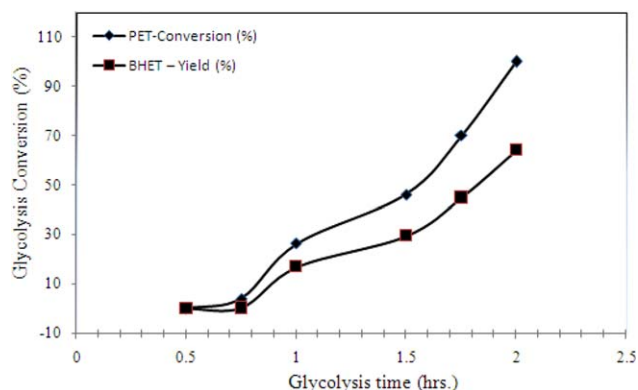

Figure 7. Effect of reaction time on the conversion of PET (1 atm, 175°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
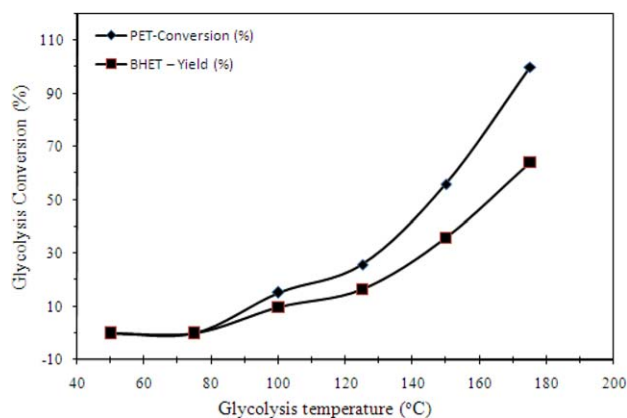
Figure 8. Effect of reaction temperature on the conversion of PET (1 atm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from Aldrich. The mass spectra strongly supported those reported in Ref. 24.

DSC

The DSC thermograms for the standard and produced BHET as well as the untreated PET are shown in Figure 5. Sharp and well-resolved endothermic peaks were observed at108°C, and at 115°C for BHET standard and BHET recovered from glycolysis process, respectively. The first melting peak for the standard occurred at slight lower temperature than the produced BHET sample. This trend was also observed from the TGA data where the onset of the first degradation stage occurred at 185°C for both samples, as shown in Table I. The shape and the broadness of the two peaks are similar to each other, which indicate the resemblance between the two materials. This corresponds very well with the same observations recorded in Refs. 13,25. Both curves have not show-ing any singe of glass transition temperature (T_g), which is a typ-ical property of polymeric materials, while the undegraded PET sample showed a shift in the base line at 81°C, which is a charac-teristic of the glass transition temperature (T_g) for the PET.[25] This indicates that the glycolysis product is certainly composed

of monomers that show no glass transition temperature, just an endothermic peak similar to the control sample.

TGA

The TGA curves for the BHET standard, BHET obtained from gly-colysis together with the PET are shown in Figure 6. The control BHET and the glycolysis product each had two degradation steps, while the PET sample had only one major step. The data obtained from the TGA are summarized in Table I. The first onset of weight loss for the glycolysis sample was between 18 and 325°C in which 37% of the material was lost. On the other hand, the first onset of weight loss for the standard sample started from 185°C, and fin-ishes at 297°C (slightly lower than the glycolysis product) in which 85% by weight was lost. These first weight losses were contributed to the thermal decomposition of the monomer. However, the sec-ond weight loss for the glycolysis product and standard occurred at almost the same temperature range, between 375 and 475°C in which 60% of the glycolysis sample was lost compare to 32% lost by the standard. Once again theses second mass losses were con-tributed to the thermal polymerization which occurred during the thermogravimetric test. This result has agreed with those reported in Refs. 2,26,27. In comparison with the untreated PET, it was found that the PET had only one major step degradation that occurred between 400 and 475°C where almost 85% of the poly-mer was lost. No self-polymerization was observed, except that the polymer residue at 600°C was higher than that of the other two samples. The temperature at 20% and 50% weight loss for all sam-ples was also recorded and listed in Table I.

Influence of Glycolysis Time

The influence of glycolysis time on the conversion of PET and the yield of BHET at 175°C was examined and the results are pre-sented in Figure 7. It indicated that the conversion of PET increases proportionally with increasing glycolysis time. When the glycolysis time was 0.5 and 0.75 h, the PET conversion was 0 and 4%, respectively. When the reaction time was extended to 1.0–2.0 h, the resulted glycolysis conversion was 26.45–100%. Furthermore, the results show that the yield of BHET reached a maximum value when the reaction time was set at 2.0 h. It was found that whenever the reaction was kept at below 1 h, the PET conversion was minimal and it increased to 100% upon 2 h.
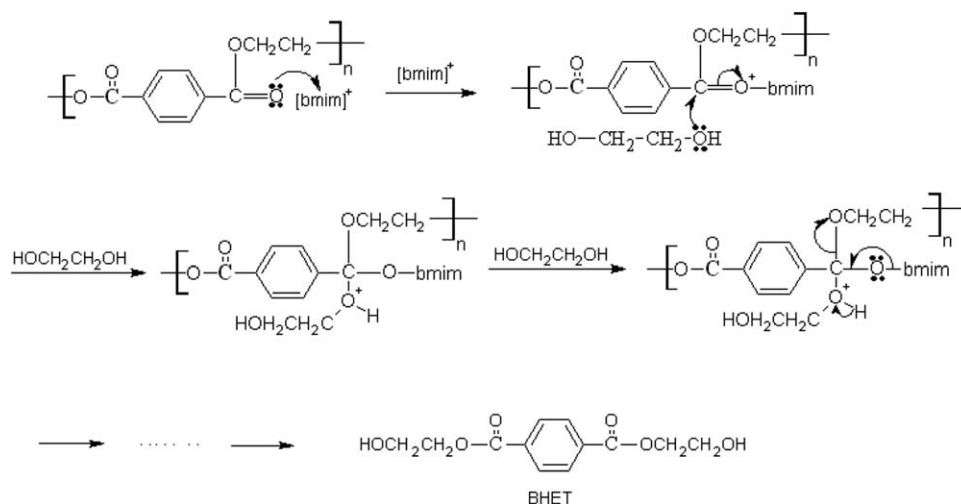

Figure 9. Mechanism of the glycolysis of PET catalyzed by [bmim]Br.[28]

Influence of Reaction Temperature

The effect of reaction temperature on the conversion of PET and the yield of BHET showed a great increase in the PET conversion and the BHET yield with increasing reaction temperature as seen in Figure 8. When the temperature was 50°C, and 75°C, the PET conversion was 0% at 2 h. Subsequently, with increasing glycolysis temperature, the conversion of PET increased rapidly reaches 100% when the temperature was set at 175°C. On the other hand, the yield of BHET increased as the reaction temperature increased. When the glycolysis temperature was 50°C, and 75°C, the yield of BHET was zero after 2 h of reaction time. Then it gradually increased to 64% when the reaction temperature rose to 175°C. Hence, high temperature was favorable for the formation of BHET.[2]

Glycolysis Mechanism

There have been several studies and discussion on the mechanism of PET glycolysis using IL and metal salts. It was accepted that the degradation occurred due to the cleavage of the ester link in PET polymeric chain.[15,19] In this process, $[bmim]^+Br^-$ catalyzed the reaction as Lewis acid.[28] The cation of the catalyst $[bmim]^+$ interacts with the carbonyl oxygen in the ester group and make the carbonyl carbon more partial positive carbon. This assist the oxygen in the hydroxyl group of EG attacks this carbon of the ester group, forming a tetrahedral intermediate. Subsequently, deprotonation of the EG occur and the bond between oxygen, and $[bmim]^+$ shifted back to form C=O. The acyl-oxygen bond cleaves, and the $-OCH_2CH_2-$ group leaves, combining with H^+ to form $HOCH_2CH_2^-$. This will finally end up with the breakdown of the polymeric chain of PET to oligomers then converted into dimer then to BHET monomer. Hence, the Lewis acid catalytic activity of 1-butyl-3-methyl imidazolium bromide ($[bmim]^+Br^-$) makes the depolymerization of PET much easier as shown in Figure 9.[28] The reaction time and temperature influence the complete conversion to BHET.

CONCLUSIONS

The glycolysis of PET catalyzed by 1-butyl-3-methyl imidazolium bromide under microwave condition gave monomer as BHET. NMR (^1H and ^{13}C) confirms the BHET monomer structure in d_6–acetone solvent. The effects of reaction parameters, such as time and temperature on the conversion of PET to BHET were investigated. The results show that the conversion of PET and the yield of BHET increase with the increase of reaction time and temperature. The use of microwave energy extremely reduces the glycolysis time as compared to the conventional heating where it takes 8–10 h. This offers a possible substantial saving in energy and cost. Ecofriendly catalyst IL such as 1-butyl-3-methyl imidazolium bromide can be used instead of metal catalyst. Thus, this method tries to gives an ecofriendly alternative over conventional depolymerization of PET with significant reduction in cost and energy.

ACKNOWLEDGMENTS

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