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Glycolysis of Postconsumer Polyethylene Terephthalate Waste

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Abstract: Chemical recycling process of polyethylene terephthalate (PET) into bis-hydroxyethyl terephthalate monomer (BHET) was investigated for that its bottle grade consumption is reaching high levels specially in bottled water and soft drinks. Although the most commonly used recycling processes are in-plant and mechanical methods, it was found that the benefits and opportunities offered by chemical recycling makes it one of the most interesting processes to develop. Glycolysis of recycled polyethylene terephthalate (PET) from consumed bottled water and soft- drink bottles was carried out with ethylene glycol (EG) for different weight ratios of PET to EG using zinc acetate as catalyst at the boiling point of EG under nitrogenous atmosphere for a constant time of 3.5 h. PET:EG ratio was studied to get information on the reaction behavior and yield results taking into account the solvent excess influence. Monomer and oligomers were characterized using FTIR technique. The possibility of improving the extraction process and the use of EG recovered from previous glycolysis reactions via distillation, membranes or other separation method could lead to an ameliorated economic and environmental process.

Keywords: *Glycolysis; BHET; monomer; depolimerization; recycling.*

1. INTRODUCTION

Plastics are commercial polymers derived from natural or chemical synthetic materials .They are made from limited resources such as petroleum; therefore, large advances are being made in the development of technologies to recycle plastic waste. The predominant ones are the petrochemical plastics which are mostly derived from polyethylene, polypropylene, polystyrene polyvinyl chloride, polyethylene terephthalate, and Polyurethane and they do not easily degrade; hence they remain in waste streams for so many years.

The material under consideration in this work is polyethylene terephthalate (PET). It is semicrystalline thermoplastic polyester showing excellent tensile and impact strength, chemical resistance, clarity, process ability and reasonable thermal stability. Although, its main application is by far in the textile industry, tremendous quantities of this material are consumed in the manufacture of video and audio tapes, x-ray films, food packaging and especially of soft-drink bottles.
PET bottles are characterized by high strength, low weight and permeability of gasses (mainly CO2) as well as by their aesthetic appearance (good light transmittance, smooth surface), while they do not have any side effect on the human organism. Many attempts are currently directed toward recycling of PET waste, because of the interests in environmental protection, energy preservation and economic benefits.

Among the different recycling techniques (primary, mechanical, chemical recycling and energy recovery), the acceptable one according to the principles of “sustainable Development” is chemical recycling, since it leads to the formation of the raw materials from which the polymer is made, as well as of other secondary value- added products [1].Chemical recycling has been defined as the process leading to total depolymerization of PET into monomers, or partial depolymerization into oligomers and other chemical substances. The main methods uses for this purpose are glycolysis, methanolysis, hydrolysis (alkaline, acidic and neutral) and other processes such as aminolysis and ammonolysis [2].
Glycolysis makes it possible to employ very low amounts of reactants, as well as applying lower temperatures, in contrast with other methods such as supercritical

methanolysis and thermal degradation [3,4] while hydrolysis under acidic or basic conditions may cause corrosion and pollution problems [5]. Recently, a growing interest has been observed in PET glycolysis for the manufacture of specialized products such as unsaturated polyesters [5], polyurethanes [6, 7, vinyl esters [8], epoxy resins [9], and polymer concretes [10,11].

2. OBJECTIVES

The objectives of this research are environmental , economical and technical in nature, PET waste from bottled water and soft drinks represents about 12% of total local plastic is to be recycled , economic benefits are achieved through recovering of monomers by de-polymerization method , a third objective is the introduction of chemical recycling techniques in Sudan, a country with limited experience in recycling

3. EXPERIMENTAL

3.1 Materials

Commercial PET Postconsumer PET bottles wastes were obtained from local market. The bottles after removing caps and labels were cut into approximately 1 cm2 chips and subsequently cleaned by boiling in weak detergent solution followed by washing and drying .

3.2 Chemicals

All the chemicals including the catalysts including ethylene glycol and zinc acetate were of analytical reagent grade. A contentious nitrogen line is supplied during the glycolysis reaction to prevent oxidation.

3.3 Glycolysis experiment

10, 20, 30 grams of PET wastes (fibres or flakes) was depolymerised using 72, 90, 54 ml of EG respectively in the presence of a zinc acetate (1 %) as a transesterification catalyst. A three-necked flat-bottom 500 ml glass reactor equipped with a thermometer, a reflux condenser, and a magnetic stirrer was used for all glycolysis experiment. In order to realize the influences of reaction conditions (especially the amount of EG) on the yield of glycolysis reaction, the experiments were allowed to proceed at 198°C under nitrogen atmosphere up to 220°C for 2.5 hour . 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. After filteration, the residual was transfered 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] . The filter cake was collected, dried and labeled as GP-2 while the glycolysed product before having water extraction ,labelled as GP-1 and some filter cake was stored in a refrigerator for 16 hrs to allow the formation of white crystalling flakes labeled as GP-3. GP-1, GP-2 and GP-3 were undergoing IR spectroscopy instrument.

3.4 Characterization of BHET

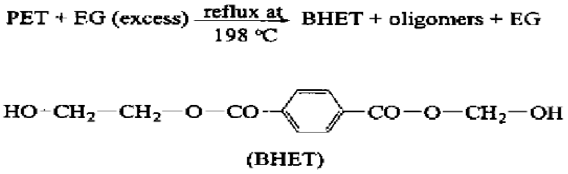
Melting point of the purified BHET was determined in an open capillary.Elemental analysis was carried out by using titration methods for obtaining acid and hydroxyl values.FTIR spectrum was recorded using KBr disc technique on Shimadzu IR Spectrophotometer (Model 8400S)

4. RESULTS & DISCUSSION

The process began with continuous rising in temperature until 195CO, then the reaction mass started boiling. the pet flakes began to dissolve and white clouds was appeared for a time until it became clear and the temperature slowed down to 190 CO, some pet wastes was still at the bottom of the flask so after stirring, the process was continued and temperature raised to 197 CO (the EG boiling point).the temperature fixed for 2.5 hours in the range between 198-220 CO. The produced yellow thick liquor was weigh and let to cool down to room temperature .a sample of the product was taken and marked as GP1(glycolysed product1). The remaining products were mixed with boiling water which would dissolve any unreacted EG and the catalyst during 45 min. This was intended to extract the BHET, which is known to be quite soluble in boiling water [12] then the mixture was filtered under vacuum (pump filter) . This filtration process was carried out avoiding the mixture cooling. The white thick wet solid obtain was dried, weight and labeled as Fraction GP2. A weigh sample of filtrate was cooled in a refrigerator for 16 hours, obtaining white crystals labeled as GP3.The filtrate, a mixture of EG and water, was distilled under vacuum, recovering the EG excess from the glycol sis reaction, thinking about the possibility of its reuse in consecutive depolimerizations.The procedure was repeated with three different mass ratio EG/PET (w: w) 8:1, 5:1and 4:1.

4.1 Glycloysis products analysis

The PET glycolysis leads to formation of bis (2-hydroxy-ethyl) terephthalate (BHET) monomer .During glycolysis, ester linkage were broken and replaced by hydroxyl terminals (Scheme 1). The process waste was converted into BHET and its oligomers with hydroxyl and carboxyl end groups (dimmer, trimmer, etc.). The extent of depolymerization of PET depended on the excess of EG taken for glycolysis. Characteristics of primary glycolysed products (GP) as well as oligomers and BHET derived thereof are presented in Table 2



Scheme (I). Chemical structure of BHET

Table (1): Gylcolysis products characteristics

Item	Melting point	Free EG%	Hydroxyl Value mg/KOH/g	Acid Value mgKOH/g
Gylcolysis Products (GP1)	58	40	312	9.2
Oligomers (GP2)	169.8	45	235	77
BHET (GP3)	110.8	0.5	337	0

Table (2). Hydroxyl and acid values of Gylcolysis products of different pet/EG ratio

Sample	Pet /EG Mass ratio	Hydroxyl Value mg/KOH/g	Acid Value mgKOH/g
1	0.25	243	59
2	0.2	255	45
3	0.125	312	9.2

It was found that the fraction (GP1) had low acid value (AV), 9.2 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, due to presence of water as impurity or formed by side reactions, and some products with carboxyl end group are also formed, especially at lower amounts of ethylene glycol. Table 2 presents the acid and hydroxyl values of the glycolysis products soluble in hot water for different molar ratios of PET/EG. It is clear that hydroxyl value (HV) increases with increasing ratio of EG/PET, which is due to increase in the amount of BHET. The hydroxyl number of pure BHET and dimer are about 337 mg KOH/g, and acid number of pure BHET is zero. The range of hydroxyl numbers shown in Table (2) fall between these two values, implying that glycolysis products consist of mixtures of BHET and mixtures.

Oligomeric PET waste is a mixture of the products of the reaction and contains 45% free EG, 3% BHET and 52% water & insoluble fraction of oligomers. According to the melting point of the oligomeric residue, the main part of this waste is a mixture of cyclic BHET dimers (melting point Tm at 169.8oC) and PET fakes traces (Tm 260oC).according to literature ,the melting point of pure BHET is 111-112 ^{o}C which is close to the obtained value 110.8 ^{o}C

products yields :

Table (3). EG, Oligmers and BHET yield

No.	PET (g)	EG(g)	EG (ml)	Pet /EG Mass ratio	BHET (g)	Oligomers (g) (Include water)	BHET Yields %
1	20	80	89	0.25	8	12	40
2	20	100	111	0.2	11.6	8.4	58
3	20	160	178	0.125	17.6	2.4	88

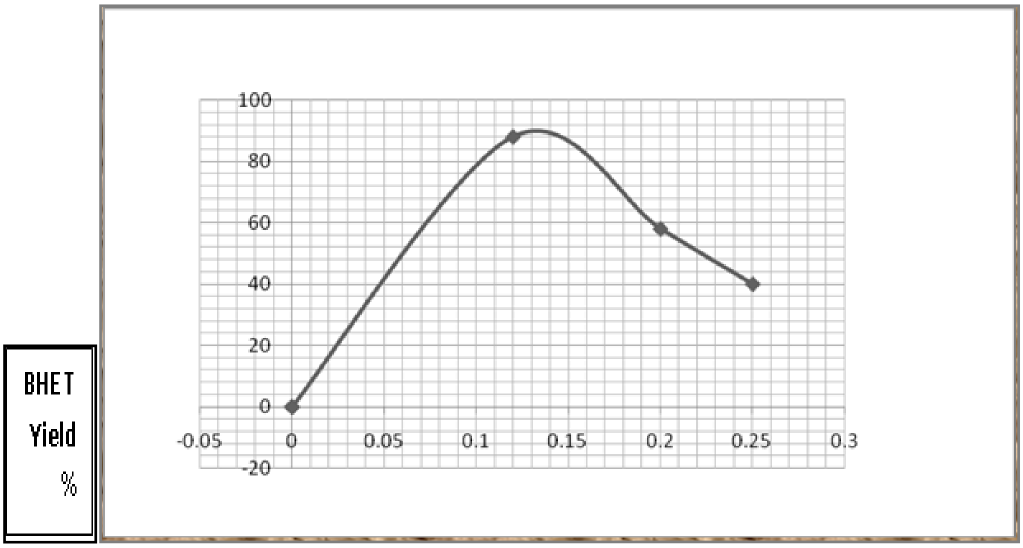


Fig. (1). Effect of EG/PET (w/w) on the yield of the BHET

The rate of depolymerization reaction under constant temperature and pressure (normal), depends on the mole ratio of PET/EG . It 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 88 % BHET was obtained at a mole ratio of PET/EG=0.125. 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 .2, the glycolyzed products consisted of oligomers having higher molecular weight. 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 maximum yield of BHET and minimum amount of oligmers were produced

Infra-red results analysis

Table (4). the characteristic FTIR transmission spectrum peaks for the PET glycolys

No.	GP1 Wavelength cm^{-1}	GP2 Wavelength cm^{-1}	GP3 Wavelength cm^{-1}
1	3460.06	3498.63	3583.49
2	3207.40	3193.90	3130.25
3	2983.67	2948.96	2948.96
4	2131.19	2310.56	2108.05
5	1922.90	1724.24	1645.17
6	1706.88	1461.94	1454.23
7	1652.88	1272.93	1276.79
8	1452.30	1128.28	1132.14
9	1400.22	1076.21	1076.21
10	1274.86	1033.77	1035.70
11	1041.49	885.27	-
12	877.55	734.83	-

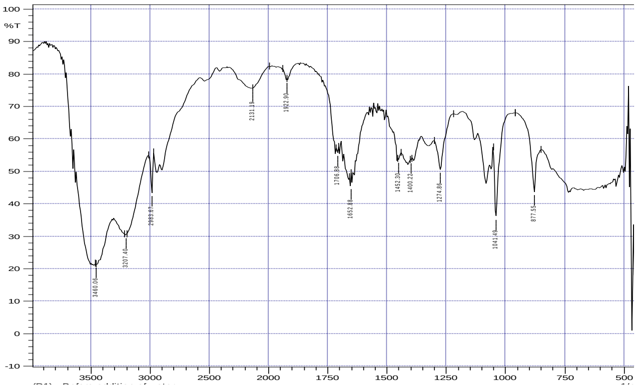


Fig. 2(a). FTIR Spectrum of the Glycolyis products(GP-1)

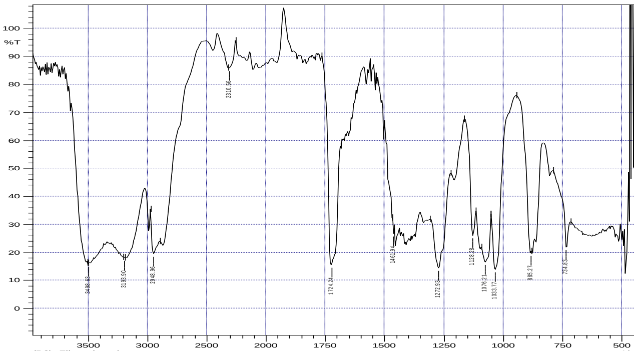


Fig. 2(b). FTIR Spectrum of Oligmers (GP-2)

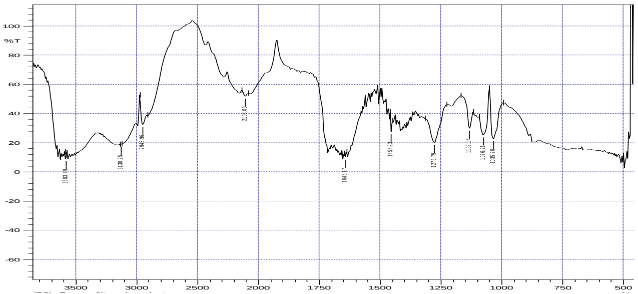


Fig. 2(c). FTIR Spectrum of the BHET crystals(GP-3)

The FTIR spectrum of the glycolysed product is shown in Fig. 2 (a,b,c) It can be seen that GP-1 and GP-2 show absorptions at 3200-3550 cm^{-1} due to the –OH, 2840-3000 cm^{-1} for the C-H stretching, 1720 cm^{-1} for the carbonyl group (C=O), 1100 cm^{-1} for C-O-C and at 675-900 cm^{-1} for the aromatic ring. Both absorption peaks are almost similar except that the peak at 3200-3550 cm-1 for GP-2 is much sharper. GP-3 shows quite a similar trend, however absorptions at 3200-3550 cm-1 is sharper and much closer to 3500 cm^{-1}. The FTIR spectrum can only reveals that the molecular structure of each sample do not defer much from each other. However due to a higher purity of sample achieved by sample GP-3, a much sharper peak is shown from the spectrum.

The BHET structure was confirmed by infrared spectroscopy fig 2(c) and assignment shown in table (5)

Table (5). Band assignment for the infrared spectrum of BHET

No.	Wave number cm^{-1}	Assignment
1	3583.49	O-H stretching of EG end group
2	3130.25	O-H stretch aromatic
3	2948.96	aliphatic C-H stretching
4	1645.17	C=O stretch carbonyl
5	1454.23	$C-H_2$ deformation
6	1276.79	C=O-O stretching in ester
7	1132.14,1076.21,1035.70	bands in this region are indicative of aromatic substitution pattern and indicate 1,3-substitution

5. CONCLUSION

The chemical degradation of PET is not easy to approach without considering the physical properties and mechanical history of the PET waste, such as the compact nature attained during processing. This may hinder or even prevent the chemical reagents from diffusing into the polymer matrix.The glycolysis of PET fibres was carried out under moderate temperature using organic solvent and catalyst. Higher amount of EG was necessary to provide higher degree of depolymerisation. Study of influence of the glycolysis amount of EG, melting point, hydroxyl and acid values showed that conversion rate increases significantly with these factors. The main products of depolymerisation of PET fibres by glycolysis, at the best conditions, were monomer BHET with the maximium yield of about 88% Solubility of lower oligomers changed with temperature and this has been used to purify the monomer (BHET) from EG and dimer. The remained EG can be recovered and reused. The ratio of cold-water soluble crystallizable fraction of pure BHET and hot water soluble fraction of dimer and higher oligomers was dependent mainly on PET/EG ratio. The amount of higher oligomers was significant at lower ratio of PET/EG .Glycolyzed PET oligoesters can be reacted directly as a polyol component with diisocyanate compounds to build up a urethane group [13].

6. RECOMMENDATION

Further investigations should be carried, especially on the re-polymerization and the effect of time and catalyst on glycolysis yield. It is therefore recommended to conduct more research on its commercial availability and technical issues bearing in mind that the technology of using recycled PET for bottle making is in need for more development and validation .

REFRENCES

[1] Achillias, D.S., Karayannidis, G.P. (2002): “The Chemical Recycling of PET in the Framework of Sustainable Development”, Proceedings of the International Conference on: Protection and Restoration of the Environment, Skiathos, Greece, Vol.6, pp. 925-936.

[2] Achillias, D.S., Karayannidis, G.P. (2004): “The Chemical Recycling of PET in the Framework of Sustainable Development”, Focus on Water, Air and Soil Pollution, Netherlands,Vol. 4, pp. 385-396.

[3] Chiu, S.J. and Cheng, W.H. (2000): Journal of Analytical and Applied Pyrolysis, Vol. 56(2),pp. 131-143.

[4] [19] Takeshi, S., Idzumi, O., Tsutomu, S., Katsuto, O., Satoshi, Y. and Yoshihiro, T. (2000):Polym. J., Vol.32 (2), pp.178-181.

[5] Karayannidis, G.P., Achilias, D.S., Sideridou, I.D. and Bikiaris, D.N. (2005): Eur. Polym.J., Vol. 41(2), pp.201-210.

[6] Vaidya, U.R. and Nadkarni, V.M. (1988): J. Appl. Polym. Sci., Vol.35, pp.775.

[7] Vaidya, U.R. and Nadkarni, V.M. (1989): J. Appl. Polym. Sci., Vol.38, pp1179.

[8] Nikles, D.E. and Farahat, M.S.(2005):, J. Macromol. Mater. Eng., Vol.290, pp.13-30.

[9] Atta, A.M., Elnagdy S.I., Abdel-Raouf, M.E., Elsaeed, S.M., Abdel-Azim, A. A. (2005): J.Polym. Res. Vol.12, pp.373.

[10] Rebeiz, K.S., Fowler, D.W. and Paul, D.R. (1992): J. Appl. Polym. Sci., Vol. 44, pp.1649.

[11] Rebeiz, K.S. (1995): J. Cem. Concr. Compos., Vol.17, pp.119.

[12] Mousa Ghaemy, Farzad Behzadi(2002): Iranian Polymer Journal/,Volume 1I ,pp. 77-83.

[13] Ikladious, N. E. Recycling of Poly(ethylene Terephthalate): Identification of Glycolysis Products Journal of Elastomers and Plastics 32 (2) 2000: pp.140 – 151.