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Nano ZnO Catalyst for Chemical Recycling of Polyethylene terephthalate (PET)

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Abstract— This paper is focused firstly on production of monomers bis (2-hydroxyethyl) terephthalate (BHET) and oligomers by using Nano zinc oxide with different particle size (55&94) nm with different weight ratio (0.05, 0.15 and 0.5) by using chemical recycling glass condenser at 190˚C. The second purpose is to study the effect of catalyst ratio, time of reaction and yield of products of the product. Elemental analysis for Carbon –Hydrogen and Nitrogen (CHN), differential scanning calorimetry (DSC), infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) have been investigated. Results indicated the catalytic activity was found to correlate with surface area; however, Nano ZnO (55) nm has shown an exceptional activity, still it is higher than Nano ZnO (94) nm in order to reduce the reaction time until 60 minutes instead of 7 hours without catalyst. The analysis of the thermograms has indicated the presence of various kinds of monomer, dimer and oligomers that are formed during the recycling; this is particularly evident due to new peaks indicating the formation of BHET monomer and oligomer of lower molecular masses.

Keywords: *Polyethylene Terephthalate (PET); Bis(2-hydroxyethyl) terephthalate; Waste bottle plastic ,Depolymerization; Glycolysis; Nano catalyst.*

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1. Introduction

Polyethylene terephthalate (PET) is a kind of semi-crystalline, thermoplastic polyester with high strength and transparency properties. Because of these properties, PET is produced in considerable amount and is used in textile industry, high strength fibers and soft drink bottles [1]. Poly (ethylene terphthalate) or PET is defined as a polyester resin which happens between terephthalic acid and ethylene glycol or dimethyl terephtalate and ethylene glycol [2]. Furthermore, It forms around (18%) of all polymers which are produced worldwide and over (60%) of its production can be used for synthetic fibers and bottles, which form approximately (30%) of global PET demand [3]. It is generally used for various applications such as bottles, moldings, fibers and sheets due to its excellent tensile and impact strength, clarity, chemical resistance, thermal stability and process ability. It is agreed up on the fact that PET, which differs from natural polymers, is considered a non-degradable polymer in the natural environment, and leads to environmental pollution when it is discarded after use. In depolymerization of PET by glycolysis, the PET chains react with ethylene glycol (EG) to produce a monomer or dimer, BHET. The overall reaction scheme of glycol with an ester bond in the PET chain is shown in Figure 1 [4].

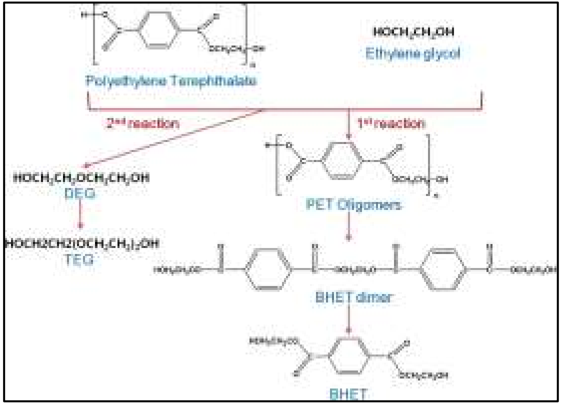

Figure 1: Scheme reaction de-polymerization of PET

In literature survey as Sojobi et al. explained the recycling of plastic bottle wastes of polyethylene terephthalate (PET) in bitumen, concrete (BC), which is used in flexible pavement construction. The mix design consists of (60/70) penetration-grade bitumen concrete, and the result showed void in mineral aggregate, and air void, and an increase in Marshall Stability [5].

Muhammad et al. [6] they study the effect of different parameters, such as catalyst type, temperature, EG/PET molar ratio, reaction time, and catalyst/PET weight ratio, on a monomer yield were studied. The results shown that the catalyst that yielded the highest amount of BHET (92.2 mol%) under significant reaction conditions (260 °C & 5.0 atm) was zinc manganite tetragonal spinel ($ZnMn_2O_4$), which has octahedral Mn^{+3} ion and tetrahedral Zn^{+2} ion organization with the spinel crystal structure [6].

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2. Materials and Methods

I. Chemical materials

Waste PET bottles were cleaned, dried and cut into square chips to particle size of 3 mm × 3mm. All of the chemicals used were of high purity degree and were used without purification. Ethylene glycol (EG) supplied by (AAG, Espana) which was used as a solvent for glycolysis. Nano zinc oxide (94nm) with total projected area (62) mm^2 supplied by (Parchem, USA) and nano zinc oxide (55nm) with total projected area (13.3) mm^2supplied by (SkySpring Nanomaterials, USA) which was used as a catalysis.

II. Experimental methods

PET (100 gm) and Ethylene Glycol (EG) (116 ml) were mixed in three neck round-bottom flask (4:1, EG: PET, molar ratio) without catalyst in 190 ° C for 7 hours until the mixture becomes in the resin state, heat treatment included totally condensation (reflux) in Batch process with (no material losing), by using glass condenser water cooling, then separation of unreacted ethylene glycol solution from the previous mixture. After reaction, the reactor was cooled to room temperature [9].

For purification product from EG, about 200 ml distilled water was added to the product mixture with heating and mixing by magnetic stirrer hot plate, which would dissolve the remaining EG. The product was cooled to room temperature and the mixture was filtered. White crystalline flakes of BHET monomers were formed in the filtrate, then separated and dried in an oven at 60 ◦C.

In the second step, used nano ZnO(94nm) as catalyst in different ratio (0.05,0.15 & 0.5) gm and used nano ZnO (55nm) as catalyst in different ratio (0.05, 0.15 & 0.5) gm. Close system of chemical recycle for (PET) and complete flow diagram have been shown in figures (2), and Figure (3) shows the product after chemical degradation of PET. In this study, the catalytic activity of catalysts on glycolysis of PET was measured by testing the conversion of PET (%) and the selectivity of BHET (%), which were calculated in Eqs. (1).

$$\text{Yield of BHET (\%)} = \frac{\text{(Weight of BHET)} \times 100\%}{\text{(Initial weight of PET)}} \quad (1)$$

[10]

Figure 2: Batch process of chemical recycling

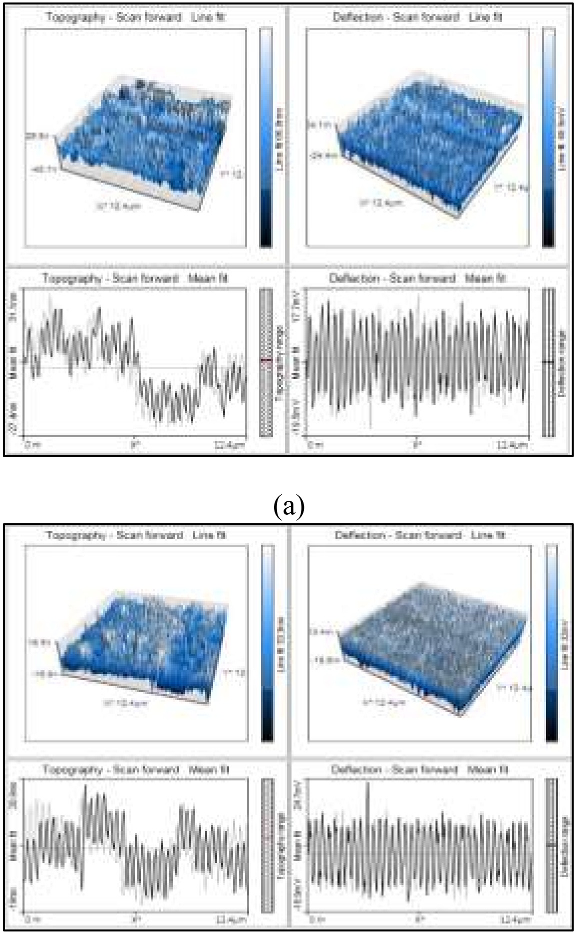
Figure 3: A- product of depolymerization before filtration, B- after purification

III. Characterization

PET for water waste bottle and solid fraction of degraded PET by glycolysis (monomer BHET, diamer DBHET and oligomers) was characterized by some instruments such as: Melting points were recorded using Stuart Digital melting points- SMP 20 (UK). Particle size distribution was carried out by Atomic Force Microscopy (AFM) in Baghdad University Laboratories by using PHYWE (GmbH und Co. KG). Spectra data were obtained by FTIR Model: WQF-520A (china) in the wave number range of 4000-400 cm-1 which included in KBr discs. The elemental analyses of the carbon, hydrogen and nitrogen contents were determined using a Euro EA CHN 3000 (Italy). DSC was performed on a Linseis DSC instrument (sample size about 10 mg) under a nitrogen stream with a standard heating/cooling rate of 10°C min–1 in the temperature range of 0–600°C. The melting (Tm) and crystallization temperature (Tc) of the BHET monomer and obtained PET were determined as the onset temperatures.

3. Results and Discussion

The particle size distribution of catalysts was carried out by Atomic Force Microscopy (AFM), the result of particle size distribution of particle ZnO is shown in Figure 3A, where the average value of diameter was (94 nm). While the result of particle size distribution of nano ZnO is shown in Figure 3B, and



(a)

(b)

Figure 3: AFM Test of (a) nano ZnO (94) (b) nano ZnO (55)

The EG attacks ester group of PET and degrades the polymer into a monomer, dimer and oligomer from BHET. The catalysts Nano (94) ZnO and (nano ZnO) were used in the glycolysis of PET to test their catalytic activity time reaction, yield percentage; color and melting point of these products are presented in Table 1.

To verify the chemical structure of the reaction product, the products BHET was analysis of elemental (CHN) for the products when used particle ZnO and nano ZnO as catalyst in

the average value diameter was (55 nm).

depolymerization PET. Table 2 show results obtained, when comparing the ratio of carbon and hydrogen for products, it was noted that it's almost similar to the theoretical ratio for carbon and hydrogen at monomer, dimer and trimer for BHET.

Figure 4 shows the time reduction through using Nano ZnO & particle ZnO, Nano ZnO as catalyst provided better conversion of PET to monomer and dimer BHET compared with particles ZnO catalysts .Where the use of few amounts of 0.05 gm from nano ZnO to get a good yield in the perfect time. The BHET yield increased dramatically in the presence of a catalyst and decreased reaction time. The BHET yield decreased with decreasing catalyst ratio. For nano ZnO with a small diameter 55 nm led to the better distribution due to their high specific surface areas and specific pore volumes and highest catalytic activity, this resulted in the highest monomer yield [10].

Table 3 shows the Infrared spectroscopic band (cm^{-1}) data of waste PET bottles & Product after recycle. Figure 5 showed the FTIR spectra of PET for waste PET bottles and the peaks, which has been obtained for PET, is nearly in agreement with that reported previously in the literatures [9]. FTIR for waste PET bottles has been presence of a carbonyl group (C=O) in conjugation with aromatic ring appear at 1714 $cm^{-1}$and second strongest peak at 1241 $cm^{-1}$is due to the asymmetric (C-C-O) stretching involving the carbon in aromatic ring. The aromatic (-C-H) wagging appears at 722cm^{-1}. The peak at 872 cm^{-1}corresponds to aromatic (-C-H) out of plane bending. The (-O-C-C) asymmetric stretching is split at 1094 cm^{-1}. There are also peak at 2961 and 2854 cm^{-1}(-C-H asymmetric stretching) 1504 cm^{-1}(aromatic C-C stretching), 1454 cm^{-1}(C-H bending). Peak at 1408cm-1 and 1371 cm^{-1} is due to deformation (-C-H alkane).

Table 1: Yield percentage, reaction time, color and melting point of products

Catalyst	The ratio used gm	Time of reaction (min)	Physical state and (Color)	Yield %	Melting point
Nano ZnO	0.05	80	Crystals white	90	179
Nano ZnO	0.15	60		89.4	178
Nano ZnO	0.5	60		89	178
Micro ZnO	0.05	90		92.2	177
Micro ZnO	0. 15	60		89.7	176
Micro	0.5	60		87.34	176

ZnO

Table 2: Elemental analysis CHN for products depolymerization PET

Sample	**C%**	**H%**	**O%**	**N%**	**S%**	Molar mass g•mol−1
Nano ZnO	63.089	4.899	-	-	-	
Particle ZnO	62.76	4.866	-	-	-	-
BHET monomer	56.69	5.55	37.75	-	-	-
BHET Dimer	58.77	5.3	35.9	-	-	254.24
BHET Dimer	59.5	5.2	35.3	-	-	490.34

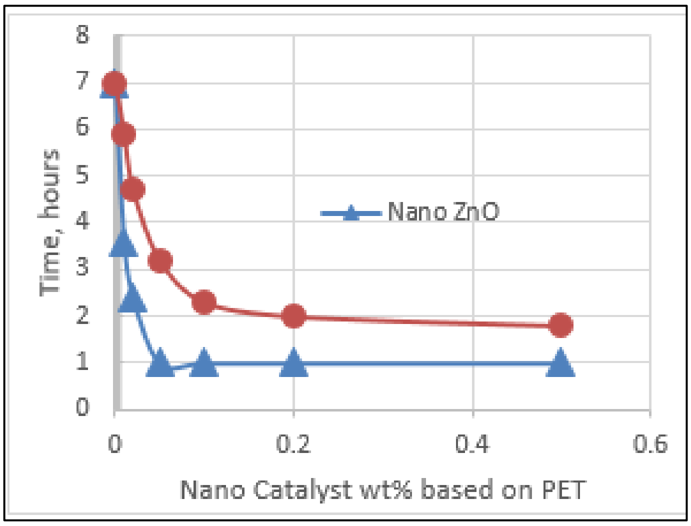


Figure 4: The time reduction through using Nano (55&94) ZnO

Table 3: Infrared spectroscopic band (cm-1) data of waste PET bottles & Product after recycle

Band name in FTIR	**Water Bottle (PET)**	**BHET (by nano ZnO)**	**BHET (by particle ZnO)**
O-H band	-	3514	3510
C-H Asymm.	2961 & 2854	2962 & 2890	2958 & 2875
C=O Ester	1714	1724	1720
Ar C-C bond	1504	1508	1504
C-H bending	1454	1456	1462
C-H def. in alkane	1408	1410	1406
C-H def. in alkane	1371	1383	1384
C-C-O Asymm.	1241	1267	1265
O-C-C Asymm.	1094	1070	1074
C-H Bend. *Inplane*	1016	1018	1018
Ar C-H *out of plane*	872	874	862
Ar C-H Wagg.	722	727	725

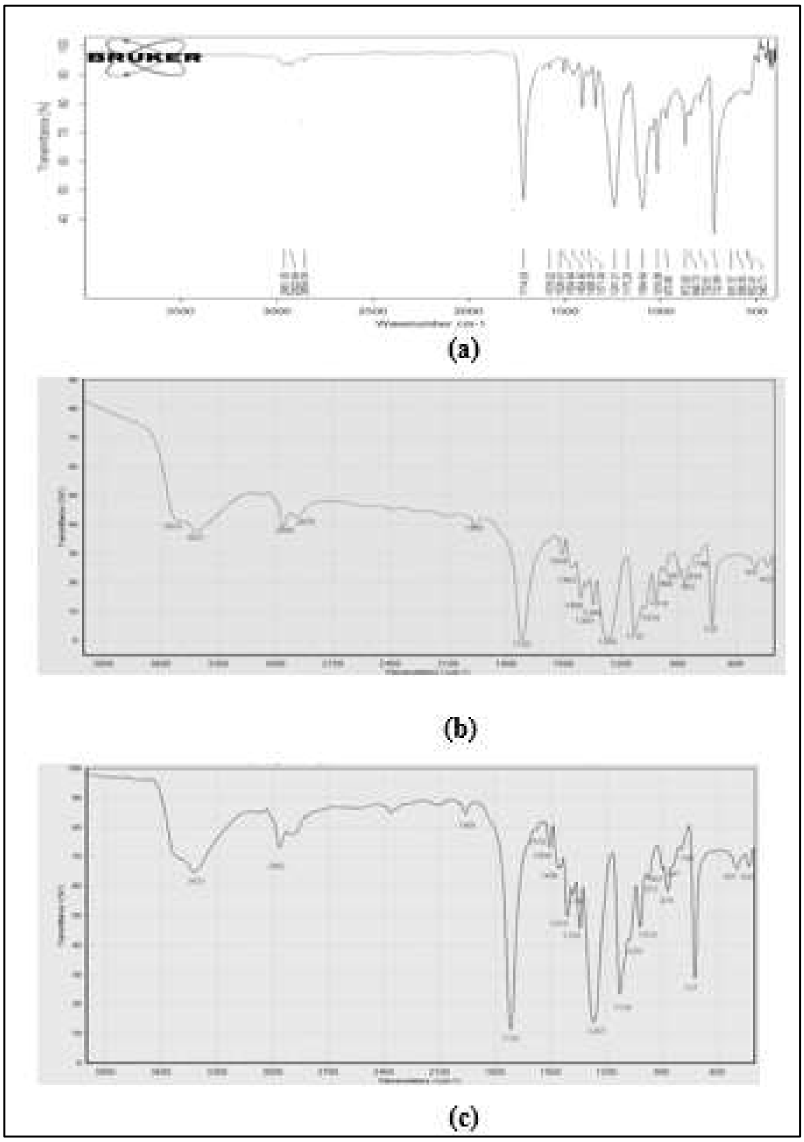


Figure 5: (a) FTIR spectra for waste PET (b) FTIR for product (BHET) by using particle ZnO & (C) FTIR for product (BHET) by using nano ZnO

After the de-polymerization of PET, the chain lengths of PET are degradation and configuration to monomer or dimer BHET this lead to different modification of the number of (–CH) groups leading to quite significant intensity changes of the bands [11]. Additionally, in the Figure 7, the bands at 3510 $cm^{-1}$and 3421 cm^{-1}indicate the presence of (–OH) groups related to the formation of oligomers or dimer (acid hydroxy and alcohol end groups) and monomer BHET due to breaking of chemical bonds in PET. The Glycolysis of PET with ethylene glycol mainly produces monomer BHET along with other products (dimers and oligomers) [10]. The FTIR in spectra for product (BHET) by using particle ZnO in Figure 7 clearly shows (-OH) band at 3421 cm^{-1}, (alkyl –CH) at 2958 cm^{-1},(C=O) stretching at 1720 cm^{-1} and aryl group at 1504 cm–1, present in monomer BHET and the FTIR spectra for product (BHET) by using nano ZnO in Fig.8clearly shows (-OH) band at 3421 cm^{-1}, (alkyl –CH) at 2962 cm^{-1}, (C=O) stretching at 1724 $cm^{-1}$and aryl group at 1508 cm^{-1}, present in monomer BHET

Figure 9 illustrates the DSC thermograms obtained for the depolymerization of waste bottle PET it can be observed that glass transition temperature (Tg) at (83°C), crystalline temperature at (146 °C) melting temperatures are at (255 °C) of PET. The value of Tg and Tm which has been obtained for PET, is nearly in agreement with that reported previously in the literatures Tg between (67 to 80 °C), Tc (150 °C) and a Tm of (267 °C) [11]. In TGA thermograms for waste water bottle PET the mass-loss were observed beginning of the thermal degradation in 479.40°C and losing 78.7 % of its initial mass.

DSC thermograms of PET glycolysis products (BHET) are presented in Figure 10 by used particle ZnO as catalyst, it can be observed that melting temperatures are (152.5 °C) of PET products obtained after glycolysis and TGA thermograms mass-loss were observed beginning of the thermal degradation in 349.04 °C and losing -13.34 % of its initial mass, and loss -77.26% at 512.99°C in the two stage.

DSC thermograms of PET glycolysis products (BHET) are presented in Figure 11 by used nano ZnO as catalyst it can be observed that melting temperatures are (151.1°C) of PET products obtained after glycolysis. The TGA thermograms mass-loss were observed beginning of the thermal degradation in 354.62°C and losing -10.78 % of its initial mass, and loss -84.47% at 476.363°C in the two stage.

Indicates presence of various types of monomer, dimer and oligomers, that are formed during the recycling, This is particularly evident due to new peaks indicating formation of BHET monomer dimer and oligomer of lower molecular masses.

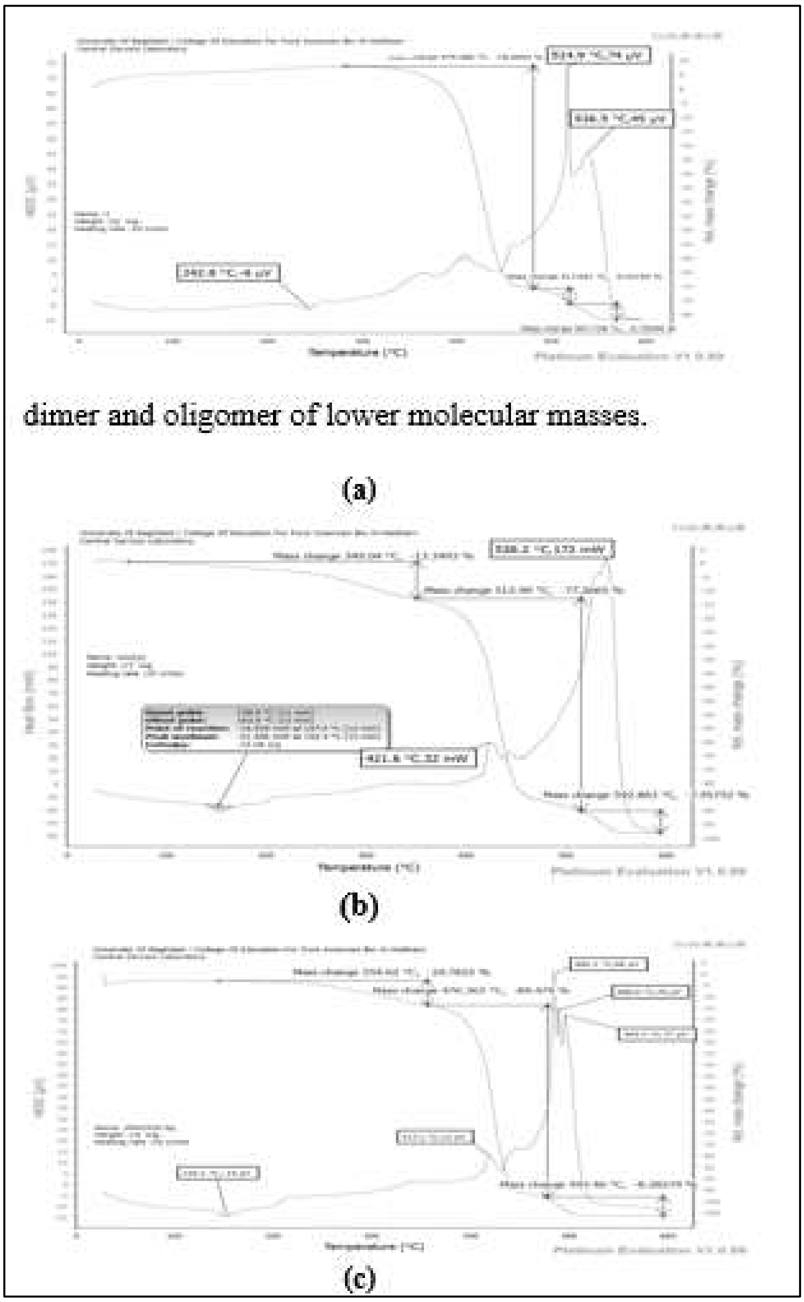


Figure 7: (a) DSC for polyethylene terephthalate (PET) , (b) DSC for BHET with nanoZnO catalyst& (c) BHET with particle ZnO catalyst

4. Conclusion

From the results, investigation could find that there is various quantities of Nano & Micro catalyst used in this work, i.e. the results of yield were convergent. Several metal catalysts quantity was screened for the depolymerization of PET. The catalytic activity was found tocorrelate with surface area; however, Nano ZnO (55) nm has shown an exceptional activity—higher than the stronger of the same catalyst Zno by reducing the reaction time until one hour instead of 7 hours without catalyst. These fundamental investigations of Nano catalysts will be beneficial to the progress of PET waste in chemical recycling. Simple close system has been used in this research; it was considered one of the most suitable methodology and low cost method. Little amount of Nano ZnO not exceed of 0.05% were enough for the depolymerization of PET to monomer and dimer BHET.

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