The conversion of post-consumer polyethylene terephthalate (PET) into a thermosetting polyester resin

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ABSTRACT

This paper covers the research carried out by the authors on the conversion of post-consumer polyethylene terephthalate (PET) into a thermosetting polyester resin. Glycolysis and hydrolysis-glycolysis were chemical recycling techniques used in the depolymerisation of PET wastes to reprocess able monomers and oligomers. The experiment was performed on PET sourced from soft drink bottles. The flakes were glycolysed using Diethylene glycol and Polyethylene terephthalate of various w/w ratios at various temperatures and reaction times, with potassium acetate (1% w/w of the total raw materials) as catalyst. For hydrolysis-glycolysis method, Diethylene glycol/ water/ polyethylene terephthalate w/w ratio at various operating temperatures and residence times were used. The w/w ratios were carefully chosen to know the trend of the yield increment at specific operating conditions. Also, water was used as hydrolysis medium in the case of hydrolysis-glycolysis to avert equipment corrosion and pollution, and is very cheap. The products obtained were purified using methanol and sun dried. From physical and chemical properties analyzed (density, refractive index, viscosity, melting point, freezing point, boiling point, acidity number, hydroxyl number and molecular weight) and a Fourier transform infrared test conducted, it was found that the glycolysed products consisted mainly of the monomers "Bis (hydroxyethylene) terephthalate (BHET)", and oligomers because of the excess Diethylene glycol used that resulted in two hydroxyl end-groups, that is, mixtures of oligoesters diols were formed. It can be used to re-synthesis ethylene terephthalate or co-polymers. Recycling of PET does not only serve as a partial solution to the solid-waste problem, but serve as a source of raw material to some industries and also contribute to the conservation of raw petrochemical products and energy which is of high importance due to high cost of energy in the World of today.

Keywords: Depolymerization, glycolysis, hydrolysis, recycling.

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INTRODUCTION

The problem of waste is now a global one, and it must be addressed in order to solve the world's resource and energy problems. Perhaps the most prevalent manufactured material in society today is plastics, they 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 methods of managing plastics are; land filling, composting, incineration, recycling, and sewage. Recycling is the most economic method of managing petrochemical plastic waste because, in addition to preventing plastic litter, recycling reduces the exploitation of non-renewable petroleum-plastic raw materials, limits the quantity of plastics sent to landfills, provides cheaper route to plastic production and above all, is a revenue earner.

The material under consideration in this work is polyethylene terephthalate (PET). It is semi-crystalline 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 does not create a direct hazard to the environment, but due to its substantial fraction volume in the plastic waste stream and its high resistance to atmospheric and biological agents; it could be considered as a noxious material. PET accounts for 8% by weight and 12 by volume of the World's solid waste [3].

PET recycling represents one of the most successful and widespread examples of polymer recycling. The main driving force responsible for this extremely increase in recycling of post-consumer PET is its widespread use, particularly in the beverage and food industry.

PET bottles are characterized by high strength, low weight and permeability of gasses (mainly CO_2) 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 and pressures, in contrast with other methods such as supercritical methanolysis and thermal degradation [5,6,12,19,23] , while hydrolysis under acidic or basic conditions may cause corrosion and pollution problems [9,11]. Recently, a growing interest has been observed in PET glycolysis for the manufacture of specialized products such as unsaturated polyesters [11,18,20], polyurethanes [13,17,21,22], vinyl esters [7,8,14] , epoxy resins [4], and polymer concretes [15,16].
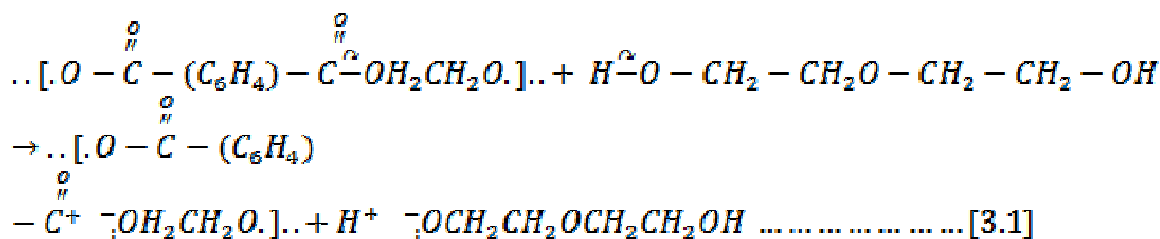
MATERIALS AND METHODS

MATERIALS: - Waste soft drink bottles made from PET plastic were washed, dried and cut into chips of small pieces (average square size of 3mm by 3mm) by a rotary cutter. Di-ethylene glycol (DEG) 98.5% w/w (BDH), Potassium acetate 99% w/w (BDH) used as a catalyst and Distilled water. Others are Toluene 99.9% w/w (BDH), Methanol 99% (BDH) used as separating solvent, Nujol used to standardized FTIR Transmission Spectrum, Acetone, Naphthalene, Sulphuric acid 98% w/w (Vickers) and Sodium hydroxide 96% w/w (Avondale). All other chemicals used were reagent grade.

PET DIGESTION BY GLYCOLYSIS: - 50g of PET plastic bottle chips and Di-ethylene glycol were measured into specific weight ratios of DEG/PET: 10/90; 20/80; 30/70; 40/60; 50/50; 60/40; 70/30; 80/20; and 90/10. 5 g of potassium acetate (1% w/w of total weight of the contents) which was added as trans-esterification catalyst was also measured. Each measured ratios were charged separately into a round bottom flask of 500 ml capacity. The respective round bottom flasks were inserted into Barnstead electro thermal heater. A thermometer was suspended inside the round bottom flask with the aid of a retort stand with clamp. The reaction operating conditions were set at 1bar and at between 180-220°C at controlled heating rate of 1.45^{o}C/min. The residence time were fixed for the different media as, 75; 90; 105; 120; and 135 minutes respectively with the set weight ratios, amidst vigorous agitation. The yields of the glycolysed PET were obtained by decanting the by-products (ethylene glycol and Di-ethylene glycol) from the product mixture and there after subjecting the recovered glycozate to drying using a tray drier operating at 60°C and1 bar.

PARTIAL HYDROLYSIS – GLYCOLYSIS: - The procedure was the same as that of glycolysis, except that potassium acetate was not use. Instead, water was used for the hydrolysis.
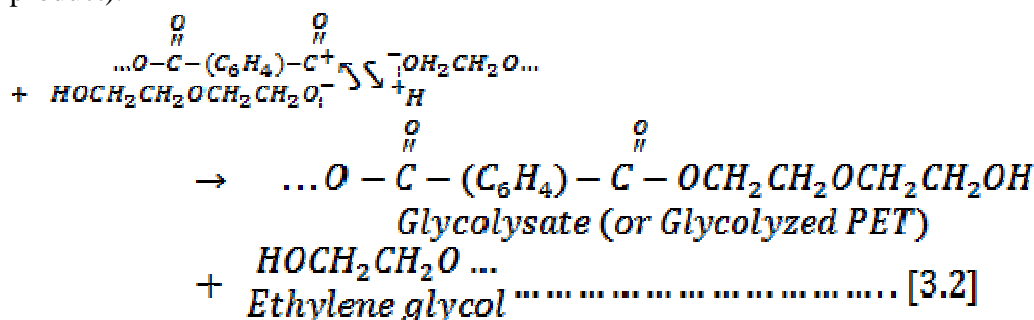
MECHANISM OF PET DIGESTION: - The mechanism of reaction is by chain scission and nucleophilic substitution.

(**A**)   **Chain Scission: -** The polyethylene terephthalate possesses polar covalent bonds in its ester linkage $O\!-\!C\!=\!O$ which is solvated by the added di-ethylene glycol. At the temperature between 180-220°C, the C-O bond in the ester linkage of the PET activates and dissociates to form ion pairs (or dipoles of carbocations and ethoxide anions as shown in equation (3.1). Similarly, the Hydroxyl linkage in di-ethylene glycol also activates and dissociates, forming a proton and di-ethoxide anion, ion pair.

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$$..[.O - \overset{\overset{O}{\|}}{C} - (C_6H_4) - \overset{\overset{O}{\|}}{C} \overset{\frown}{-} OH_2CH_2O.]..+ H\overset{\frown}{-}O - CH_2 - CH_2O - CH_2 - CH_2 - OH$$

$$\rightarrow ..[.O - \overset{\overset{O}{\|}}{C} - (C_6H_4)$$

$$- \overset{\overset{O}{\|}}{C}{}^+ \ \bar{;}OH_2CH_2O.]..+ H^+ \ \bar{;}OCH_2CH_2OCH_2CH_2OH \ ....\text{[3.1]}$$
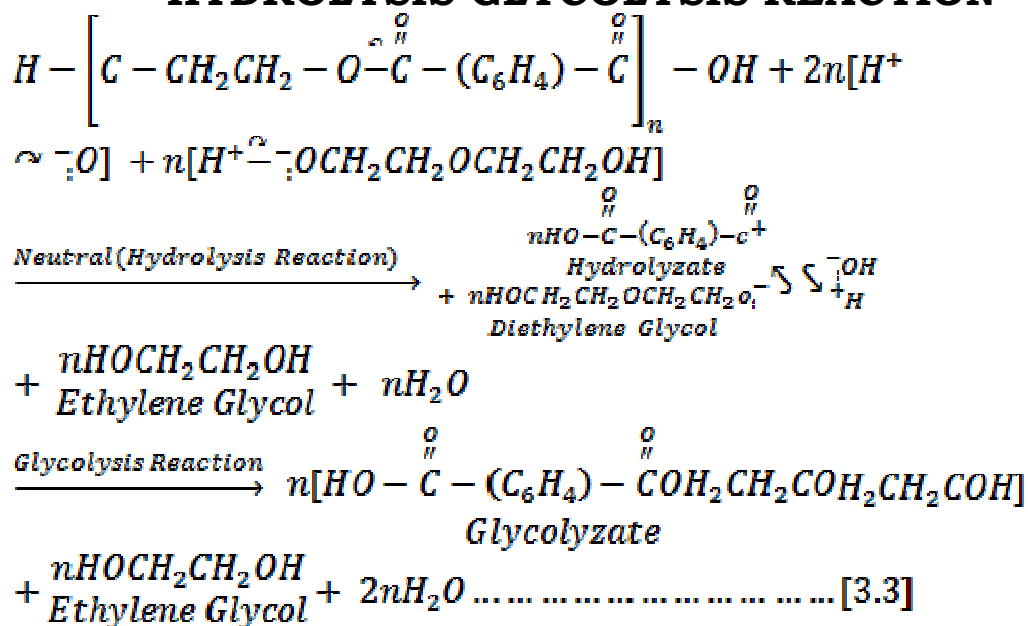
(B)   Nucleophilic Substitution

The nucleophilic end of the activated di-ethylene glycol, attacks the positive end of the activated polyethylene terephthalate carbocation to from glycozate or glycolyzed PET and ethylene glycol (by product).

$$+ \ HOCH_2CH_2OCH_2CH_2O\bar{;} \quad \overset{...O - \overset{\overset{O}{\|}}{C} - (C_6H_4) - C^+}{\underset{\overset{+}{H}}{\nearrow\swarrow}} \ \bar{;}OH_2CH_2O...$$

$$\rightarrow \quad ...O - \overset{\overset{O}{\|}}{C} - (C_6H_4) - \overset{\overset{O}{\|}}{C} - OCH_2CH_2OCH_2CH_2OH$$
$$\text{Glycolysate (or Glycolyzed PET)}$$

$$+ \ \begin{matrix} HOCH_2CH_2O \ ... \\ \text{Ethylene glycol} \end{matrix} \ ....\ \text{[3.2]}$$

HYDROLYSIS-GLYCOLYSIS REACTION

$$H - \left[C - CH_2CH_2 - O\overset{\frown}{-}\overset{\overset{O}{\|}}{C} - (C_6H_4) - \overset{\overset{O}{\|}}{C} \right]_n - OH + 2n[H^+$$

$$\sim \bar{;}O] + n[H^+\overset{\frown}{-}\bar{;}OCH_2CH_2OCH_2CH_2OH]$$

$$\underrightarrow{Neutral(Hydrolysis\ Reaction)} \quad \begin{matrix} nHO - \overset{\overset{O}{\|}}{C} - (C_6H_4) - c^+ \\ Hydrolyzate \\ + \ nHOCH_2CH_2OCH_2CH_2O\bar{;} \\ Diethylene\ Glycol \end{matrix} \overset{\bar{;}OH}{\underset{\overset{+}{H}}{\nearrow\swarrow}}$$

$$+ \begin{matrix} nHOCH_2CH_2OH \\ Ethylene\ Glycol \end{matrix} + \ nH_2O$$

$$\underrightarrow{Glycolysis\ Reaction} \quad n[HO - \overset{\overset{O}{\|}}{C} - (C_6H_4) - \overset{\overset{O}{\|}}{C}OH_2CH_2COH_2CH_2COH]$$
$$Glycolyzate$$

$$+ \begin{matrix} nHOCH_2CH_2OH \\ Ethylene\ Glycol \end{matrix} + \ 2nH_2O ....\ \text{[3.3]}$$

METHOD OF SAMPLE ANALYSIS: - Some parameters were measured and work done to analyzed the samples. Refractive index was measured using Abbe refractometer (Barcelona). Determination of molecular weight by freezing point depression using Rast method was done. This is known as the cryoscopy method, and may be expressed mathematically as a formula for the calculation of molecular weight by this method.

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$$Mn = \frac{K \times 1000 \times m}{M \times \Delta T} \quad \ldots\ldots.4$$

Where, Mn = Number average molecular weight (g/mole); K= Molecular depression constant; m = Mass of the sample (g); ΔT = Freezing point depression (^{o}C); M = Mass of pure solvent (g). Specific gravity of the sample was determined using standard gravity bottle method and calculated using the relationship:

$$S.G. = \frac{(W_2 - W_1)}{(W_3 - W_1)} \quad \ldots\ldots\ldots.5$$

Where, W_1 = Mass of empty bottle; W_2 = Mass of bottle filled with sample; W_3 = Mass of bottle filled with water. Density was determined using the specific gravity gotten above. It was determined from the relationship:

$$Density\ of\ the\ material(\rho_m) = S.G.\ X\ Density\ of\ water\ (\rho_w), \quad \rho_w = 1000\ g/cm^3. \quad \ldots.6$$

Melting and boiling points were gotten with the aid of one-end sealed capillary tube coupled with the METTLER FP 62 (a programmable heating instrument). A rotational viscometer manufactured by J.P. Selecta's Technical Services, Barcelona was used in measuring the viscosities of the samples. A Microprocessor – based Bench PH/mV/^{o}C meters manufactured by HANNA Instruments was used to measure the PH of the samples. Temperature was taken into consideration in order for the meter to measure the PH accurately, because the PH is affected by temperature. Determination of acid value of the glycolyzate by ASTM NO.141 method 5071 (Gardner and Sward, 1972) was done. The acid value of the sample was calculated as shown:

$$Acid\ value = \frac{A \times B \times Mw}{M} \quad \ldots\ldots.7$$

Where, A = cm^3 of alkali solution (KOH); B = mg of KOH per cm^3 of solution; Mw = molecular weight of the alkaline (KOH); M = mass of the sample. The hydroxyl number of digested polyethylene terephthalate is estimated from the following equation:

$$Hydroxyl\ number = \frac{(B - A)N \times 56.1}{g - sample} \quad \ldots\ldots\ldots.8$$

Where, A = titre value, cm^3, Hydroxyl number = mg $_{KOH}$/g; B = titre value of blank, cm^3 N = normality of KOH, molarities. FTIR spectrophotometer was implored for proper bonds identification. A Fourier transform infrared spectrophotometer (FTIR) was used to identify the chemical bonds in the digested polyethylene terephthalate obtained from the glycolysis and the partial hydrolysis – glycolysis reactions. The chemical bonds in the sample were identified at the peaks of the displayed infrared spectra for a specific transmittance and wave number. This was achieved by stretch and bend vibrations, while a standard spectra library table was used to identify the actual bonds present on the basis of specific range of wave numbers and transmittance.

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RESULTS AND DISCUSSION

Table 1:- Yields of Pet Glycolysis at 180°C - 220°C and 1 Bar

Deg/Pet (W/W) Ratio	RUN 1		RUN 2		RUN 3	
	Mean Residence Time (Min.)	Yield (%)	Mean Residence Time (Min.)	Yield (%)	Mean Residence Time (Min.)	Yield (%)
10/90	180	90.0	195	92.0	210	93.9
20/80	165	88.4	180	90.3	195	92.2
30/70	150	88.0	165	89.9	180	91.8
40/60	135	80.4	150	82.1	165	83.9
50/50	120	75.8	135	77.4	150	79.1
60/40	105	72.0	120	73.6	135	75.1
70/30	90	12.6	105	12.9	120	13.1
80/20	75	7.0	90	7.2	105	7.3
90/10	60	4.6	75	4.7	90	4.8

Table 2:- Yields of pet glycolysis at 180°C - 220°C and 1 bar

Deg/Pet (W/W) Ratio	RUN 1		RUN 2	
	Mean Residence Time (Min.)	Yield (%)	Mean Residence Time (Min.)	Yield (%)
10/90	225	95.9	240	97.9
20/80	210	94.2	225	96.1
30/70	195	93.7	210	95.7
40/60	180	85.6	195	87.4
50/50	165	80.7	180	82.4
60/40	150	76.7	165	78.3
70/30	135	13.4	150	13.7
80/20	120	7.5	135	7.7
90/10	105	4.9	120	5.0

Table 3:-Partial Hydrolysis -Glycolysis at Deg/H_2O/Pet(w/w) ratio of 20/40/40 at 1 bar

RUN	Operating Temperature (°C)	Mean Residence Time (Min.)	Yield (%)	Heating Rate (°C/Min.)
	90	60	45.4	1.50
	90	90	46.4	1.00
RUN 1	90	120	47.3	0.75
	90	150	48.4	0.60
	90	180	49.3	0.50
	120	60	65.7	2.00
	120	90	67.1	1.33
RUN 2	120	120	68.6	1.00
	120	150	70.0	0.80
	120	180	71.4	0.67
	150	60	70.9	2.50
	150	90	72.4	1.67
RUN 3	150	120	74.0	1.25
	150	150	75.5	1.00
	150	180	77.1	0.83

	180	60	80.8	3.00
	180	90	82.6	2.00
RUN 4	180	120	84.3	1.50
	180	150	86.1	1.20
	180	180	87.8	1.00
	210	60	85.8	3.50
	210	90	87.7	2.33
RUN 5	210	120	89.5	1.75
	210	150	91.4	1.40
	210	180	93.3	1.17

Table 4:- Glycolysis at 180°C - 220°C and 1 Bar

Deg/Pet (W/W) Ratio	10/90	20/80	30/70	40/60	50/50	60/40	70/30	80/20	90/10
Mean Residence Time(Min.)	210	195	180	165	150	135	120	105	90
Mean Yield (%)	93.94	92.24	91.82	83.88	79.08	75.14	13.14	7.34	4.80
Density(g/cm³)	11.5	10.8	8.4	8.3	8.2	8.1	8.0	7.4	6.9
Refractive Index	1.6161	1.6115	1.5569	1.5336	1.5250	1.5044	1.4838	1.4530	1.4231
pH	4.56	4.63	4.84	4.90	6.28	6.38	6.47	6.50	6.52
Viscosity ,μ, (g/cm.s , at 70^0C X10^{-5})	9.965	9.700	8.400	8.350	8.200	7.865	7.500	7.260	6.880
Melting Point (^{O}C)	65.0	43.0	37.0	36.0	34.0	33.0	32.0	31.5	31.0
Freezing Point (^{O}C)	78.0	74.0	65.0	64.5	63.0	62.0	60.0	59.5	58.0
Boiling Point (^{O}C)	114	82	78	76	72	70	68	66	62
Naphthalene Depressed Freezing Point (^{O}C)	149.7	132.5	128.2	126.5	122.7	117.4	116.1	115.9	115.6
Acidity Number(AN) (mg KOH/g)	243.484	149.600	51.612	50.864	48.994	47.872	47.124	44.880	41.514
Hydroxyl Number (HN) (mg KOH/g)	0.000	94.248	192.236	192.984	194.854	195.976	196.724	198.968	202.334
MN (g/mol)	1344	800	726	701	650	590	577	575	572

Table 5:-Partial Hydrolysis-Glycolysis at Deg/H$_2$O/Pet (W/W) ratio of 20/40/40 at 1 Bar

Deg/Pet (W/W) Ratio	90	120	150	180	210
Mean Residence Time(Min.)	120	120	120	120	120
Mean Yield (%)	47.36	68.56	73.98	84.32	89.54
Density(g/cm³)	0.87	1.16	1.45	1.74	2.03
Refractive Index	7.0	7.4	8.0	8.7	8.9
pH	1.4533	1.5033	1.5184	1.5317	1.5391
Viscosity ,μ, (g/cm.s , at 70^0C X10^{-5})	4.39	4.50	4.64	4.73	4.85
Melting Point (^{O}C)	9.200	8.950	8.650	8.300	8.250
Freezing Point (^{O}C)	50.0	41.0	39.5	38.0	37.0
Boiling Point (^{O}C)	72	68	67	65	63
Naphthalene Depressed Freezing Point (^{O}C)	85	81	79	78	76
Acidity Number(AN) (mg KOH/g)	131.5	130.3	128.4	128.2	126.4
Hydroxyl Number (HN) (mg KOH/g)	142.120	95.370	52.734	51.238	50.116
MN (g/mol)	101.728	148.478	191.114	192.610	193.732
	782	761	730	726	700

These properties when compared with the standard properties of bis (hydroxyethylene) terephthalate as obtained in Aldrich's Chemicals Catalogue, showed close similarities. This was shown on Table .6.

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Table 6:- comparison of properties of glycolsed and hydrolyzed-glycolyzed products with standard properties of bis(hydroxylethylene) terephthalate

S/N	properties	values		
		glycolyzed product	partial hydrolyzed – glycolyzed product	literature bhet
1	Density(g/cm^3)	8.62	8.00	8.20
2	Refractive index	1.5230	1.5092	1.4250
3	Viscosity(at 70°C, g/cms)	8.236x10^{-5}	8.670 x10^{-5}	8.223 x10^{-5}
4	Melting point(^{o}C)	38.1	41.1	37
5	Freezing point(^{o}C)	64.9	67.0	65
6	Boiling point(^{o}C)	76.4	79.8	80
7	Acidity number(mgKOH/g)	80.7	78.3	
8	Hydroxyl number(mg KOH/g)	163.065	165.532	196.2
9	Molecular weight(g/mol)	726.11	739.8	726.0

GRAPHS
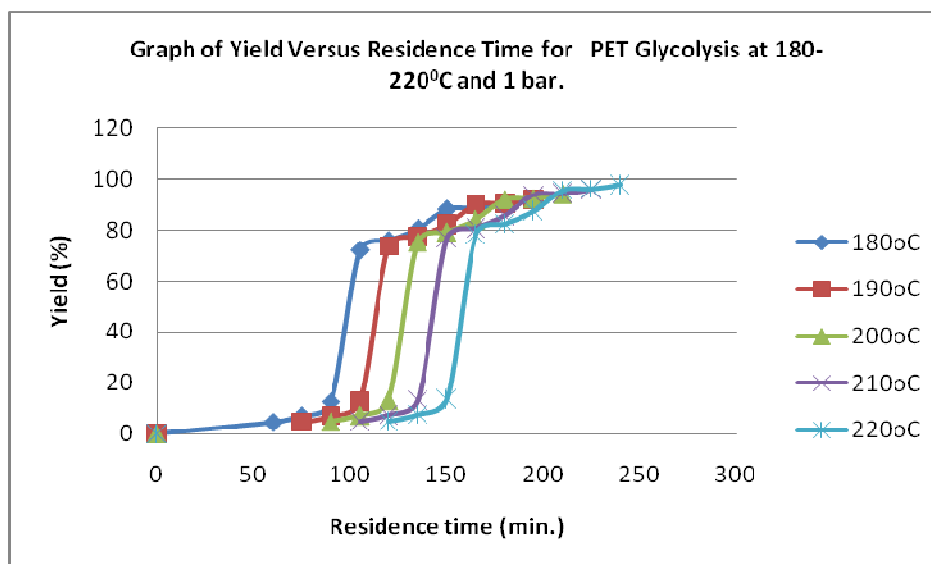
FIGURE 1: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PET GLYCOLYSIS AT 180°C - 220°C AND 1 BAR

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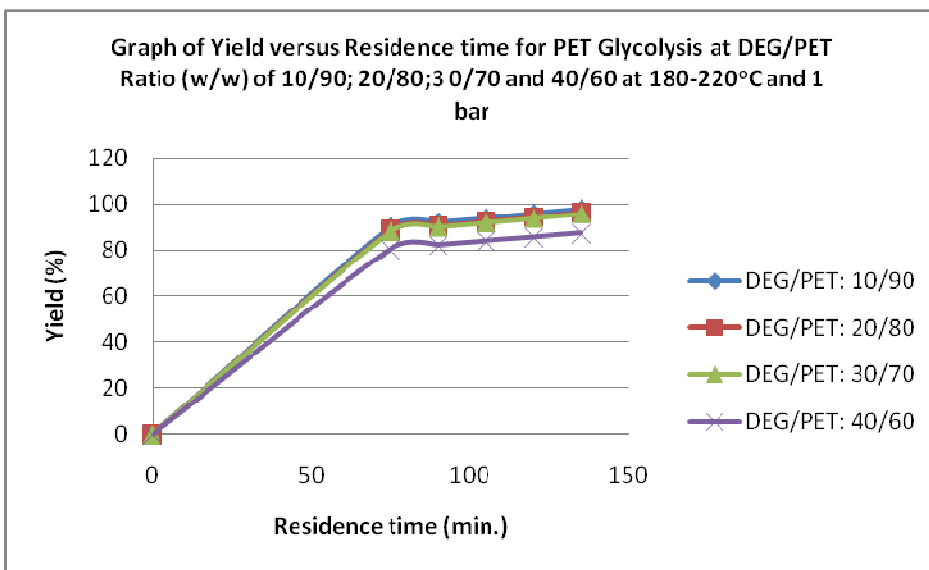
**FIGURE 2: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PET
GLYCOLYSIS AT DEG/PET RATIO (w/w) OF 10/90; 20/80; 30/70; AND 40/60 AT
180ºC - 220ºC AND 1 BAR.**
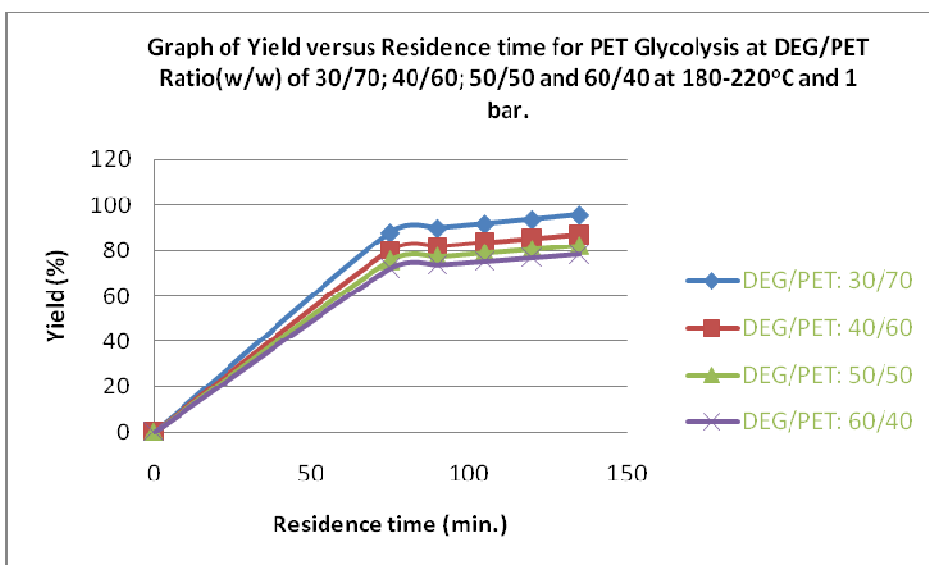
**Figure 3: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PET GLYCOLYSIS AT
DEG/PET RATIO (w/w) OF 30/70; 40/60; 50/50; AND 60/40 AT 180ºC AND 1 BAR.**

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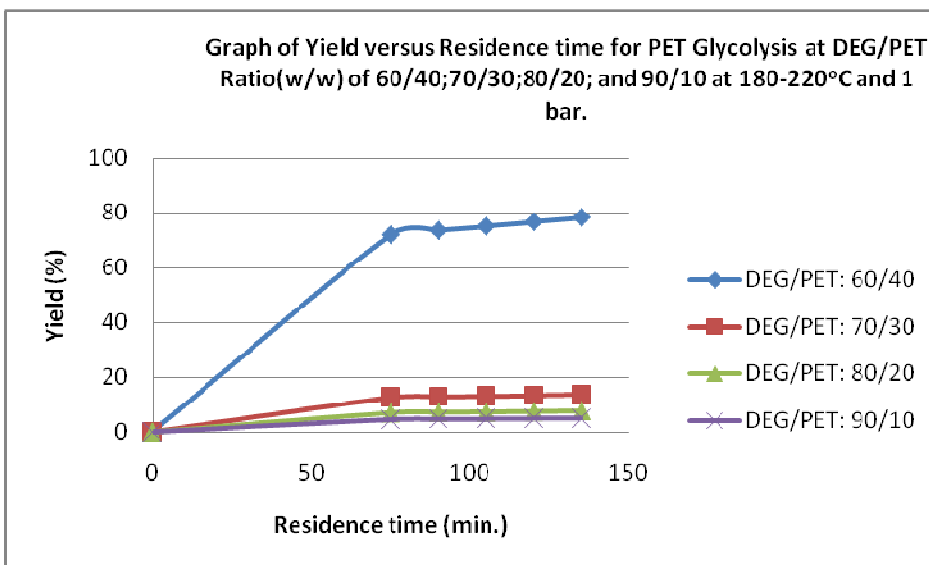
Figure 4: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PET GLYCOLYSIS AT DEG/PET RATIO (w/w) OF 60/40; 70/30; 80/20; AND 90/10 AT 180-220ᵒC AND 1 BAR.
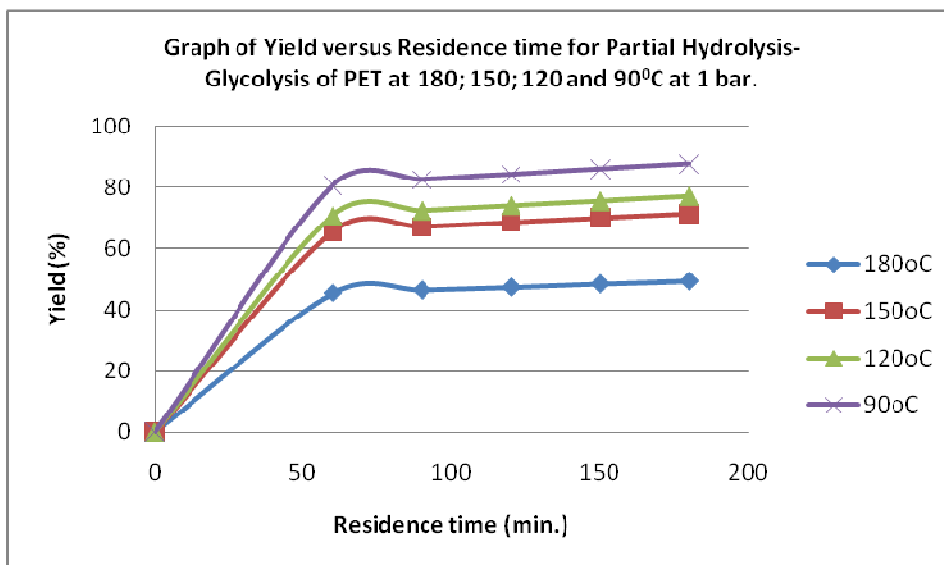
FIGURE 5: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PARTIAL HYDROLYSIS-GLYCOLYSIS OF PET AT 180ᴼC; 150ᴼC; 120ᴼC; AND 90ᴼC AND 1 BAR.
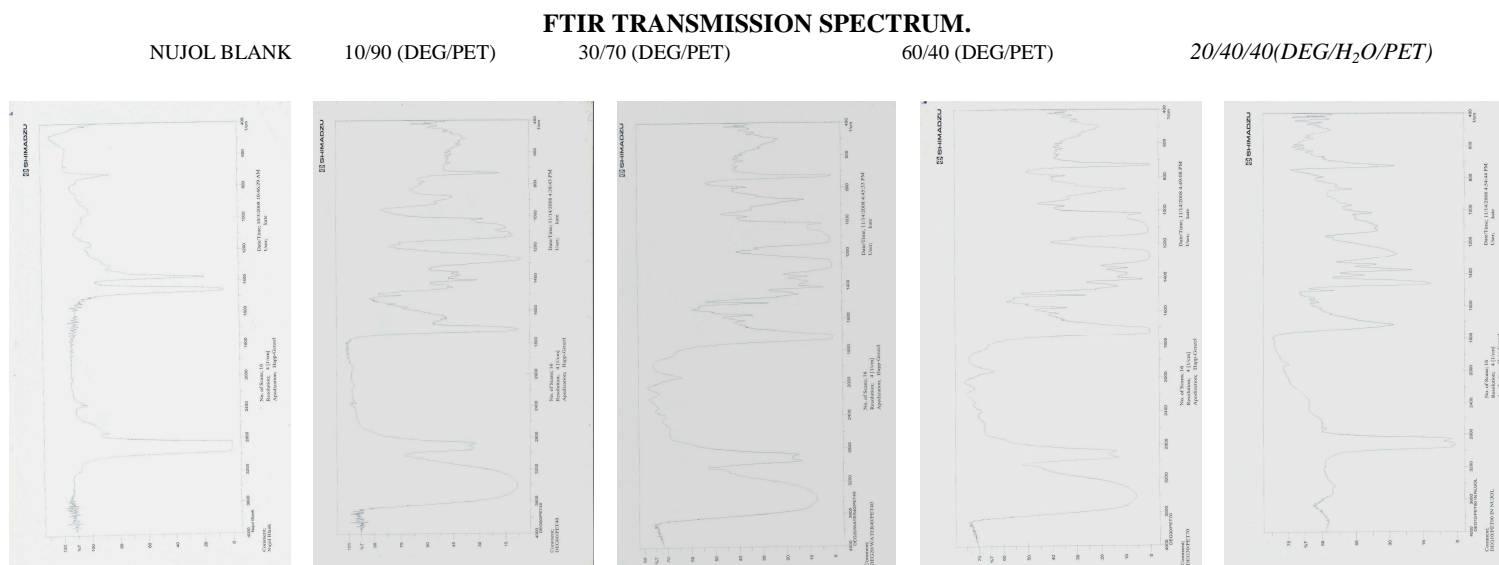
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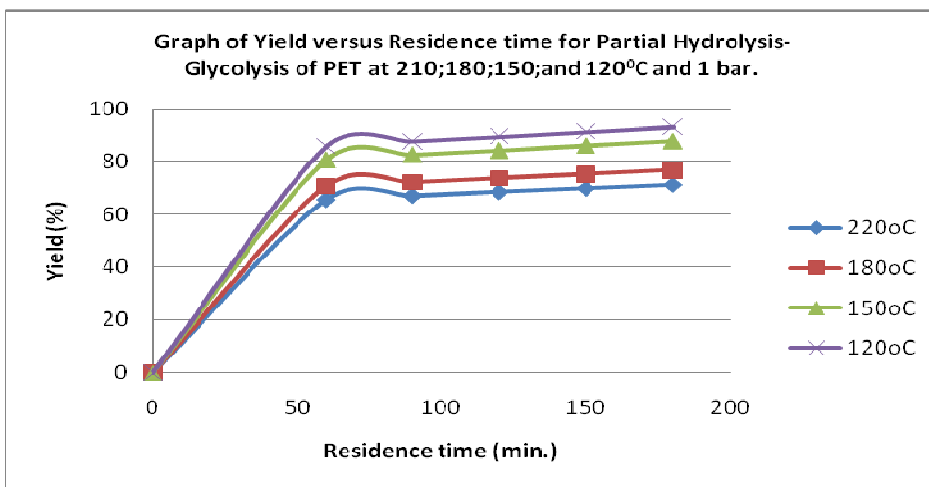
FIGURE 6: A GRAPH OF YIELD VERSUS RESIDENCE TIME FOR PARTIAL HYDROLYSIS-GLYCOLYSIS OF PET AT 210°C; 180°C; 150°C; AND 120°C AND 1 BAR.

UV SPECTROMETER TRANSMISSION SPECTRUM
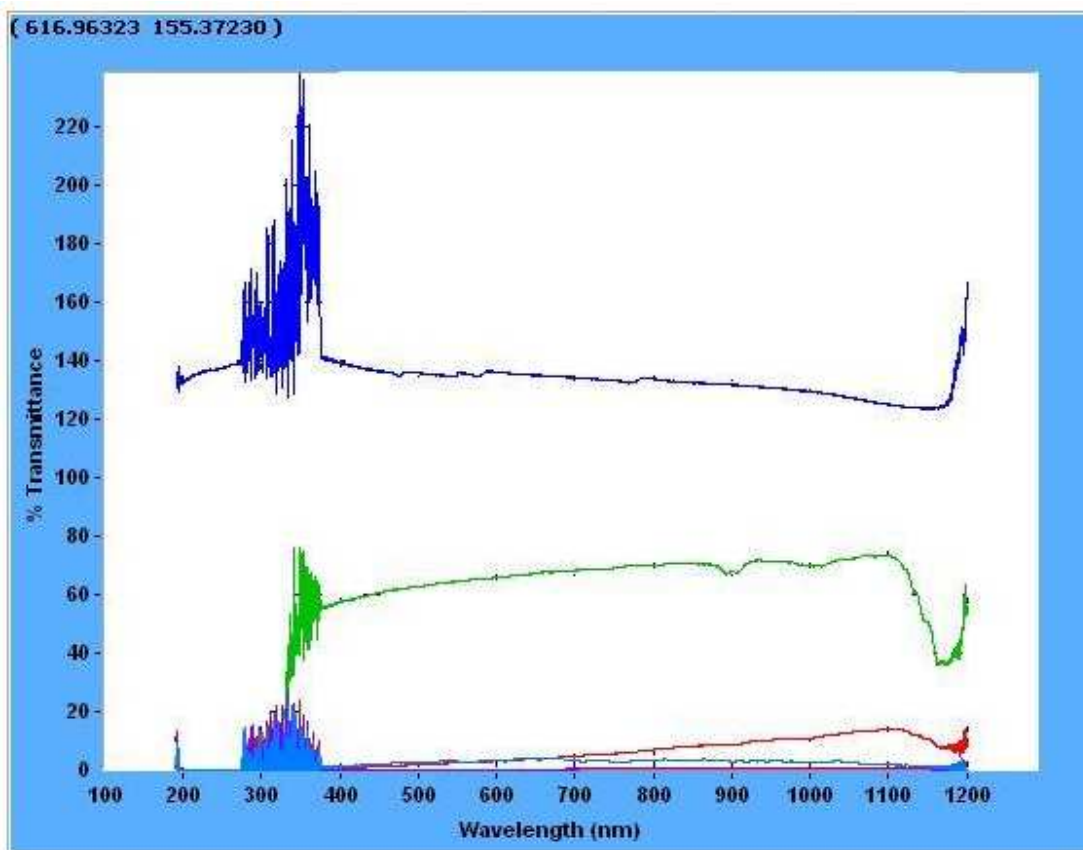
FIGURE 7: UV SPECTROMETER TRANSMISSION SPECTRUM.

FTIR TRANSMISSION SPECTRUM.

NUJOL BLANK   10/90 (DEG/PET)   30/70 (DEG/PET)   60/40 (DEG/PET)   *20/40/40(DEG/H₂O/PET)*

FIGURE 8:- FTIR TRANSMISSION SPECTRUM.

DISCUSSION

The alcoholysis of PET with Diethylene glycol proceeds according to the reactions shown in Equations (1) to (3). The alcoholysis consists of the transesterification of PET and the depolymerization of its polymer chain, resulting in the decrease of its molecular weight. Using a small excess of glycol in the depolymerization of PET, the oligoesters obtained have mainly two hydroxyl end-groups, that is, mixtures of oligoesters diols are formed. The choice of DEG to carryout the glycolysis and partial hydrolysis-glycolysis is usually determined by the necessity of having good flexural properties in the product, since the long chains containing this glycol improve flexibility. In this study, the glycolysis of PET was carried out to obtain small degrees of depolymerizations and, as a consequence, oligomers of relatively high molecular weights. These could partly maintain the primary features of PET and impart improved mechanical properties to the final product, that is, the presence of more terephthalate repeating units between the cross-links can result in the existence of harder domains and better separation between the cross-links in the packed cross–linked structures leading to improved mechanical properties. For all the glycolysis and partial hydrolysis-glycolysis cases, the yield (%) versus reaction time (min.) graphs show that yields increases with increases in residence time, but at about 4hrs, each and all the products have attained their respective ultimate yields. Also, the higher the DEG/PET (w/w) ratio, the lower the yields obtained (Tables 1-6). Density, refractive index, viscosity, melting point, freezing point, boiling point, acidity number and molecular weight decreases down the trend. PH and hydroxyl number increases down the trend. At a specific operating temperature, heating rate decreases with increases in residence time. Figures above show the graphs of yield (%) versus residence time (min.).

For glycolysis: reaction started at about 60 minutes, yield increases drastically at about 100 minutes, at about 150 minutes the increment is gradual but after 240 minutes (4hrs), the increment is infinitesimal. For hydrolysis-glycolysis: reaction starts at about 60 minutes also, but

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increases gradually till about 180 minutes (3hrs), after which the increment is infinitesimal. Thus, it can be deduced that 240 minutes (4hrs) is the utmost reaction time for the glycolysis where as 180 minutes (3hrs) is for hydrolysis-glycolysis of the PET materials.

The Mn, of the obtained glycolysate without excess DEG was calculated by determining the hydroxyl number (HN), which was found to be 134.8644 mg KOH/g of the Sample. Based on this value, the Mn calculated was found to be 393. The obtained glycolysate with excess DEG hydroxyl number was found to be 198.5005 mg KOH/g of the sample and the corresponding Mn was calculated to be 579. The Mn calculated from the freezing point depression (Naphthalene) was 726.11. Also, for hydroxyl-glycolysate method, the hydroxyl number (HN) was found to be 165.532 mg KOH/g of the sample and the corresponding Mn calculated was found to be 483. The lower values of Mn, that is, 393 and 483 confirmed the presence of monomers in glycolysate obtained without excess DEG in glycolysis and hydrolysis-glycolysis products. The Mn calculated from the freezing point depression was 739.8. If it is considered that the oligoesters produced is a dihydroxyl compound, the Mn estimated based on the HN, is very near with that obtained from freezing point depression method. On trying to identify the oligoesters diols produced the structures in Figures 9 to 10 were proposed. According to these structures if one replaces m with 0, 1 and 2, the following molecular weights were obtained: 342, 534 and 726, respectively. By comparing these values with the values obtained by both HN and freezing point methods, it can be concluded that the above structure is confirmed with m = 0,1and 2. The FTIR transmission spectrum figures (Figure 8) confirmed the proposed chemical structure for the glycolyzed PET product. It was observed that the UV Transmission Spectrums peaks could not be read clearly, thus UV Spectrometer cannot handle the work.

The characteristic FTIR transmission spectrum peaks for the PET glycolysate are the following:-
DEG/PET: 10/90 IN NUJOL:-1275(CO), 1350, 1375(CH), 1410(CH), 1460(CH), 1505, 1545, 1585(C=C), 1615, 1650 (C=C), 1730($-COOH$), 1825, 1955, 2120, 2360, 2690, 2750(OH), 2850, 2930, 2950(OH), 3440, 3540, 3590(OH).

DEG/PET: 30/70 IN NUJOL:- 1245-1295(CO), 1340, 1375(CH), 1410(CH), 1455(CH), 1505, 1580(C=C), 1615, 1635, 1645, 1655(C=C), 1700-1730($-COOH$), 1960, 2110, 2260, 2290, 2320, 2390, 2530(OH), 2580 (OH), 2630, 2880, 2950(OH), 3090, 3110(OH), 3420-3430 (OH).

DEG/PET: 60/40 IN NUJOL:- 1275(CO), 1360, 1380, 1410, 1440, 1450(CH), 1505, 1530, 1535, 1555, 1580(C=C), 1620, 1635, 1645, 1655, 1660, 1665, 1670, 1680(C=C), 1720($-COOH$), 1760, 1775, 1790, 1795, 1805, 1810, 1840, 1865, 1885, 1920, 1940, 1955, 2110-2140, 2310, 2350, 2380, 2880, 2950(OH), 3380-3420(OH).

DEG/H_2O/PET: 20/40/40 IN NUJOL:- 1250-1295(CO), 1340, 1375(CH), 1410(CH), 1455, 1470(CH), 1505, 1555, 1575(C=C), 1615, 1635, 1650(C=C), 1710-1730($-COOH$), 1825, 1960, 2120, 2260, 2290, 2350, 2390, 2540(OH), 2580(OH), 2630, 2880, 2950(OH), 3060, 3100, 3400-3430(OH).
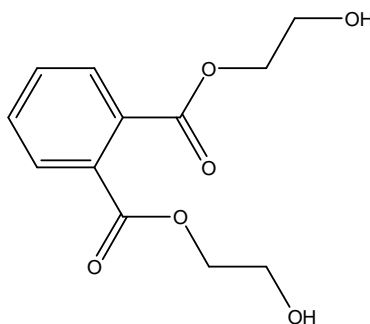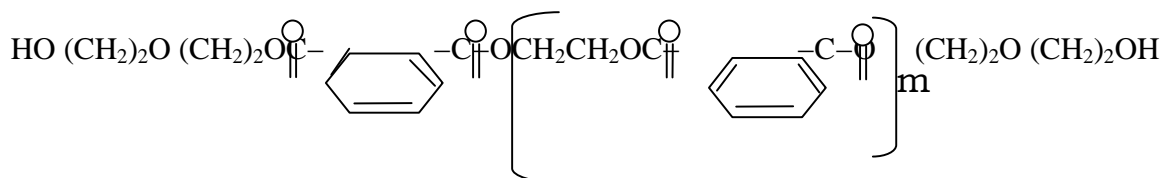
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PROPOSED STRUCTURES

Figure 9:- Bis (Hydroxyethylene) Terephthalate (BHET).

Figure 10:- Proposed structure of the Oligoesters diols resulting from PET glycolysis using DEG. m=1 – 3.

CONCLUSION

In this work, PET glycolysis for the production of the Glycolysate was carried out. By finding the M_n of the PET Glycolysate according to end-group analysis, it is obvious that the glycolysis of post consumed PET using exact or a small excess of DEG to obtain respective monomer or oligomer is attainable. The above glycozate can be easily converted to the respective poly (ethylene terephthalate), which could be applied as a raw material in the textile, video, audio tapes, x-ray films, food packaging and especially of soft-drink bottles industries. In the frame of chemical recycling, a significant amount of post- consumed PET could be used as raw material in a value-added application in the near future, instead of ending up at city landfills. Certainly, the whole attempt requires further investigation in order to let the polymerization of the produced Glycolysate be in commercial quantity.

Recommendation
I recommend that further investigation should be done on the work, most especially on the re-polymerization and blending of the products with various additives to improve its qualities. Also, the technology for use of recycled PET for bottle making is still at development and validation stage. I am recommending that people should work more on this option to make it commercially available.

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