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Chemical Recycling of Postconsumer Poly(ethylene-terephthalate) Bottles – Depolymerization Study

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Poly(ethylene-terephthalate), PET bottles waste was chemically recycled by glycolysis process. The glycolysis reaction was carried out at three temperatures 170, 180 and 190 °C in different time intervals (1, 3, 6 hours) with a weight ratio of ethylene glycol (EG) to PET 1 : 18 and the zinc acetate as a catalyst. The glycolysis reaction leads to formation of monomers bis(2-hydroxyethyl)terephthalate (BHET) and ethylene glycol as well as various types of PET oligomers. Depolymerization products were further characterized by infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). From the results it can be seen that remained PET products i.e. oligomers are thermally very stable and they are suitable for obtaining other polymers.

Key words:
Bis(2-hydroxyethyl)terephthalate, chemical recycling, glycolysis, oligomers, poly(ethylene-terephthalate)

Introduction

Recycling of poly(ethylene-terephthalate), PET, represents one of the most successful and widespread examples of polymer recycling. This material is fully recyclable and may be used for manufacturing new products in many industrial fields such as packaging for detergents, cosmetics, carpets, foils, car parts or back into PET bottles. Its versatility in the many industries therefore makes it irreplaceable. Nevertheless, the excellent properties of PET needed for its many applications are also responsible for the difficult degradation of PET and an accumulation of polymer waste, which in turn creates serious environmental problems connected to littering and illegal landfilling or incineration. A large amount of research has been carried on the subject of recycling process of PET and chemical decomposition, and conversion into reusable chemical products of added value is one of the important recycling strategies for this material [1–4]. Chemical recycling processes for PET are divided as follows: glycolysis, methanolysis, hydrolysis and other processes such as aminolysis or ammonolysis [5–9]. One of the attractive methods of recycling is glycolysis reaction into the monomer bis(2-hydroxyethyl)terephthalate, BHET and oligomers of various structures. The obtain monomer BHET has been widely used in the synthesis of a number of polymeric materials like unsaturated polyester resins which are used in polyurethanes, foams and various copolymer production as well as novel biocompatible systems on the base of PET polymer [10–13]. The purpose of the present study was to investigate the formation of various structures of PET products (oligomers) and monomer BHET obtained by glycolysis during the chemical recycling. Depolymerized products (monomer BHET and oligomers) were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

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Experimental

Materials

Post-consumer PET bottles were cleaned, dried and cut into square chips with cryogenic rotary cutter (Retsch SM 2000) to particle size of 3 mm × 3 mm. Samples were first conditioned with an aqueous diluted sodium hydroxide solution (2 wt) for 30 minutes to remove any surface impurities, and subsequently washed with water and dried in an oven at 80 °C to eliminate moisture. Ethylene glycol (EG), which was used as a solvent for glycolysis (Merk, Darmstadt), sodium hydrate (Kemika, Zagreb) and zinc acetate (Kemika, Zagreb) were of analytical reagent grade. The glycolysis reaction was carried out in a four-necked glass reactor equipped with a thermometer, electromagnetic stirrer and a reflux set. Reaction of PET waste chips and EG (molar ratio of PET/EG was 1 : 18) was catalyzed with a 1 mass % of zinc acetate and reaction was carried out at three temperatures (170, 180 and 190 °C) and different times (1, 3 and 6 hours). The reactor and the mixture of EG and the catalyst were preheated to the selected temperature prior to the addition of the PET scraps in order to minimize the time required to reach the reaction temperature. At the end of reaction, two fractions were obtained; solid-degraded PET that was separated and further characterized and liquid ethylene glycol (EG).

Characterization

The solid fraction of degraded PET by glycolysis (BHET monomer and oligomers) was characterized by FTIR, DSC and TGA. FTIR spectra were recorded on Perkin Elmer Spectrum One spectrometer in the range of 4000–500 cm^{-1}. All samples were ground in a laboratory mill (IKA WERKE M20) and prepared as pellets with KBr. DSC was performed on a MettlerToledo DSC 823^e T 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 25–280 °C. The melting (Tm) and crystallization temperature (Tc) of the BHET monomer and obtained PET oligomers were determined as the onset temperatures. The thermal properties of the PET glycolysis products were investigated in the temperature range of 25–550 °C using an instrument TA Instruments Q500. Experiment was carried out in a nitrogen flow rate of 100 ml min^{-1} at heating rate of 5 °C min^{-1}.

Results and discussion

Analysis of glycolysis products

Chemical recycling of PET by glycolysis reaction involves a partial to full depolymerization of high molecular weight polymer consisting of terephthalate and ethylene glycol. The presence of glycol in reaction mixture causes chain scission by attacking the ester linkages along the polymer backbone.

Theoretically, the main product of PET depolymerization by glycolysis is monomer bis(2-hydroxyethyl)terephthalate (BHET) along with oligomers to a lesser extent, out of which BHET was separated by repeated crystallization. The reaction pathway of BHET formation, along with other side products, is shown in Fig. 1.

After a referred time of glycolysis, the mixture was cooled down at room temperature by plunging of reactor into cold water and then the mixture was separated into solid PET residue and liquid phase (ethylene glycol) by filtration, Table 1. Remaining residue was dried, weighed and calculated according to the equation

$$Y_{oligomers} \ (\%) = (weight \ of \ oligomers/weight \ of \ monomer \ and \ oligomers) \times 100 \qquad (1)$$

Further, solid residue was split up on the oligomers and monomer BHET that were extracted with boiling water three times, Table 2. The liquid fraction that contained extracted monomers was collected after filtration and stored in a refrigerator for 24 h at 5 °C to induce the precipitation of white crystals of BHET monomer. BHET crystals were further washed with cold distilled water in order to remove the remaining zinc acetate, then dried under vacuum at 40 °C for 24 h and its mass fraction was determined according to the following equation

$$Y_{BHET} \ (\%) = (weight \ of \ BHET \ monomer \ / \ theorethical \ yield \ of \ BHET) \times 100 \qquad (2)$$

In Table 1 are given both obtained fractions of the PET products (solid and liquid) at three different temperatures and various depolymerization times (1, 3 and 6 h). The solid fraction includes oligomers, trimers, dimers and monomer BHET. From the results it can be seen that after 6 hours of glycolysis, PET was negligibly degraded at 170 °C (only 12 mass % of EG was obtained) and for the reaction carried out at 180 °C (only after 6 hours), higher values of EG are observed (30 %). In contrast, after 6 hours of glycolysis at 190 °C the highest fraction of PET (cca 70 mass %) was converted to the EG monomer. Low concentration of EG monomer indicates the lower level of PET depolymerization and presence of high concentration of polymer of high molecular masses. This is supported by the obtained results of mass fraction of monomer BHET and oligomers in Table 2. For example, after depolymerization of PET at 170 °C for 1 h, 1.11 mass % and 3.2 mass % after 6 h of
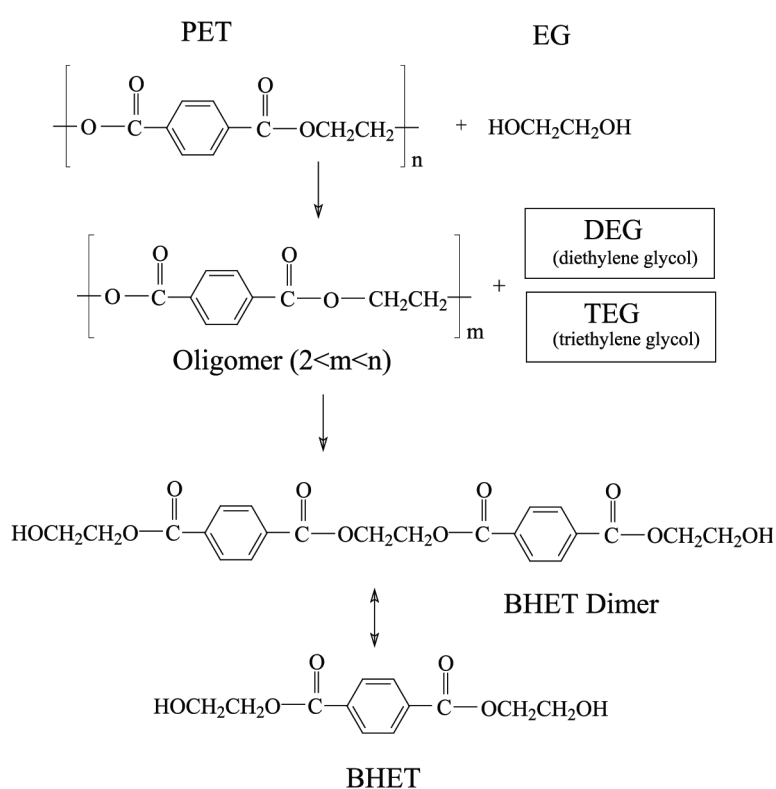
F i g . 1 – *Depolymerization of PET*

T a b l e 1 – *Solid PET residue and EG formed after glycolysis reaction at 170, 180 and 190 °C in various depolymerization times (1, 3, 6 h)*

Depolymerization time	T=170 °C		T=180 °C		T=190 °C	
	solid residue	EG	solid residue	EG	solid residue	EG
t / h	mass %					
1	98,01	1,99	90,32	9,68	99,29	0,71
3	92,34	7,66	81,52	18,48	35,15	64,88
6	88,56	11,44	72,70	27,30	31,75	68,25

T a b l e 2 – *Mass fractions of BHET monomer and PET oligomers obtained by glycolysis reaction at 170, 180 and 190 °C in various depolymerization times (1, 3, 6 h)*

Depolymerization time	T = 170 °C		T = 180 °C		T = 190 °C	
	BHET	oligomers	BHET	oligomers	BHET	oligomers
t/h	mass %					
1	1,11	98,89	1,19	98,81	1,32	98,68
3	1,40	98,60	9,45	90,55	28,88	71,12
6	3,20	96,80	61,04	38,96	87,28	12,72

BHET is obtained. It is obvious that after glycolysis at lower temperature (170 °C), solid fraction mostly consists of oligomers and its concentration increases with shift to higher gylcolysis temperature. Very low content of PET depolymerization at 170 °C (even with the extended reaction time) is obtained, which is explained with low solubility of PET in EG at 170 °C.[14] The highest fraction of BHET monomer (87 mass %) is obtained at 190 °C and after 6 hours of depolymerization. An excess of EG in the reaction mixture shifts the reaction equilibrium to PET depolymerization because EG is the solvent and catalyst at the same time. Besides that, the presence of EG could cause the side reaction, which can yield unexpected oligomers and side products. Obtained oligomers differ by size of molecular masses and by end groups (hydroxyl end groups and/or products with hydroxyl and carboxylic end groups) that are formed. Monomers are also subjected to reverse reactions forming di- and tri- monomers (diethylene glycol, triethylene glycol, dimer BHET). The main problem that appears is the equilibrium between depolymerization reagents and the reverse reaction of polycondensation of produced monomers/oligomers [15–17]. In order to achieve an efficient recycling of PET by glycolysis, higher temperatures and longer reaction time are required. High concentration of the formed oligomers is also important and useful product of recycling because they are used as intermediates for obtaining other polymers.

FTIR analysis

The degradation of PET with respect to the changes in the structure during the chemical recycling process was monitored using the changes in intensity of the characteristic PET bands, and the spectra are shown in Figs. 2a–d. Noticeable band changes are observed in all presented spectra in comparison to the neat PET and we are particularly focused on changes at –CH at 2919 and 2850 cm^{-1}, CH$_2$ stretching at 725 cm^{-1} and C=O stretching at 1720 cm^{-1}. The meaningful changes (in comparison to neat PET) in the intensities and shape of the –CH bands are observed for all studied samples. This observation could be attributed to the partial distortion of the polymer structure during the degradation process i.e. by the loss of high molecular structure resulting in formation of PET oligomers and monomers. Also, this can be attributed to the variety in the electronic environment of the aliphatic carbon-hydrogen chains [18]. During the depolymerization, the chain lengths of PET are modified (decreased)
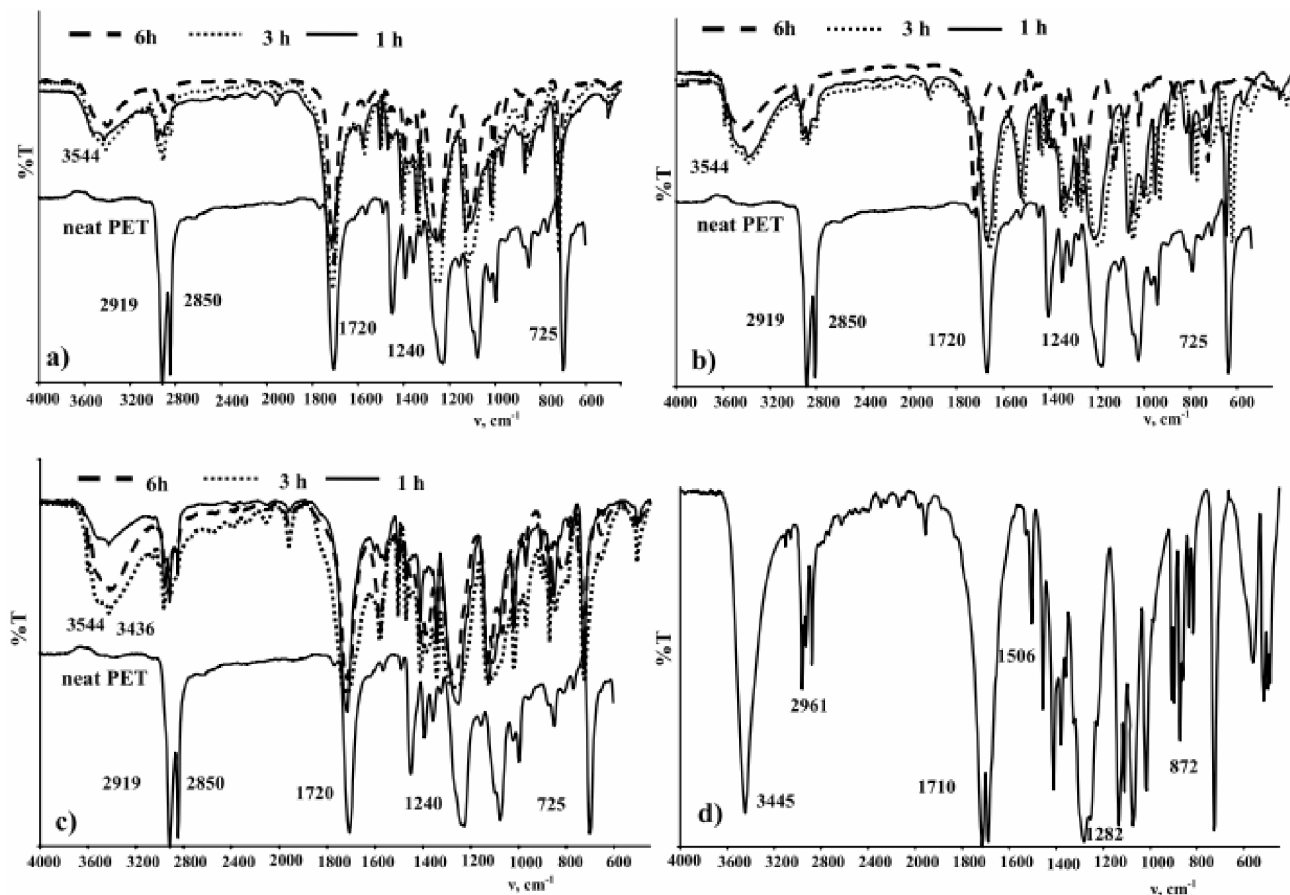
F i g . 2 – *FTIR spectra of neat PET polymer and spectra of glycolysis products recorded after 1, 3 and 6 h at: a) 170 °C, b) 180 °C, c) 190 °C and d) FTIR spectra of extracted monomer BHET*

andconfiguration of created components (oligomers and monomers) are different causing modification of the number of –CH groups leading to quite significant intensity changes of the bands. Examination of the ester bands at 1240 cm^{-1} enables us to verify the information about the conformational changes obtained from the bands associated with the –CH, CH$_2$ and C=O modes. Additionally, in the presented spectra (Figs. 2a–2c), the bands at 3544 and 3436 cm^{-1} indicate the presence of –COOH and –OH groups related to the formation of oligomers (alcohol and acid hydroxyl end groups) and monomer BHET due to breaking of chemical bonds. The highest intensity of the -OH end groups was observed for the sample which was glycolized for the longest time (6 h) and at the highest reaction temperature (190 °C), Fig. 2c. Such observation can be explained by the presence of higher concentration of oligomers with –OH and –COOH end groups that can be linked by hydrogen bonds.[19]

Glycolysis of PET with ethylene glycol mainly produces monomer BHET along with other products (oligomers and dimers) and the spectra of separated and purified BHET is presented in Fig. 2d). The FTIR spectrograph clearly shows -OH band at 3448 cm^{-1}, alkyl –CH at 2961 cm^{-1}, C=O stretching at 1710 cm^{-1} and aryl group at 1506 cm^{-1}, present in monomer BHET.[13]

DSC analysis

DSC thermograms of PET glycolysis products (oligomers) are presented in Fig. 3. The analysis of the thermograms indicates presence of various types of oligomers, Figs. 3a–3c and monomer BHET, Fig. 3d. Oligomers that are formed during the depolymerization, consist of various numbers of repeating monomer units n, that can be in interval of $n = 2$–20. Generally, it is known that experimentally obtained melting endotherms of oligomers can give an idea of their structure and detect the side reaction products.[14,15,20]

For example, there are PET oligomers with specific structure as H(GA)OH, H(GA)$_2$OH, H(GA)$_3$OH and H(GA)$_2$–G–H (detected by FTIR) and with molecular masses in the range of 210–595 gmol^{-1}. In the cited structures, the mark A stands for –OCC$_6$H$_4$CO– and G for –OCH$_2$CH$_2$O–. From the endotherms at Figs. 3a and 3b it can be observed that melting temperatures are in interval from 249–254 °C (also Table 3) of PET products
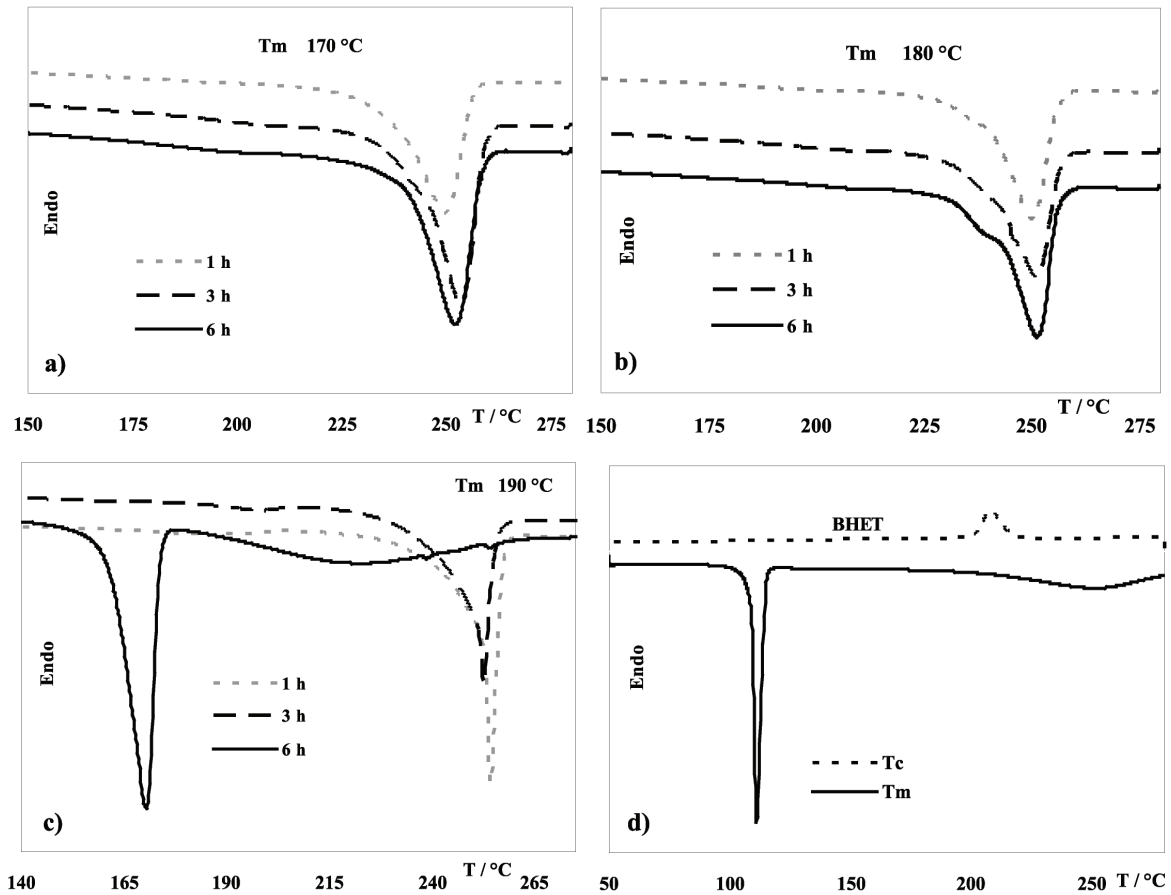
F i g . 3 − *Melting temperatures (T_m) of PET oligomers recorded after 1, 3 and 6 h at a) 170 °C, b) 180 °C, c) 190 °C and d) melting and crystallization (T_c) temperatures of extracted monomer BHET*

T a b l e 3 − *Melting (Tm) and crystallization temperatures (Tc) of BHET monomer and PET oligomers obtained by glycolysis reaction at 170, 180 and 190 °C in various polymerization times (1, 3, 6 h)*

Depoly-merization time	170 °C		180 °C		190 °C	
t/h	Tm/°C	Tc/°C	Tm/°C	Tc/°C	Tm/°C	Tc/°C
1	249,01	195,44	251,26	182,66	255,29	206,13
3	253,66	205,84	252,11	190,73	252,46	207,63
6	252,64	195,44	252,24	191,23	170,62	182,49

	Tm/°C	Tc/°C
neat PET	252,21	196,04
monomer BHET	110,22	207,05

obtained after glycolysis. These results denoted that the formed PET oligomers have complex structure HO–A–(GA)$_4$OH and HO–A–(GA)$_5$OH and molecular masses between 935 and 1127 gmol^{-1}.[20] Slight differences in values of melting temperature (Tm) and crystallization temperature (Tc) indicate pres-

ence of other structured oligomers. This is particularly evident due to new peaks at Fig 3b indicating formation of oligomers of lower molecular masses and with various chain ends. Additionally, it can be seen that extended depolymerization time leads to polycondensation reaction if we consider the results of Tm and Tc at 170 °C. DSC thermogram of the sample glycolysed 6 hours at 190 °C, Fig. 3c, consists of two endothermic melting peaks: the first peak centered at 170 °C is considered the melting point of dimer BHET.[21,22] The second maximum is detected around 225 °C and it is quite broad and can be related to the presence of low content of a mixture of oligomers. If we now look at Table 2 it can be seen that 12.7 mass % of oligomers mainly consist of BHET dimer. High concentration of BHET dimer indicates that dimer is not soluble in hot water and it is present due to reverse reaction. Such high concentration of dimer BHET confirms that after 6 h of glycolysis at 190 °C almost complete depolymerization of PET polymer is achieved, which is concluded from the endothermic melting peaks that are well separated from each other.[15,22] Thermogram in Fig. 3d, shows a reasonably sharp endothermic peak at 110 °C and a peak at 207 °C of

crystallization temperature, which agrees with the melting and crystallization point of monomer BHET reported in the literature and this is confirmation that neat monomer BHET was obtained from the solid phase.[22–25]

TG analysis

The solid fraction of PET products was also studied using TG analysis and the thermograms are reported in Figs. 4a, 4b, 4c and for BHET monomer in Fig. 4d. It was assumed that various oligomer structures should show different thermal behavior. Comparison of the TG traces obtained under nitrogen flow for the polymers glycolysed at 170 and 180 °C, Figs. 4a and 4b, reveals almost no differences in the mass-loss behavior in contrast to samples exposed to depolymerization reaction for 6 hours and at 190 °C, Fig. 4c. Samples of PET that
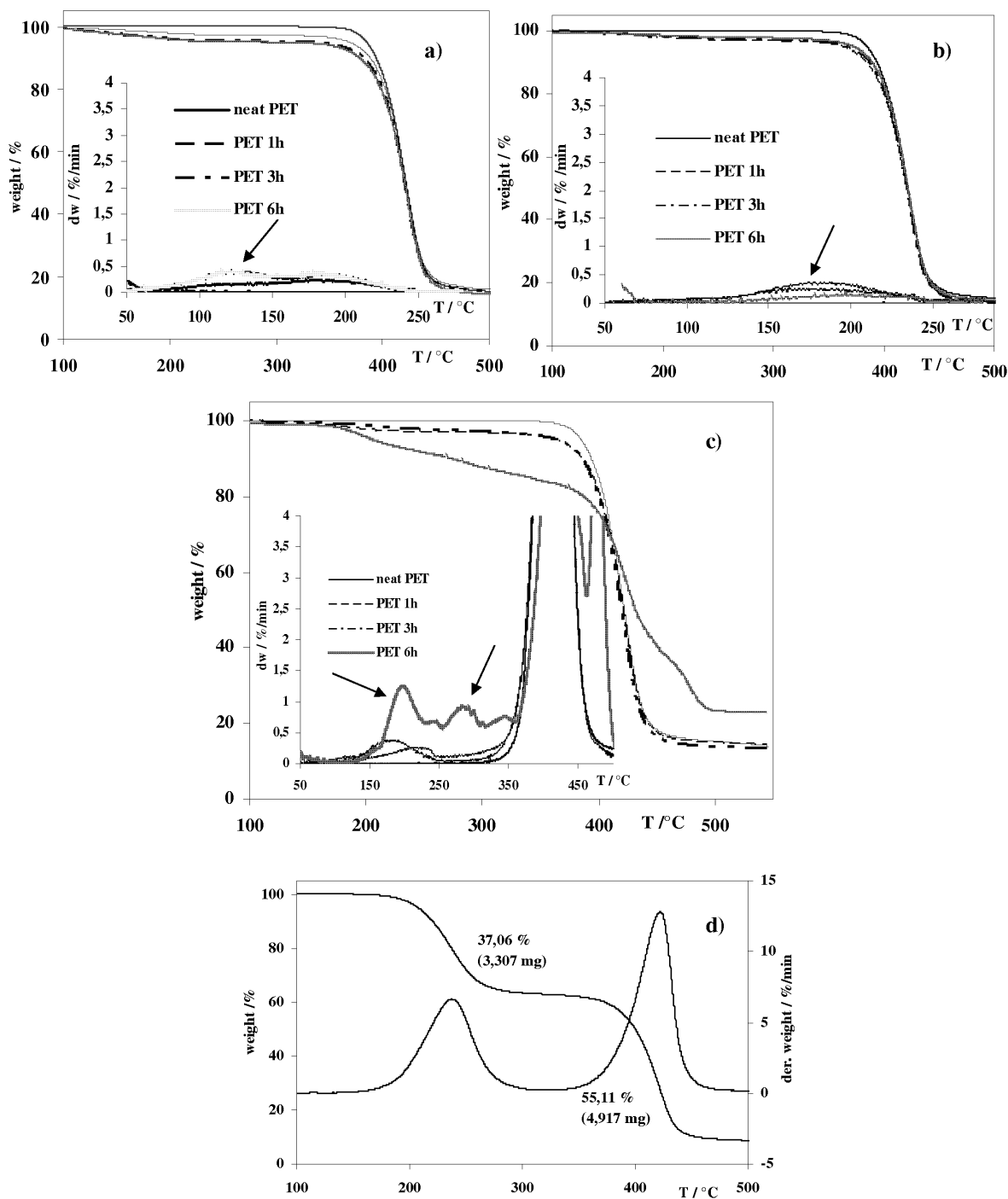

F i g. 4 − *Thermograms of neat PET and of glycolysis products (solid residue) recorded after 1, 3 and 6 h at: a) 170 °C, b) 180 °C, c) 190 °C and d) thermogram of extracted BHET monomer. Inset: corresponding DTG curves*

were glycolysed 1, 3 and 6 hours at 170 and 180 °C as well as these at 190 °C for 1 and 3 h undergoes one step of mass-loss stretching between 180 and 480 °C and losing 85 % of its initial mass. Slight mass-loss were observed in the beginning of the thermal degradation between 145 and 280 °C, which is evident as a new maximum decomposition rate temperatures from the all DTG curves at Fig. 4. This 15 % of initial mass of PET samples represents thermal degradation of newly formed oligomers of lower molecular masses showing different thermal behavior than polymer chain. It is assumed that solid residues of 85 % consist of oligomers of high molecular mass due to their higher thermal stability, which is equal to those of the neat PET polymer. On the contrary, PET that were glycolysed 6 hours at 190 °C sees 20 % of its initial mass evolved in the first and the second step starting at 200 °C and 300 °C, before undergoing the third and fourth mass-loss step, starting at 423 °C and at around 460 °C, Fig. 4c). The first mass-loss step can be attributed to the evolution of oligomers of low-molar mass and other species like benzoic acid, vinyl benzoate chain-ends, and other various degradation products[26] The other temperature maximums describe degradation of dimer BHET. According to the thermal analysis using DSC it can be seen that similar degradation behavior was observed, with onset temperatures matching those found in TG analysis. Fig. 4d) presents the thermogram of the extracted monomer BHET and the two-steps of monomer degradation are clearly visible, where in the first step 37 mass % ofmonomer decomposed at 237 °C while the residue of monomer decomposed in the second stage at 422 °C.[27]

Conclusion

Glycolysis reaction with ethylene glycol was employed to decompose PET and from the result obtained after chemical recycling it can be concluded that high concentration of PET oligomers of high molecular mass is formed at lower temperatures (170 and 180 °C). This is confirmed with the results obtained by DSC and TG analysis. On DSC endotherms slight changes in melting and crystallization temperatures were observed indicating the presence of oligomers of lower molecular masses. PET products obtained by glycolysis are thermally stable as is the neat PET polymer. High concentration of monomer and dimer BHET confirmed that almost complete depolymerization of PET polymer to monomers is achieved at 190 °C after 6 h of glycolysis. Hence, the optimal conditions are reaction time of 6 hours at 190 °C and the yield of obtained BHET is about 87 % under these conditions.

Presence of monomer and dimer BHET is confirmed by both thermal methods due to thermal degradation in two steps by TGA and by melting peak at 170 °C obtained by DSC.

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