Glycolytic Depolymerization of PET Waste in a Microwave Reactor

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ABSTRACT: Recycling of waste PET bottles was examined using glycolytic depolymerization with diethylene glycol, under microwave irradiation. The objective was to investigate if depolymerization using microwave energy could provide the same product distribution, while carried out in milder experimental conditions and/or shorter reaction times, resulting, thus besides to polymer recycling, in substantial energy saving. The reaction was carried out in a sealed microwave reactor in which the pressure and temperature were controlled. Experiments under constant temperature or microwave power were carried out at several time intervals. The main glycolysis product was analyzed and identified by FTIR measurements. The average molecular weight of the PET residues was found to decrease with the percentage of PET degradation. In the experiments carried out under constant microwave power, complete depolymerization was observed at irradiation powers greater than 150 W for 2 min, or 100 W for 5 min. In the constant temperature experiments, it was clear that at temperatures below 150°C no degradation occurs, whereas complete depolymerization takes place at temperatures greater than or equal to 180°C for 5 min. These results when compared to the conventional heating, where more than 4 h are needed for complete with PET degradation, confirm the importance of the microwave power technique and the substantial energy saving achieved. Finally, from a simple kinetic model the activation energy of the reaction was evaluated. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3066–3073, 2010

Key words: recycling; plastics; glycolysis; microwave irradiation; poly(ethylene terephthalate)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the versatile engineering plastics showing excellent thermal and mechanical properties, chemical resistance, and clarity. Although its main application was by far 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 water and soft-drink bottles. The overall world consumption of PET amounts to about 26 million tons a year[1] compared with about 13 million tons, reported in 1997.[2] As the duration of life of PET wastes (mainly from mineral-water and soft-drink bottles) is very small, there is a vast waste stream that reaches each year to the final recipients creating a serious environmental problem. PET accounts for 8% by weight and 12% by volume of the world's solid waste.[3] Disposing of the waste to landfill is becoming undesirable, because of legislation pressures, rising costs, and the poor biodegradability of commonly used polymers such as PET. Therefore, other ways of treatment, such as recycling, should be adopted.

PET recycling represents one of the most successful and widespread examples of polymer recycling. The main driving force responsible for this extremely increased recycling of post-consumer PET is its widespread use, particularly in the beverage and food industry. PET bottle collection in Europe is growing steadily. By 2008, Petcore announced that European post-consumer PET collection rates reached 1 260,000 tons, an increase of more than 11% over the previous year[4] and almost double the value reported in 2004 (665 000 tones). The recycling of waste polymers, including PET, can be carried out in many ways. Four main approaches have been proposed:[5–8] *Primary recycling* refers to the "in-plant" recycling of the scrap material of controlled history. *Mechanical Recycling*, where the polymer is separated from its associated contaminants, and it can be readily reprocessed into granules by conventional melt

extrusion. *Chemical recycling*, defined as the process leading to total depolymerization of PET to its monomers, or partial depolymerization to oligomers and other chemical substances. *Energy recovery* referring to the recovery of plastic's energy content usually by incineration. Among the recycling techniques, incineration meets with strong societal opposition and mechanical recycling can be carried out only on single-polymer waste streams. Therefore, we focused our attention on chemical recycling, which also conform to the sustainable development principles.[5,9]

Chemical recycling processes for PET are divided as follows:[2,6,10,11] (i) Glycolysis, (ii) Methanolysis, (iii) Hydrolysis, and (iv) other processes: Glycolysis involves the insertion of ethylene glycol (EG) (or diethylene glycol (DEG) and propylene glycol) in PET chains to give bis (2-hydroxyethyl) terephthalate, which is a substrate for PET synthesis and other oligomers. The glycolysis makes it possible to employ very low amounts of reactants, as well as the application of lower temperatures and pressures, in contrast with other methods. Recently, a growing interest has been observed in PET glycolysis for the manufacture of specialized secondary products such as unsaturated polyesters, polyurethanes, vinyl esters, epoxy resins, and polymer concretes.[6,12–15] Methanolysis actually is the degradation of PET by methanol at high temperatures and high pressures with main products: dimethyl terephthalate and EG. Hydrolysis of PET can be carried out in an acid, alkaline, or neutral environment to produce the monomers terephthalic acid (TPA) and EG.[16,17]

Microwave assisted organic synthesis has revolutionized the chemical research.[18,19] Microwave irradiation as a heating technique offers many advantages over the conventional heating such as instantaneous and rapid heating with high specificity without contact with the material to be heated. It is, therefore, a popular technique for heating and drying materials and is utilized in many household and industrial applications.[19,20] The main advantage of microwaves over conventional heating sources is that the irradiation penetrates and simultaneously heats the bulk of the material. Research efforts have thus lead to numerous applications in material processing techniques that have resulted in shorter reaction times and greater convenience.

Although the use of microwave irradiation in chemical reactions is a rather well-established technique, the articles published on PET recycling are very limited. A survey is reported next. Nikje and Nazari[21] used microwave irradiation during a hybrid hydro-solvolytic depolymerization of PET with alcohols, such as methanol, ethanol, butanol, pentanol, and hexanol. Reactions were performed at short times (less than 1 h) with main products TPA

and EG. Hydrolytic depolymerization of PET in closed system under microwave irradiation and 2 MPa pressure (220°C) for 90–120 min led to the formation of TPA, EG, and DEG as degradation products.[22] In a subsequent study carried out by Li et al.,[23] it was found that the optimal conditions for PET hydrolytic depolymerization in neutral conditions under microwave irradiation were: reaction temperature 220°C, pressure 200 psi, microwave power 260 W, time 210 min, and ratio of water to PET equal to 10/1. Krzan,[24,25] carried out the depolymerization of PET in a microwave oven. Methanol, propylene glycol, and polyethylene glycol 400 were used as solvolysis reagents and zinc acetate as catalyst. The microwave irradiation power was kept constant at 500 W during all experiments and almost complete solubilization of PET was achieved in about 10 min. Finally, Pingale and Shukla[26] used a modified microwave oven to carry out glycolysis of PET bottle waste in presence of sodium carbonate, sodium bicarbonate, and barium hydroxide catalysts. The experiments were carried out under reflux in microwave irradiation and showed that the time of reaction reduced to 35 min as compared to 8 h under conventional heating system.

Following previous works from our group on polymer recycling,[27–32] in this study, PET waste taken from common soft-drink bottles, was subjected to glycolysis with DEG in a laboratory-scale microwave reactor, to study the effect of microwave irradiation on the reaction kinetics. The reaction was carried out in a sealed microwave reactor in which pressure and temperature were controlled. The main product was an oligoester diol, which was analyzed and identified. Properties of PET oligomers were also measured. The effect of several process parameters, including degradation temperature and time, on the degree of PET depolymerization was studied. The main objective was to investigate if microwave irradiation applied during depolymerization of PET could result in the same final products with those obtained from a conventional process, but using either lower reaction temperatures or shorter reaction times with substantial energy saving.

EXPERIMENTAL PART

Materials

PET taken from post-consumer clear bottles was used from which the polyethylene caps and the polypropylene label were removed. The bottles were cut and fed to a rotary cutter with a max size of 6 mm. The DEG was used in all the glycolysis experiments. Manganese acetate [$Mn(CH_3COO)_2 \cdot 4H_2O$] with a purity of 99% was used as a transesterification catalyst.

Microwave assisted glycolysis of PET

The PET decomposition experiments were conducted in a microwave reactor (CEM corporation) equipped with a digital temperature control system and pressure sensors inserted directly into the 10 mL PTFE reaction tube. PET waste flakes (0.5 g) together with 2.5 mL of DEG (molar ratio of PET:-DEG = 1:10) and the transesterification catalyst (0.5% w/w) were added into the reactor, sealed in a nitrogen atmosphere and the heat-up period to the desired set-point started. When the set temperature reached, the reaction time began and PET decomposition was followed for prespecified time periods. In a second set of experiments, the microwave irradiation power was set to a specific value and PET decomposition was also followed for prespecified time periods. After that time period, the reaction vessels were automatically cooled and the reaction mixture was filtered through a G3 glass filter to remove the unreacted PET solids. The filtrate was extracted with dichloromethane and the extract finally washed with water to remove traces of DEG excess, catalyst, and EG coming from the PET molecules. The final unreacted PET was washed with water, dried in a vacuum oven at 40°C and weighed.

The percent degradation and the unreacted PET are calculated using the following equations:

$$\text{PET Degradation (\%)} = \frac{W_{\text{PET},0} - W_{\text{PET},f}}{W_{\text{PET},0}} 100 \qquad (1)$$

$$\text{Unreacted PET (\%)} = \frac{W_{\text{PET},f}}{W_{\text{PET},0}} 100 \qquad (2)$$

where, $W_{\text{PET},0}$ and $W_{\text{PET},f}$ refer to the initial and final weight of PET, respectively.

Product characterization

Fourier-transform infra-red (FTIR)

The chemical structure of the final glycolized product was confirmed by recording its IR spectra. The instrument used was an FTIR spectrophotometer of PerkinElmer, Spectrum One. The resolution of the equipment was 4 cm^{-1}. The recorded wavenumber range was from 450 to 4000 cm^{-1} and 32 spectra were averaged to reduce the noise. A commercial software Spectrum v5.0.1 (PerkinElmer LLC 1500F2429) was used to process and calculate all the data from the spectra. The KBr tablet technique was used.

Viscosimetry

Intrinsic viscosity [η] measurements of PET residues were performed using an Ubbelohde viscometer at

25°C, in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). The samples were maintained in the above mixture of solvents at 90°C for some time (approximately 15–20 min) to be completely dissolved and solutions of 1% w/v were prepared. The solutions were then cooled to room temperature and filtered through a disposable Teflon membrane filter. Intrinsic viscosity was calculated after the Solomon-Ciuta equation.[33]

$$[\eta] = [2\{t/t_o - \ln(t/t_o) - 1\}]^{1/2}/c \qquad (3)$$

where c is the concentration of the solution; t, the flow time of solution, and t_o the flow time of pure solvent.

The number-average molecular weight ($\overline{M}_n$) of the samples was calculated from intrinsic viscosity [η] values, using the Berkowitz equation:[34]

$$\overline{M}_n = 3.29 \times 10^4 [\eta]^{1.54} \qquad (4)$$

RESULTS AND DISCUSSION

As it was previously mentioned, two different sets of experiments were carried out. The first at constant reaction temperature, whereas the second at constant microwave irradiation power. Subsequently, results from these experiments are presented.

Experiments at constant temperature

Conventional glycolysis of PET is usually carried out at temperatures above 200°C (around 210°C) and prolonged time (~ 4 h).[13] Therefore, for the experiments of PET glycolysis using microwave irradiation temperatures below 200°C were used. As such 150, 160, 170, 180, and 200°C were selected. In all the experiments the amount of catalyst was kept constant at 0.5% w/w, which has been found to be sufficient for maximum yield of the glycolized product.[26] Indicative results on the variation of reaction temperature and pressure, as well as microwave power with depolymerization time for two experiments at 150 and 180°C, are illustrative in Figure 1. It can be seen that, in both cases the temperature set-point is achieved soon after some initial small-scale oscillations. The time needed to achieve the constant value, decreased with temperature. To maintain the reaction mixture at the desired temperature the microwave power undergoes much more pronounced oscillations. The final almost constant value of power varied with temperature in the following order 11, 39, 46, and 80 W for temperatures equal to 150, 160, 180, and 200°C, respectively. Moreover, the reaction pressure initially increased with
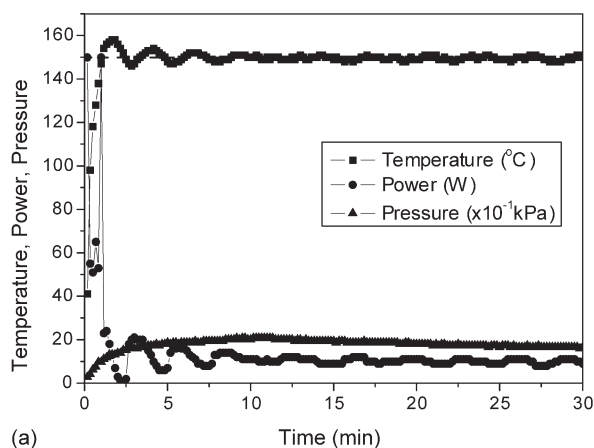
(a)
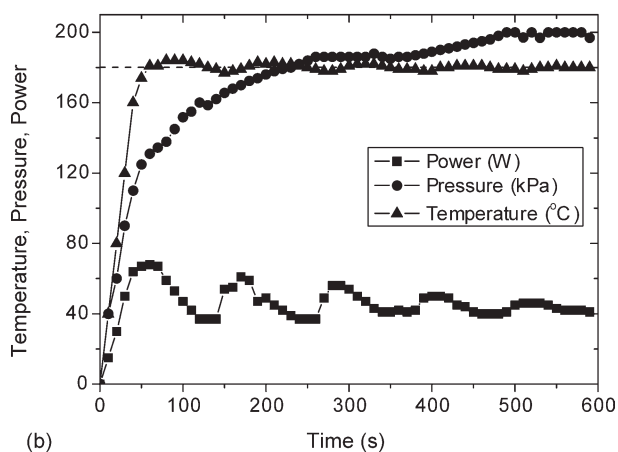
(b)

Figure 1 Variation of reactor temperature and pressure, as well as microwave irradiation power with time during PET glycolysis at 150°C for 30 min (a) and 180°C for 10 min (b).

time in order to reach an almost constant value, which also varied with temperature as follows, 170, 190, 200, and 227 kPa for the temperatures 150, 160, 180, and 200°C, respectively.

Furthermore, the effect of depolymerization time on the amount of unreacted PET and oligomers recovered is illustrated in Figure 2. It is observed that after 1 h of reaction time almost 24% of PET has reacted, whereas the rest 76% is unreacted. From these results, it can be concluded that glycolysis of PET is indeed carried out under microwave irradiation at relatively low temperature (i.e. 150°C) but at a slow rate. Therefore, higher depolymerization temperatures (i.e. 160, 170, 180, and 200°C) at different times were further tested. The effect of depolymerization temperature on the amount of PET reacted with time is illustrated in Figure 3. It was observed that at high temperatures (i.e. 200°C), it takes only 2 min for complete PET degradation. These results when compared with the conventional heating, where more than 4 h are needed for complete PET degradation, confirm the importance of the microwave power technique and the substantial energy
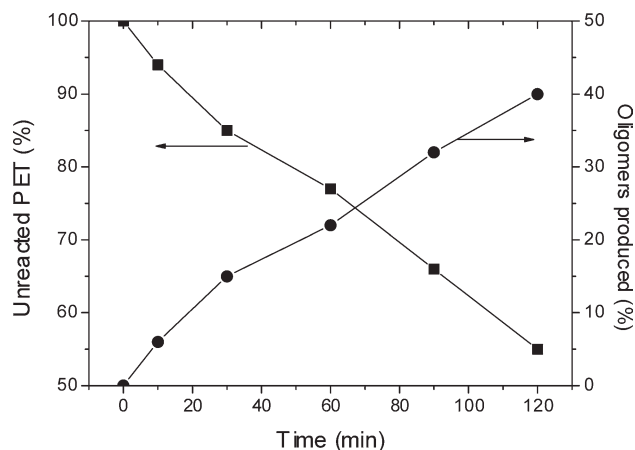

Figure 2 Amount of unreacted PET and oligomers produced as a function of time during PET glycolysis at 150°C under microwave irradiation.

saving achieved. At 180°C after only 5 min the degradation of PET has also reached 100%. However, when temperature is decreased to 160°C, only 65% of the PET has reacted even after 60 min of microwave irradiation. At the intermediate temperature of 170°C, it is also needed almost a 1 h to achieve 90% PET depolymerization. The same results but expressed as unreacted PET as a function of temperature are presented in Figure 4. It is clear that at temperatures below 150°C no degradation occurs, whereas at those above 180°C, almost complete depolymerization takes place at 5 min.

Furthermore, a simple theoretical model was used to predict the time evolution of the reaction conversion. It should be pointed out that, the derivation of a comprehensive mathematical model is rather complicated since mass transfer phenomena (between
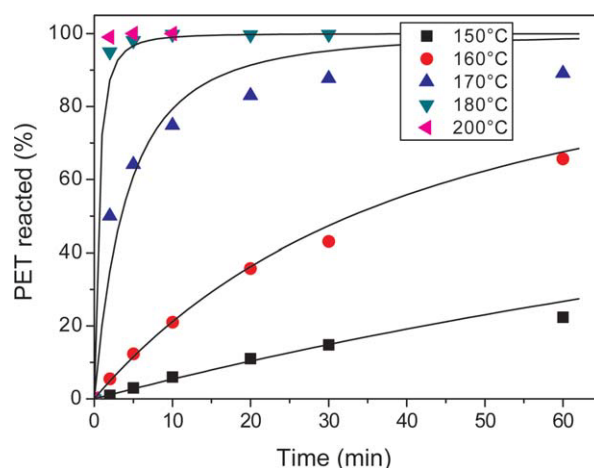

Figure 3 Effect of depolymerization temperature on the amount of PET reacted with time during microwave assisted PET glycolysis. Discrete points refer to experimental data and continuous lines to the results of the simulation model. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
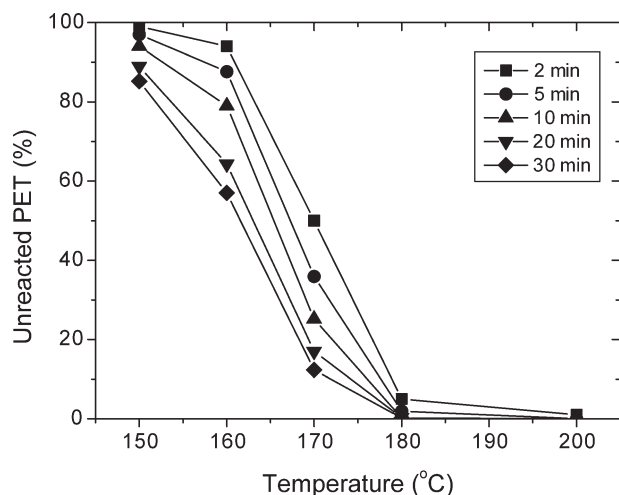
Figure 4 Effect of depolymerization time on the amount of PET reacted at different temperatures during microwave assisted PET glycolysis.

the solid and the liquid phase) occur in parallel to the chemical reaction. The model successfully used by our group[6,16] during alkaline hydrolysis of PET was employed. Accordingly, the initial assumption is that glycolysis of esters is proportional to the ester and the glycol concentration, C_A and C_B, respectively. Next, according to a shrinking-core model,[35] the reaction rate must be proportional to the surface area of PET flakes, S_A. The molar balance of PET molecules then can be expressed as:

$$\frac{dN_A}{dt} = -kS_A C_A C_B \qquad (5)$$

where k is the kinetic rate constant in (m^3/mol) (m/s).

On the assumption that, the reaction proceeds on the flake surface, the concentration of ester on the surface, C_A, can be considered roughly constant for a certain period of time.[36] Furthermore, if the reaction conversion is defined as, $X = (N_{A0}-N_A)/N_{A0}$, equation (5) becomes:

$$\frac{dX}{dt} = \frac{kS_A}{V_0} C_{B0}(1 - X) \qquad (6)$$

where C_{B0} denote the initial glycol concentration.

Equation (6) can be integrated if the dependence of the effective surface area, S_A, on X is defined. The surface area is considered proportional to the degree of unreacted PET according to $S_A = S_0 (1 - X)^a$ where a is a constant $(0 \leq a \leq 1)$,[35] and $a = 0$ refers to a constant surface area during the reaction, whereas $a = 1$ refers to a conversion dependence according to a first order model. In this study, the arithmetic mean value was considered, that is, $a = 0.5$. Because

this value fitted the experimental data points best. Hence, equation (6) will be:

$$\frac{dX}{dt} = k\frac{S_0}{V_0} C_{B0}(1 - X)^{1.5} \qquad (7)$$

Which is easily integrated to the following simple expression:

$$(1 - X)^{-0.5} - 1 = k't \qquad \text{or} \qquad X = 1 - (1 + k't)^{-2} \qquad (8)$$

with:

$$k' = 0.5k\frac{S_0}{V_0} C_{B0} \qquad (9)$$

Using the theoretical model [eq. (8)] the apparent rate constant, k', was estimated for every temperature (150–180°C) and theoretical simulation lines produced were in good agreement to experimental data (Fig. 3). An Arrhenius expression was assumed for k' and the corresponding plot appears in Figure 5. As it can be seen, very surprisingly for such a simple model, all values follow a very good straight line having a correlation coefficient equal to 0.996. The calculated apparent activation energy was estimated equal to 305 kJ/mol.

Experiments at constant microwave power

In the second set of experiments, the irradiation power was kept constant and the amount of PET reacted was recorded as a function of time and temperature. The investigated irradiation power ranged between 50 and 200 W, whereas the reaction time was constant at 2, 5, and 10 min. Results on the percentage of PET degradation appear in Table I. It was found that, at the two higher microwave powers used (i.e. 150 and 200 W), the PET has been
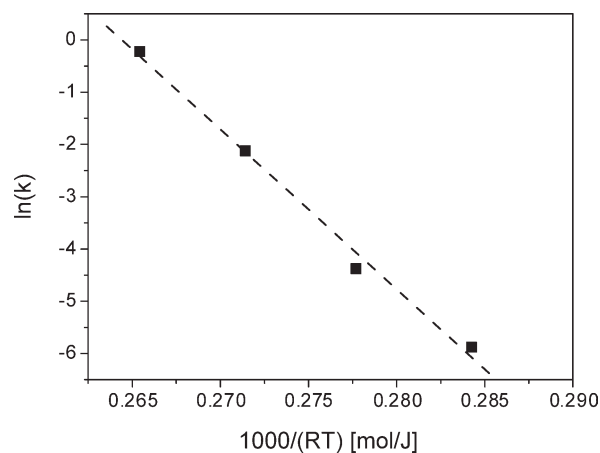

Figure 5 Arrhenius-type plot of the overall kinetic rate constant with temperature.

TABLE I
**Effect of the Microwave Power Applied, on the
Percentage of PET Degradation at Different Times,
During Microwave Assisted PET Glycolysis**

Power (W)	Depolymerization time (min)		
	2	5	10
50	3.5	12.7	100
100	32	100	100
150	100	100	100
200	100	100	100

Figure 7 Variation of reactor pressure with time during PET glycolysis at different constant irradiation powers.

completed degraded even after 2 min of irradiation time. Only at 50 W, it took ∼ 10 min for complete PET degradation. Therefore, it seems that the experimental conditions of 100 W constant microwave power and 5 min are adequate for 100% PET degradation. To explain these results, the variation of reaction temperature and pressure with time was recorded again. It should be noted that in all experiments, the irradiation power was absolutely constant at the prespecified value. A comparative plot showing the variation of temperature with time at several constant microwave irradiation powers is illustrated in Figure 6. A sharp increase in temperature was observed at the first 1–2 min followed by a further increase but with a lower slope, indicating that prolonging irradiation time results in a relatively small temperature increase. The final temperature values reached were 170, 230, 260, and 280°C for irradiation at 50, 100, 150, and 200 W, respectively. It was thus observed that, at power values greater than 150 W the melting point of PET is reached and exceeded. Hence, the reaction does not have also to overcome diffusion limitations between the solid (PET) and the liquid (DEG) phase, and it is much facilitated, resulting in complete degradation at small times. In contrast, at the 50 W experiment, the temperature was much lower, and therefore the reaction was slower
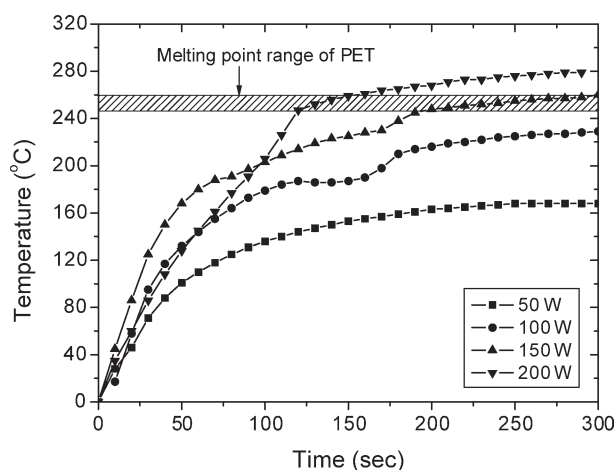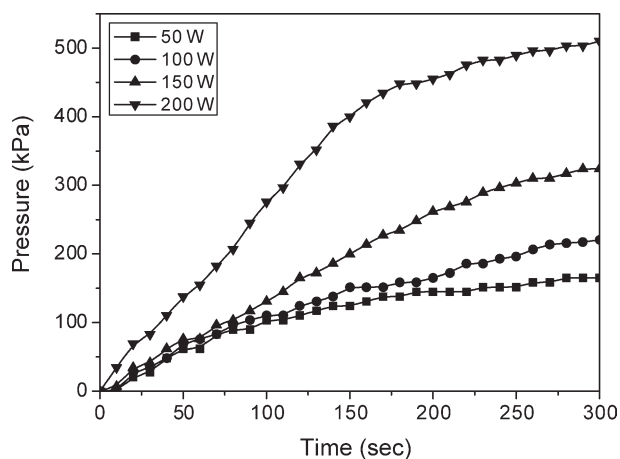
resulting in degradation, but after a much larger time. Furthermore, the reaction pressure was also recorded and appears in Figure 7. Again pressure continuously increases with time and is much affected by the microwave power. The final values reached were 165, 220, 324, and 510 kPa for irradiation at 50, 100, 150, and 200 W, respectively. A great increase in pressure at the highest power used was obvious, whereas at 50 W the final value is slightly above the atmospheric pressure.

Characterization of the oligomers received

The alcoholysis of PET with DEG proceeds according to the following reaction,
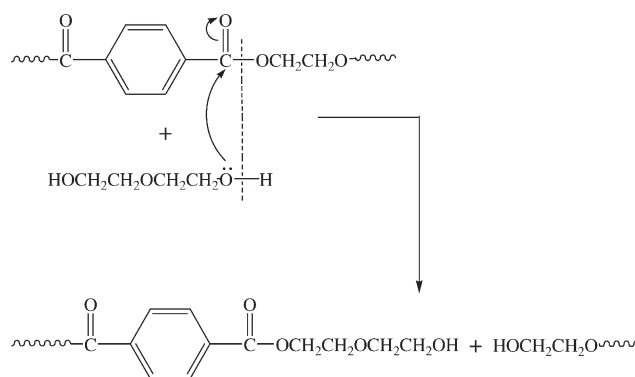
The alcoholysis consists of the transesterification of PET and the depolymerization of its polymer chain, resulting in the decrease of its molecular weight. Using a small excess of glycol in the depolymerization of PET, the oligoesters obtained have mainly two hydroxyl end-groups, that is, mixtures of oligoester diols are formed. The choice of DEG to carry out the glycolysis is usually determined by the necessity of having well flexural properties, because the long chains containing this glycol improve flexibility. Use of other glycols such as propylene glycol
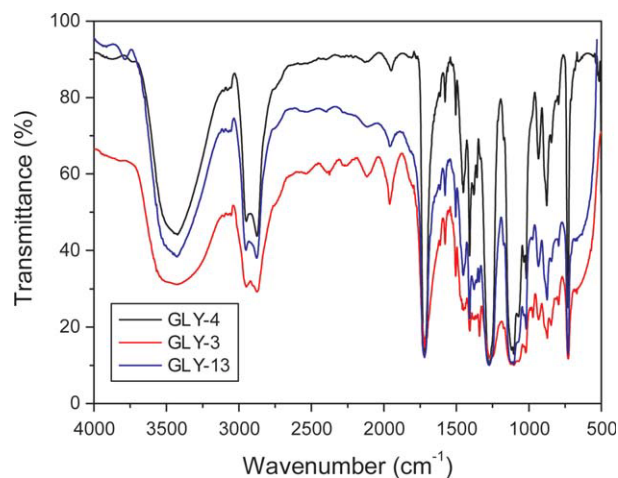

Figure 6 Variation of reactor temperature with time during PET glycolysis at different constant irradiation powers.

Figure 8 Comparative FTIR spectra of the oligomer produced from the microwave glycolysis of PET at 180°C and 30 min (GLY-4), 150°C and 60 min (GLY-3), and 180°C and 5 min (GLY-13). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

or dipropylene glycol results in products, which in a further step of the polyesterification reaction produce two-phase unsaturated polyesters.

On trying to identify the oligoester diols produced the following structure was proposed:
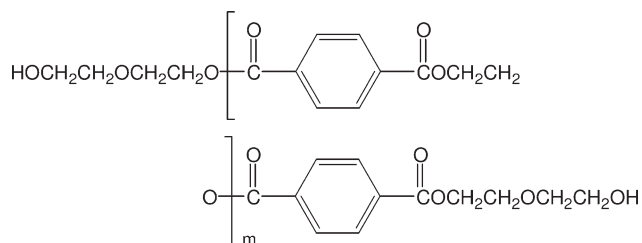

where $m = 0$–3.

The chemical structure of the oligomers received was investigated by FTIR analysis. Characteristic FTIR spectra of the product obtained from different experimental conditions appear in Figure 8. The characteristic peaks for the PET glycolysate are the following.

- The broad peak between 3570 and 3200 cm^{-1} denotes the existence of hydroxy groups and particular the stretch of H-bond in —OH.

- The absorption peaks at 1720 cm^{-1} as well as at 1272, 1018, and 730 cm^{-1} denote the existence of an aromatic carboxylic acid ester of the type.
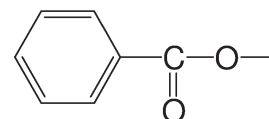
- The absorption peaks at 1504 cm^{-1}, as well as at 1408, 1105, 1018, and 874 or 877 cm^{-1} are characteristic of the existence of a terephthalate type carboxylic acid ester.
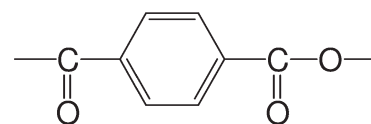
- The peaks at 2950 cm^{-1} and 2877 or 2875 cm^{-1} are characteristic of the asymmetric/symmetric stretch of C—H in the methylene groups —CH$_2$—. The same group is also identified by the peaks at 1452 cm^{-1} and 1379–1377 cm^{-1}, which characterize the methyl C—H asymmetric/symmetric bend.
- The absorption peak at 1578 cm^{-1} proves the existence of an aromatic phenyl ring.
- All spectra taken were similar meaning that similar products were produced.

The aforementioned FTIR transmission spectra, just confirms the proposed chemical structure for the glycolized PET product. However, a definite identification of the components could be done for example by using ^{13}C NMR, or ^{1}H NMR spectroscopy.

Moreover, it was found interesting to investigate the structure of the oligomers denoted as PET residues. Therefore, the intrinsic viscosity of some selected samples was measured and using eq. (4) their number-average molecular weight was estimated. The samples were selected in such a way to correspond to different degrees of PET degradation. Results, including the percentage of PET degradation and the corresponding

TABLE II
Intrinsic Viscosity and Number-Average Molecular Weight of PET and Selected PET Residues Produced Under Different Experimental Conditions

Sample	P (W)	T (°C)	t (min)	PET degree of degradation (%)	$[\eta]$ (dL g^{-1})	$\overline{M}_n$
PET	–	–	–	–	0.79	22930
Oligomer	50	–	5	13	0.62	15920
Oligomer	–	160	10	21	0.52	12140
Oligomer	–	160	30	43	0.35	6380
Oligomer	–	170	2	50	0.32	5580
Oligomer	–	170	5	64	0.25	3850

experimental conditions from which these samples were synthesized, appear in Table II. The average molecular weight of the PET used in the degradation experiments was also measured with the same method and results are included also in this Table. From the estimated values, it was clear that the average molecular weight of all samples was much less compared with the original PET, which was found equal to 22,930. In advance, there was a clear correlation of the intrinsic viscosity values with the degree of PET degradation, meaning that the [η] values decreased following the increase in the percentage of PET degradation. When PET degradation reached a value of 64%, the $\overline{M}_n$ of the PET residue was only 3850. Therefore, from these results, it can be postulated that during degradation experiments, it is not only the mass of the PET that is decreased but also its average molecular weight. It seems thus that glycolytic depolymerization of PET obeys a random chain-scission mechanism to some extent. This was also observed during hydrolytic depolymerization of PET by Liu et al.[22]

CONCLUSIONS

The potential use of microwave irradiation in PET recycling and recovery of secondary value-added products was investigated. The glycolytic depolymerization of PET from waste bottles with DEG in a microwave reactor was studied to produce an oligomeric diol, which was identified by FTIR measurements. In the experiments carried out under constant microwave power, complete depolymerization was observed at irradiation powers greater than 150 W for 2 min or at 100 W for 5 min. At the constant temperature experiments, it was clear that at temperatures below 150°C no degradation occurs, whereas complete depolymerization occurs at temperatures greater than or equal to 180°C at only 5 min. In general, PET depolymerization, is favored by increasing temperature, time and microwave power. The average molecular weight of the PET residues was found to decrease with the percentage of PET degradation. Therefore, it seems that use of microwave irradiation in PET recycling results in the same product distribution but using a much lower temperatures or reaction times leading thus to substantial energy saving.

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