Post-consumer PET Bottles Recycling

II. PET depolymerization using microwaves

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The chemical recycling of poly(ethylene terephtalate) PET using a unconventional method employing microwave radiation was studied. The reaction parameters were varied in order to study their influence. The reactivity of several glycols was compared and results showed consistency with conventional solvolysis methods. The dissolution of PET polymer into the glycol solution is one of the key parameters in determining the reaction time. The modification of the microwave field power afforded a 50% reduction of the reaction time. This method presents certain advantages compared to conventional glycolysis methods such as: energy and time saving through a rapid and a more uniform heating capacity, leading to a complete depolymerization in the presence of the catalyst.

Keywords: PET waste, glycolysis, microwave, oligomers, viscosity

One of the most intensely used thermoplastic elastomers, poly(ethylene terephthalate) (PET) is a semi-crystalline thermoplastic polyester [1-3], which has found large scale applications in the manufacture of fibers, photographic films, packages or soft-drink bottles.

As early as the 1980's, the amount of PET strictly used in the beverages industry was estimated to reach over 320 million kilograms, representing more than 1 billion bottles [4-7]. The continuous demand growth for PET, resulted in the need for a production of over 49 million tons/year and a forecasted value of the market to reach over ∈24 billion [8-9] in 2011. In order to avoid the increase of waste amount generation, different states of the world developed not only education programs to reduce consumption, but also engaged industrial branches to encourage the use of recycled materials from PET bottles [9-11]. Thus, more than 1 million tons of PET flakes are recycled every year in Europe, due to the environmental policy imposed by European Union [12]. While part of PET waste is converted into energy [13], most of the resulted derivates from PET processing can be used as raw materials for certain applications as fibres [14], adhesives [15], synthetic dyes [10], polyurethane foams [16], concrete composites [5] leading to cost savings in the manufacturing type of products.

PET waste is chemically processed by depolymerization into monomers, dimers and other low molecular weight oligomers [2, 11]. The monomers are then re-polymerized and the regenerated or reconstituted polymer is formed into new article. Regenerated monomer, polymer, or both may be blended with virgin materials. The regeneration process may involve a variety of monomer/polymer purification steps in addition to washings, such as distillation, crystallization, and additional chemical reaction [17-18].

Different recycling processes for chemical reprocessing or chemolysis of PET waste are available and most of them consist of reacting the polyester with an excess of reactant such as diols, diamines or alcohols. PET conversion products are used as monomers for further synthesis of PET, polyurethanes, or polyesters. G.P. Karayannidis and D.S. Achilias [19] define *hydrolysis* as the method of PET waste recycling by the reaction of PET with water in an acid, alkaline or neutral environment, leading to total depolymerization to its monomers terephthalic acid and ethylene glycol.

Methanolysis is the degradation of PET by methanol at high temperatures and high pressures with the main products being dimethyl terephthalate and ethylene glycol. The dimethyl terephthalate produced can be purified and used to create new PET [2, 20-23]. Methanolysis is relatively tolerant to the contents of impurities in the input materials.

Aminolysis of PET proceeds under the action of amine and terephtalamide is obtained. Depolymerisation of the PET waste using different amines such as allylamine, morpholine, hydrazine, and polyamines can be implemented [24-25].

Glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with hydroxyl terminals. PET waste can be depolymerized by glycolysis to obtain oligomeric diols and polyols, or glycolyzed into its monomeric units, bis(2-hydroxyethyl) terephthalate or dimethyl terephthalate [26-29, 35]. Bis(2-hydroxyethyl) terephthalate can be used as a substrate to create PET and other polymers [30]. The focus is mainly on new trends of glycolysis reactions, as this process is more advantageous from the economical point of view than other kinds of chemolysis. The companies such as “Eastman Kodak“, “Goodyear“, “Du Pont“, “Zimmer“ use mainly glycolysis for PET recycling.

The glycolysis of PET has been found to depend on the reaction conditions represented in the glycolysis time, glycolysis temperature, catalyst concentration and glycol concentration.The researchers found that the sequence of the main effects on the glycolysis conversion of recycled PET is in the following descending order: catalyst concentration>glycolysis temperature>glycolysis time [27,31].

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The objective of the current paper is to realize PET chemical recycling by non-conventional methods. The depolymerization step will be realized using a glycolysis process in microwave field. This method presents certain advantages such as: energy and time saving as well as a rapid and uniform heating possibility for a complete depolymerization in the absence/presence of the catalyst. Using microwave irradiation a homogenous reaction mixture can be attained more easily due to a highly efficient heat transfer. This last aspect is of high importance in the recycling step, more precisely in the reutilization of the obtained oligomers. In the ideal case, depolymerization can lead to the obtaining of the monomer. Our team attained this result by using a microwave field to conduct the reaction and by selecting the optimal parameters for the process.

Experimental part

Materials and methods

In the round bottom glass flask of 500 mL with which the microwave reactor was equipped, the selected PET amount was introduced. This solid PET samples were added in the reaction in two varieties:

-as small pieces, with almost granular characteristic, obtained by industrial recovering of post-consumer PET bottles (designed as G);

-as small, plane pieces with rectangular shape with a diagonal of around 10-12 mm, resulted by manual cutting of same PET raw material (designed as B).

The selected amounts of glycol and the catalyst were added to the PET samples. Then, the flask was introduced in the microwave oven and equipped with the condenser followed by nitrogen purging for elimination of the oxygen. Nitrogen bubbling was conducted for 10 min prior to the installation starting of the reaction by activation of the command key (3), respectively the switch (4), and using the timer (2) the reaction time was set. The controller (5) and the gage (6) allowed the control of the microwave field power at which the reaction mixture was exposed.

All the reactions were performed at glycol boiling temperature. The reaction was considered completed when no visual decrease of PET mass could be detected. Usually this coincided with a complete dissolution and/or glycolysis of more than 95% of the initial PET and was considered as conversion degree of the process.

As a result of reaction progress, the pieces of PET are transferred to the glycol by dissolution and by glycolysis with the formation of oligomers presenting molecular weights lower than the starting material. After the reaction time elapsed, the reaction mixtures were allowed to cool to temperature lower than 100°C and filtered, for unreacted PET elimination, and analyzed.

The microwave reactor set-up is presented in figure 1 and comprises the following principal elements:

a)Microwave generator with controllable power settings (lower part);

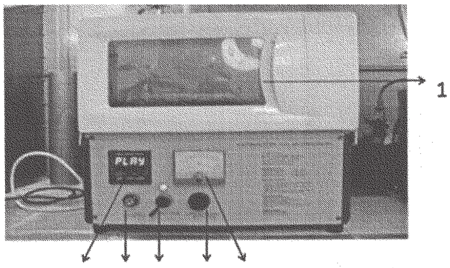


Figure 1 Microwave oven reactor components: 1) reaction cavity and reaction vessel; 2) timer (time controller); 3) command key; 4) on/off switch; 5) power setting handle; 6) power reading gage

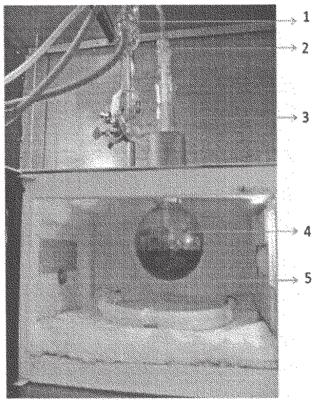


Figure 2 Reaction cavity and experimental set-up: 1) condenser; 2) nitrogen bubbler; 3) ramification equipped with glass-joints; 4) reaction vessel 0.5 L; 5) microwave cavity.

b)Microwave reaction cavity and reaction vessel.

The reaction cavity and experimental set-up are presented in figure 2.

The post-consumer PET bottles solvolysis reactions and analysis involved the use of the following materials:

·Glycols: monoetylene glycol (MEG), diethylen glycol (DEG), monopropylene glycol (MPG) and dipropylene glycol (DPG)

·Catalyst: zinc acetate

The PET glycolysis reaction was monitored determining the following characteristics of the reaction product:

a) conversion of PET (percent degradation) was calculated using the equation:

$x=[(G_i - G_f)/G_i] \times 100$, where G_i-the initial mass and G_f-final mass of PET involved in the reaction;

b) dynamic viscosity of the product was determined using a Brookfield viscometer. Two analysis were performed, one at product unloading (using spindle 62, 30 rpm) and one after 24 h (using spindle 63, 50 rpm). The determinations were realized at ambient temperature, the spindles and the rotation speed were selected in order to cover a wide range of viscosities;

c) kinematic viscosity was determined using an Ubbelohde viscometer, size 3 with a constant of k=4.2852 at 50°C;

d)Visual inspection of the product.

Results and discussions

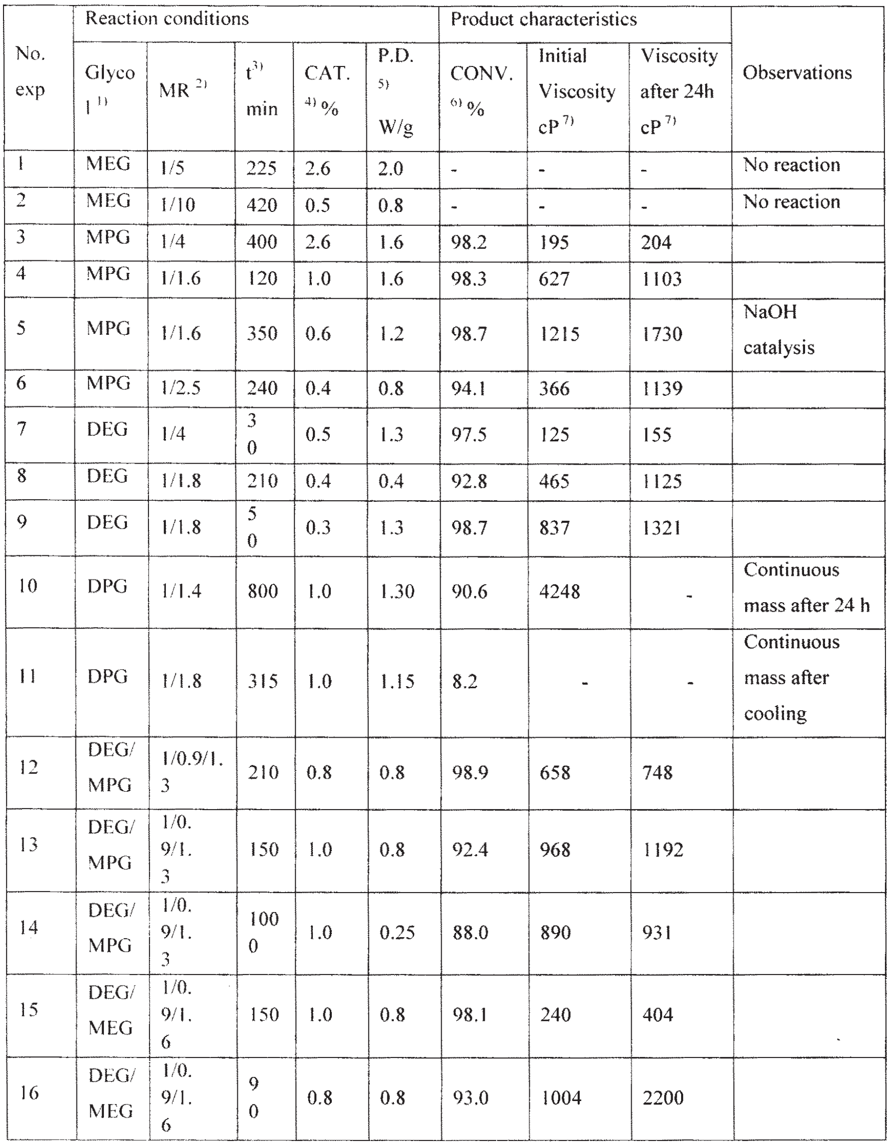
After a literature data study, the catalyst selected for the solvolysis reaction was zinc acetate - $Zn(CH_3COO)_2$. The choice was justified in part by the reported performances in conventional glycolysis and in part by the affordable price range; stringent requirements for an industrial application of the process [7].

In order to determine the type of glycol best suited for the glycolysis process, a series of experiments employing four glycols, two presenting only primary hydroxyl groups (MEG and DEG) and two having primary and secondary hydroxyl groups (MPG and DPG isomeric mixture). Also, based on literature data, the use of different mixtures of glycols was investigated in several experiments [28].

In all preliminary experiments, type B PET raw material was used (resulted by manual cutting of PET bottles). Part of the results of these experiments is presented in table 1. The data presented represents the average value of two distinct experiments.

The analysis of the presented data affords the following observations:

- in the case of MEG, the solvolysis does not take place despite the use of high molar ration glycol/PET, catalyst and long reaction time. The explanation consists in the fact that all the experiments were conducted at atmospheric pressure; the installation did not allow a procedure under pressure. In these conditions the reflux



No. exp	Reaction conditions					Product characteristics			Observations
	Glycol [1]	MR [2]	t [3] min	CAT. [4] %	P.D. [5] W/g	CONV. [6] %	Initial Viscosity cP [7]	Viscosity after 24h cP [7]	
1	MEG	1/5	225	2.6	2.0	-	-	-	No reaction
2	MEG	1/10	420	0.5	0.8	-	-	-	No reaction
3	MPG	1/4	400	2.6	1.6	98.2	195	204	
4	MPG	1/1.6	120	1.0	1.6	98.3	627	1103	
5	MPG	1/1.6	350	0.6	1.2	98.7	1215	1730	NaOH catalysis
6	MPG	1/2.5	240	0.4	0.8	94.1	366	1139	
7	DEG	1/4	30	0.5	1.3	97.5	125	155	
8	DEG	1/1.8	210	0.4	0.4	92.8	465	1125	
9	DEG	1/1.8	50	0.3	1.3	98.7	837	1321	
10	DPG	1/1.4	800	1.0	1.30	90.6	4248	-	Continuous mass after 24 h
11	DPG	1/1.8	315	1.0	1.15	8.2	-	-	Continuous mass after cooling
12	DEG/MPG	1/0.9/1.3	210	0.8	0.8	98.9	658	748	
13	DEG/MPG	1/0.9/1.3	150	1.0	0.8	92.4	968	1192	
14	DEG/MPG	1/0.9/1.3	1000	1.0	0.25	88.0	890	931	
15	DEG/MEG	1/0.9/1.6	150	1.0	0.8	98.1	240	404	
16	DEG/MEG	1/0.9/1.6	90	0.8	0.8	93.0	1004	2200	

Table 1
PET GLYCOLYSIS EXPERIMENTAL DATA

Notes: [1]MEG monoethylene glycol; MPG-monopropylene glycol; DEG – diethylene glycol; DPG-dipropylene glycol.
[2] molar ratio PET/glycol; [3] reaction time; [4] catalyst, weight percent ratio compared to PET;
[5] power density of the microwave field.
[6] Conversion of PET (percent degradation) was calculated using the equation: $x=[(G_i - G_f) / G_i]\,x100$, where G_i-the initial mass and G_f-final mass of PET involved in the reaction; [7] Dynamic viscosity of the product was determined using a Brookfield viscometer. Two analysis were performed, one at product unloading (using spindle 62, 30 rpm) and one after 24 h (using spindle 63, 50 rpm). The determinations were realized at ambient temperature, the spindles and the rotation speed were selected in order to cover a wide range of viscosities.

temperature of the glycol is 195°C insufficient for glycolysis activation;

- in the case of MPG, the solvolysis took place in all cases with a reasonable reaction time (environ 2 h) for a catalyst concentration and microwave power density at the upper limit of the studied domain. In this case a molar ration PET/MPG 1/1.6 affords a conversion of over 98% (experiment 4);
- the best results were obtained using DEG, thus a conversion of over 95% was obtained for a reaction time of around 1 h although low glycol and catalyst ratio, a condition being the microwave power density setting at relatively high values (experiment 9);
- DPG presents relatively low reactivity insufficient for further development of unsaturated polyester resins. Even the product initially solubilized, after 24 h is transformed to a waxy mass;
- in the case of glycol mixtures, at a PET/glycol weight ratio of 1/1, a decrease of reaction rate is registered. This can be explained by the decrease in reaction temperature: the boiling points for the components are DEG 245°C, MEG 195°C, MPG 188°C. The most promising result can be considered experiment 13, which would allow the obtaining of polyester oligomers with an increased flexibility thanks to the DEG component and a higher compatibility with styrene due to the MPG constituent.

In general, the results presented in table 1 confirm the reactivity order suggested in [32-33] DEG>>MPG> DPG>MEG. Based on these results, DEG was selected for further experiments. Thus, the conversion being dependent on the reaction conditions: PET/glycol ratio, reaction time, microwave power density and catalyst amount; further experiments were aimed at determining optimal parameters for the reaction. These results will be discussed in the following sections.

Parameters systematic study

The parameters systematic study involved the study of parameters such as PET/DEG molar ratio, catalyst amount, microwave power density and reaction time on the process parameters (reaction rate and conversion) as well as product characteristics (initial viscosity and viscosity after 24 h).

No. exp.	Molar ratio PET/DEG		Reaction time [min]	Initial viscosity[cP]	Viscosity after 24h [cP]
1	1/5	0.20	30	77	90
2	1/4	0.25	30	125	139
3	1/3	0.33	35	256	256
4	1/2	0.50	40	538	815
5	1/1.8	0.55	60	823	1212
6	1/1.5	0.66	120	1584	2135

Table 2
REACTANTS MOLAR RATIO
INFLUENCE ON THE SOLVOLYSIS
PROCESS

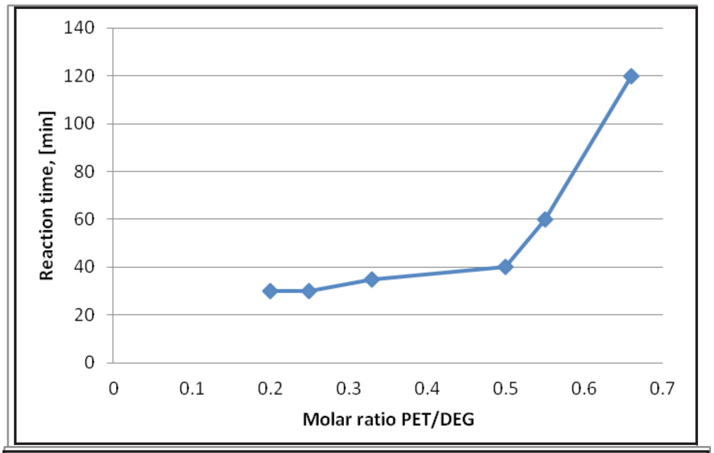


Fig. 3. Reaction time dependence on the molar ratio

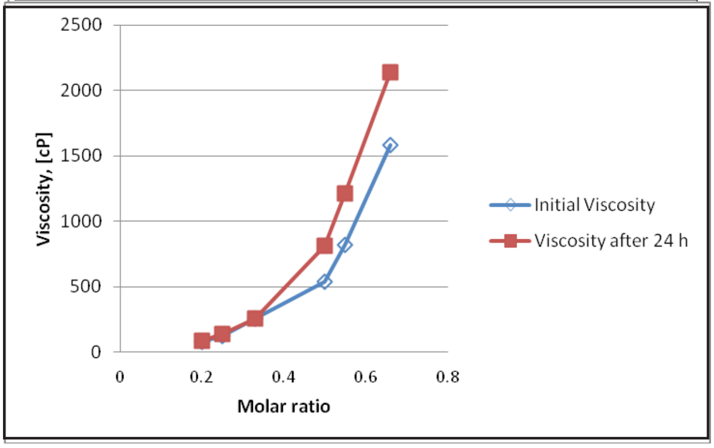


Fig. 4. Viscosity depending on the molar ratio

Influence of the reactants molar ratio

During these experiments the following parameters were kept constant: microwave power density 1.3 W/g; catalyst concentration 0.16 % weight ratio, type G PET raw material. The results are presented in table 2 and figure 3, respectively figure 4. These experiments were conducted to a conversion of 95-98%.

The presented data reflect the significant influence of the reactant molar ratio on the reaction rate as well as on the characteristics of the obtained product. These results, confirm literature data on conventional glycolysis, presenting a reaction rate directly proportional with the increase of DEG molar ratio.

The increase of viscosity (initial, respectively final) directly correlated with the reduction of glycol amount, can be explained by the decrease of unreacted glycol in the product mass so its solvent effect for the oligomers resulted from the reaction is limited and also the molecular weight of the oligomers at low molar ratio is increased.

It has to be noted that the end of the solvolysis reaction was considered when no decrease in PET amount could be observed. Since the consumption of PET raw material is due to dissolution and solvolysis process, it is not clear if the reaction time taken into consideration in these experiments is the necessary duration for reaching the equilibrium state. In order to elucidate this problem, the product resulted in the case of experiment 5, was subject, subsequently, with the addition of another 0.1% catalyst, to a second microwave irradiation with the same power density for a period of 3 h. The two viscosities revealed the same values, confirming the possibility that the consumption of all PET pieces coincides with the equilibrium state of the reaction. Nevertheless, to completely confirm this aspect, further experiments are needed such as chromatographic and mass determination analysis.

Hence the glycolysis products are characterized by instability in time, an opacifying tendency, more pronounced at low glycol quantities. For PET/DEG ratio 1/5 – 1/3, the clouding process takes place after several days whereas for lower ratio, the clouding process takes place overnight or even faster. The phenomenon can be attributed to several factors: incomplete glycolysis, recombination of polyesters oligomers resulting in higher mass products, lower solubility of oligomers on their crystallization. Upon heating the products return to transparent characteristics after which the clouding process repeats after cooling.

In all experiments presented in table 2, the conversion was situated between 97 and 98.8%. Due to economic constraints, the optimum molar ratio PET/DEG of 1/1.8 was selected, corresponding to a weight ratio between the two components of 1/2.

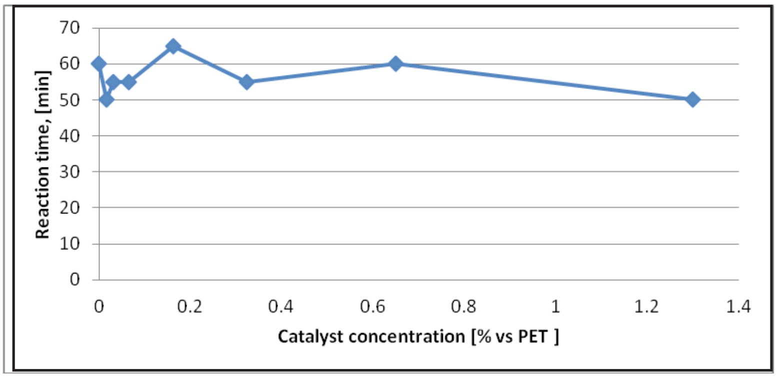


Fig. 5. Reaction time depending on the catalyst concentration

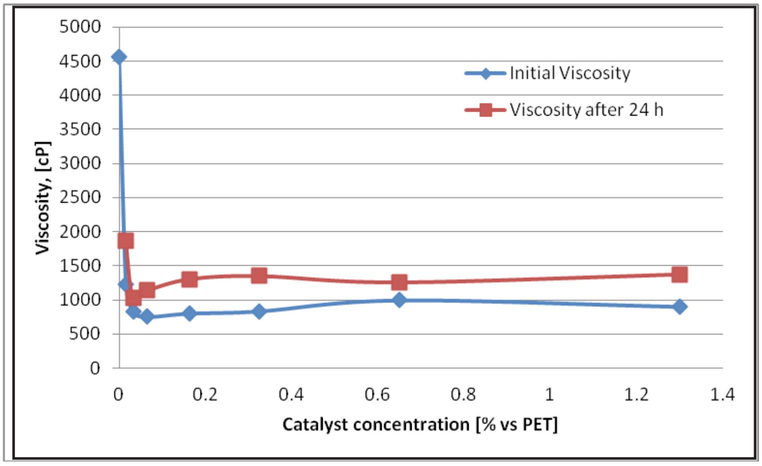


Fig. 6. Viscosity depending on the catalyst concentration

Catalyst amount influence

During these experiments the following parameters were kept constant: microwave power density 1.3 W/g; PET/DEG molar ratio 1/1.8, type B PET raw material. The results are presented in the figure 5 and 6. These experiments were conducted to a conversion of 97-98.5%, an exception being represented by the free catalyst experiment in which the conversion was 92.7%.

The catalyst concentration were: 0; 0.016; 0.032; 0.162; 0.324; 0.65; 1.3% weight ratio compared to PET amount.

The results present that the reaction time varies in an interval of 50 to 65 min, without any real modification induced by catalyst amount.

An important decrease of viscosity can be noted for the catalyst concentration domain of 0-0.032% (weight compared to PET), after which a nearly constant value is registered. In the case of 0% catalyst, the viscosity of the obtained product after 24 h could not be measured due to the fact that it became a continuous mass with waxy characteristics.

By analyzing the obtained results, we can consider a catalyst concentration of over 0.05% required in order to attain the activation of the glycolysis reaction.

Microwave power density influence

During these experiments the following parameters were kept constant: catalyst concentration 0.3 % (weight ratio vs PET); PET/DEG molar ratio 1/1.8, type G PET raw material. The results of these experiments are presented in figure 7 and table 3.

The analysis of the obtained data allows the following conclusions:

-The reaction time is drastically reduced (at less than 50%) by increasing the power density for the studied reaction conditions;

-The conversion is increased by higher microwave power density values, reaching easily 98%;

- Both viscosity measurements (initial and after 24 h) present a slight increase that can be related to the conversion variation. It is possible that the solvolysis process

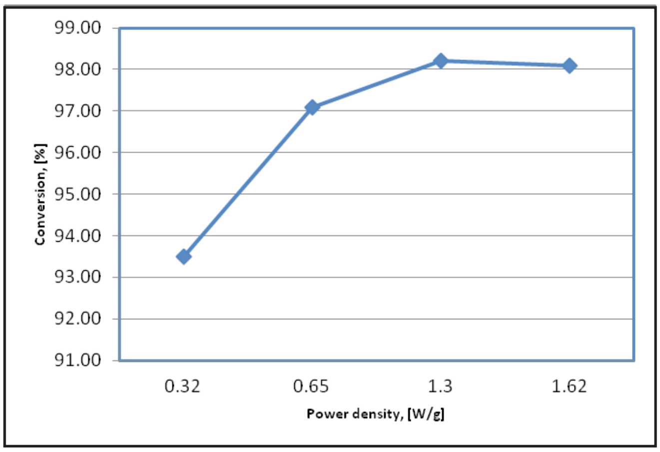


Fig. 7. Conversion depending on the microwave power density

	Reaction conditions		Product characteristics		
No. exp.	Power density [W/g]	Time [min]	Conversion %	Initial Viscosity [cP]	Viscosity after 24h[cP]
1	0.32	130	93.50	759	965
2	0.65	110	97.10	795	1193
3	1.30	60	98.20	823	1260
4	1.62	50	98.10	842	1258

Table 3
VARIATION OF PRODUCT CHARACTERISTICS DEPENDING ON MICROWAVE POWER DENSITY

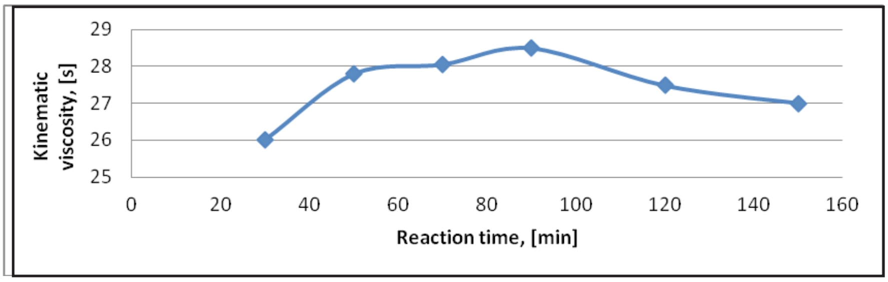


Fig. 8. Kinematic viscosity dependence on the reaction time

Characteristic	PET type G	PET type B
Reaction time (min)	60	55
Conversion (%)	98,2	98,7
Initial viscosity (cP)	823	837
Viscosity after 24h (cP)	1260	1321

Table 4
INFLUENCE OF THE PET TYPE RAW MATERIAL

to be more advanced, however for a clear determination of this aspect molecular weight measurements are needed.

Reaction time influence

As previously mentioned, we considered the solvolysis process practically finished when no decrease in PET quantity, from the reaction mixture, could be observed. Further glycolysis after this point (see experiment 5 - Influence of the reactants molar ratio), revealed that after an additional 2h reaction time, the value of the dynamic viscosity did not change sustaining the hypothesis that the attaining of the equilibrium state prior to the second reaction time period. Thus, the first considered reaction time was sufficient.

To further study this aspect kinematic viscosity measurements (using an Ubbelohde viscometer) were realized at different time intervals. The measurements were realized at 50°C in order to maintain a homogenous mixture by avoiding the clouding of the samples. The experiment was realized using the optimal parameters resulted from the systematic studies:

-PET/DEG 1/1.8 molar ratio;

-Microwave power density 1.3 W/g;

-Catalyst concentration 0.3% weight ration compared to PET.

The results of the measurements are presented in figure 8.

An increase in kinematic viscosity for the time interval 30-90 min was registered, followed by a decrease in the next hour. This behaviour can be explained as an initial diffusion of PET into de glycol solution leading to higher viscosity values (the first sample was taken at a conversion close to 90%). The resulting oligoesters from the glycolysis reaction presenting a lower mass than PET, the decrease in kinematic viscosity is correlated with the progress of the reaction.

Using figure 8, the optimal reaction time for the given parameters should be 60 min , which corresponds to the consumption of PET raw material from the mixture.

The duration of the process was longer than reported data in the literature for glycolysis in a microwave field [34], but slightly lower than in the case of conventional methods. This increase in reaction time can have several explanations:

a) the reported reactions were carried out in monomod installations, whereas in this case the reaction was carried out in a multimod reactor [34];

b) our study utilized a reaction scale of hundred grams whereas the literature data present the scales in the order of several grams mostly a dozen [34].

The glycolysis reaction was carried out as previously mentioned on two types of PET wastes:

- as small pieces, with almost granular characteristic, obtained by industrial recovering of post-consumer PET bottles (designed as G);
- as small, plane pieces with rectangular shape with a diagonal of around 10-12 mm, resulted by manual cutting of same PET raw material (designed as B).

Between the two varieties of PET there are slight differences in the progress of the reaction and on the characteristics of the final product. Data from a compared experiment are presented in table 4.

The acceleration of the solvolysis process (50 min compared to 60 min) and the insignificant conversion increase are explained by the fact the PET glycolysis is a process governed in the first stage by the dissolution of PET; type B raw material has a surface area higher and thus more susceptible for a glycol attack. The viscosity modification is unimportant.

Conclusions

A microwave reactor was used to study the depolymerization of PET and an investigation of the process parameters was realized. In terms of glycol type and molar ratio, the best results were obtained using a PET/DEG molar ratio of 1/1.8, thus a conversion of over 95% was obtained for a reaction time of around 1 h at an optimal catalyst amount of 0.3% (weight ratio compared to the PET amount), respectively 0.16 % (weight ratio as regard to the mixture). The reactivity order of the studied glycols was DEG>>MPG>DPG>MEG.

The study of microwave field power influence revealed that the reaction time can be drastically reduced (at less than 50%) by increasing the power density for the studied reaction conditions and the conversion can be increased by higher microwave power density values, reaching easily 98%.

An influence of PET particles size was observed using two types of raw material, and the reduction of reaction time in the case of type B raw material can be explained by its higher surface area which makes it more susceptible for a glycol attack. The diffusional parameter of the PET glycolysis process is very important and the microwave field for large scale applications can increase reactor efficiency.

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