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Simple and convenient method of chemical recycling of poly(ethylene terephthalate) by using microwave radiation

Summary — Microwave assisted ester bond breaking of poly(ethylene terephthalate) (PET) to tere-phthalic acid (TPA) was performed by using glycerin, diethylene glycol (DEG) or monoethanolamine (MEA) as transesterification reagents and KOH or NaOH as the catalysts and results were compared with PET degradation by conventional heating method. Comparisons of reaction times showed significant enhancement of reaction rates in the microwave assisted experiments in comparison with the process going with use of conventional heating. In addition, collected data cleared the intense dependence of the recycled TPA recovery on the catalyst concentration and the minimum time observed for 1.3 mol L^{-1} of KOH and 1.9 mol L^{-1} of NaOH, respectively.
Key words: poly(ethylene terephthalate), microwave radiation, chemical recycling, depolymerization, terephthalic acid.

PROSTA I DOGODNA METODA CHEMICZNEGO RECYKLINGU POLI(TEREFTALANU ETY-LENU) Z ZASTOSOWANIEM PROMIENIOWANIA MIKROFALOWEGO
Streszczenie — Przedmiotem badań była degradacja poli(tereftalanu etylenu) (PET) do kwasu terefta-lowego (TPA) prowadzona pod wpływem mikrofal (MW). Jako czynniki solwolizujące stosowano glicerynę, glikol dietylenowy (DEG) lub monoetanoloaminę (MEA), a katalizatorem był wodorotlenek sodu bądź potasu. Przebieg takiego procesu porównano z przebiegiem rozpadu PET w warunkach ogrzewania konwencjonalnego (tabele 1—3). Wykazano, że czas potrzebny do całkowitej degradacji polimeru z wykorzystaniem MW jest wielokrotnie krótszy. Zbadano również wpływ mocy promieniowania MW oraz stężenia katalizatorów na szybkość przebiegu omawianego procesu (rys. 1—5). Skuteczniejszym katalizatorem okazał się wodorotlenek potasu: minimalny czas niezbędny do całkowitego odzyskania TPA z PET odpowiada stężeniu KOH wynoszącemu 1,3—1,5 mol/l a NaOH — 1,9 mol/l.
Słowa kluczowe: poli(tereftalan etylenu), promieniowanie mikrofalowe, recykling chemiczny, depolimeryzacja, kwas tereftalowy.

The consumption of poly(ethylene terephthalate) (PET) has increased in the recent years and caused demand for effective utilization of PET waste. In this area, the main driving force responsible for the increased recycling of post consumer PET is its widespread uses, particularly in the beverage industry, which has made PET the main target for plastics recycling.

Chemical recycling of PET wastes to the versatile intermediates constitutes effective resource utilization, because the processes are applicable without substantial waste formation. One of the most common processes of PET chemical recycling is hydrolysis of ester bonds at acidic or basic media [1]. In such conditions of hydrolysis process, PET is depolymerized to terephthalic acid (TPA) and ethylene glycol (EG) [2—11]. Depolymerization of PET in non-aqueous alkaline media is analogous

to the base hydrolysis reactions and TPA salt is recovered in significant yields [12, 13].

The main purpose of use of microwave energy is decreasing the reaction time and greater convenience. Recently, rapid PET depolymerization using microwave (MW) radiation was described, by using methanol or glycols as solvolytic reagents in a closed reactor under elevated pressures [14, 15]. Liu and coworkers investigated the effect of crystallinity on PET depolymerization under MW radiation and found the crystallinity of PET decreasing during the hydrolysis reaction [16]. In addition, in these reactions it has been proved that after 35 min 99.9 % of PET is decomposed in a microwave assisted process in ethylene glycol media and different catalysts have been used in PET hydrolysis reactions [17, 18].

As well as the glycolysis process that is the object of many research studies, it has been tried to determine the

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optimum reaction time and find most useful catalysts [14, 15, 19, 20]. It is worth to mention that hydrolysis process can also run under microwave radiation [21].

Jeziorska has been studied reactive extrusion of polyamide/PET wastes derived from post consumer carpets [22].

In our previous work [23] some low-boiling monofunctional alcohols as reagents, namely methanol, ethanol, 1-butanol, 1-pentanol, and 1-hexanol in the presence of different simple basic catalysts (potassium hydroxide, sodium hydroxide, sodium acetate, zinc acetate) under normal pressure in PET chemical recycling were used. In continuation of this previous work, now we applied high-boiling reagents, namely diethylene glycol (DEG) as a diol, monoethanolamine (MEA) as an aminoalcohol or glycerin as a triol in PET chemical recycling, catalyzed by KOH or NaOH.

EXPERIMENTAL

Materials

Commercial PET flakes (3 mm × 3 mm) were used in recycling process without any purification. All destroying reagents, namely glycerin, DEG or MEA, were purchased from Iranian Petrochemical Company. Potassium and sodium hydroxides (Merck, Germany) were used as catalysts in all experiments. For titration of unreacted KOH or NaOH from the reaction mixture, standard HCl (37 %) solution was diluted to 0.2 N.

General procedure

Degradation experiments were performed using a Mileston Ethos 1600 microwave system at atmospheric pressure.

In a typical recycling process, base catalyst (1.25 mmol) was dissolved in the destroying reagents, namely glycerin, DEG or MEA (7.0 ml) and followed by addition of PET flakes (1.0 g). All reactions were performed in a three-necked flask equipped with a condenser, thermometer and magnetic stirrer at different microwave powers in the range 500—1000 W. MW radiation was programmed for defined reaction times and to avoid over oxidation reactions, the reaction mixture was cooled rapidly by immersing the flask into the crushed ice water, and quenched by pouring into the distilled cold water (100 ml). To determine the consumed KOH or NaOH for hydrolysis reaction — which is equivalent to disodium or dipotassium terephthalate (TPA-Na$_2$ or TPA-K$_2$) salts — the remained bases were titrated by HCl solution. The reaction mixture was filtered to remove residual unreacted PET flakes and the filtrate was acidified by excess of HCl to crystallize terephthalic acid from liquid phase. Finally TPA was characterized by spectroscopy methods and data were compared to authentic samples.

Methods of testing

^{1}H NMR and ^{13}C NMR spectra were obtained using a BRUKER DRX-300 AVANCE instrument, with d$_6$-DMSO as a solvent and TMS as an internal standard. FT-IR spectra were recorded by a BOMEM MB-100 spectrometer.

RESULTS AND DISCUSSION

In order to study the effect of MW radiation (500—1000 W) in PET chemical recycling, a series of experiments were performed by using at first glycerin as a destroying reagent in combination with sodium or potassium hydroxides. In one set of reactions NaOH was used as the catalyst and irradiations followed for complete PET dissolution. By increasing of MW power, the required time for complete PET dissolution reduced from 750 s to 150 s at 950 W (Fig. 1). Another set of reactions was done by using KOH as the catalyst instead of NaOH. The results show the better performance of glycerin/KOH system under MW radiation in PET glycolysis — required time for complete PET dissolution were reduced at defined MW power in comparison with glycerin/NaOH system. Namely, the total required time for complete recovery of TPA from PET structure was 135 s at 950 W.
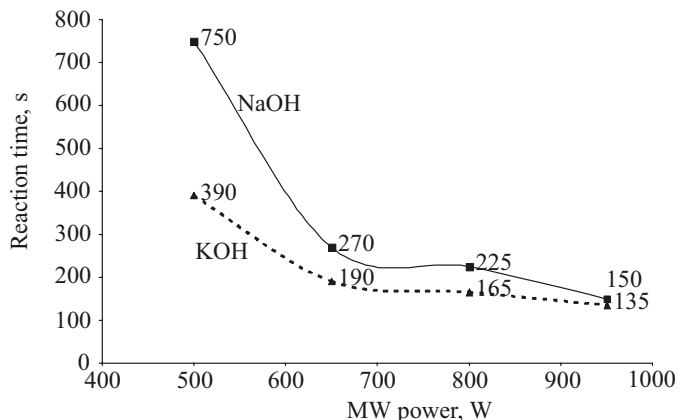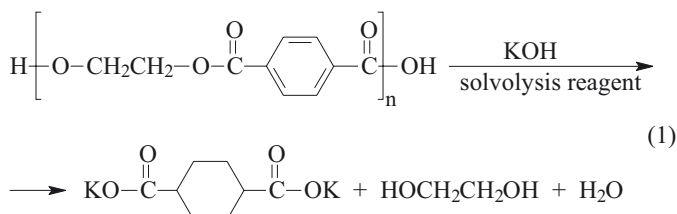

Fig. 1. Reaction times for complete degradation of PET at various MW radiation doses in glycerin/KOH or glycerin/NaOH systems

As a typical experiment, PET was recycled by using glycerin/KOH system at 650 W and the data were compared with the results obtained with use of conventional heating method. As shown in the Table 1, the data get at conventional heating show an additional required time (835 min) for incomplete PET recycling (47.4 %) in comparison with required the much shorter reaction time (190 s) for complete PET recycling (*i.e.* TPA recovery) under MW radiation.

Complete PET dissolution as well as breaking of ester bonds of PET chains in the presence of glycolysis agents and a base catalyst is shown in equation (1).

T a b l e 1. Comparison of PET depolymerization processes by MW radiation at 650 W and conventional heating at 160 °C in glycerin/KOH system (1 g of PET and 0.5 g of KOH)

Heating method	Reaction time	TPA yield mol %	Unreacted PET mol %
MW	190 s	90.2	0
Thermal	853 min	47.4	34

$$H \left[O\text{—}CH_2CH_2\text{—}O\text{—}\overset{\overset{O}{\|}}{C}\text{—}\bigcirc\text{—}\overset{\overset{O}{\|}}{C} \right]_n OH \xrightarrow[\text{solvolysis reagent}]{KOH}$$

$$\longrightarrow KO\text{—}\overset{\overset{O}{\|}}{C}\text{—}\bigcirc\text{—}\overset{\overset{O}{\|}}{C}\text{—}OK + HOCH_2CH_2OH + H_2O$$

(1)

Fig. 3. Reaction time for complete degradation of PET at various MW radiation power, in KOH/MEA and NaOH/MEA systems

The reaction (1) mechanism is the same in both processes, with use of microwave or conventional heating methods.

As shown in the reaction scheme the main product is TPA salt, which is converted to TPA by treatment with an acid. The results of TPA characterization by spectroscopic methods were as follows:

^{1}H NMR (δ, ppm): 2.60 (d_6-DMSO), 3.30 (H_2O as impurity), 7.90—8.10 (aromatic ring protons, s, 4H), 12.0—14.0 (carboxylic acid protons).

^{13}C NMR (δ, ppm): 41.0 (d_6-DMSO), 132 (unsubstituted aromatic ring carbons), 137 (*ipso* carbons — attached aromatic carbons to carboxylic acid groups), 168 (carbonyl groups of carboxylic acid functional group).

IR (KBr, cm^{-1}): 1287 (carboxylic acid C-O stretching vibration), 1600 (aromatic C=O), 1689 (carboxylic acid C=O stretching vibration), 3000 (OH stretching vibration).

All these spectroscopy data were comparable with those authentic sample data [23].

Figure 2 illustrates the results of DEG efficiency in depolymerization reaction of PET. Comparison of the results obtained wit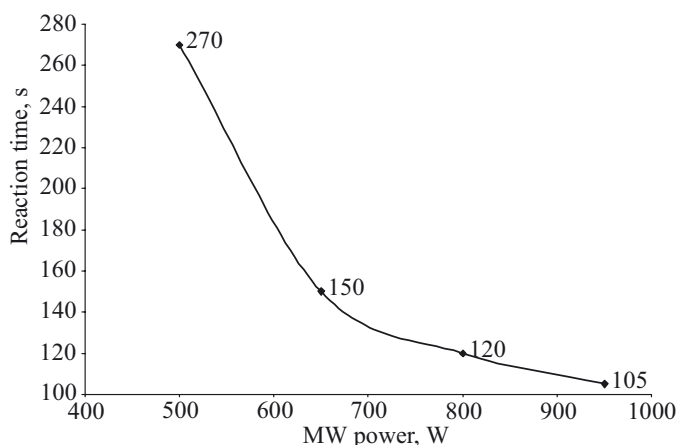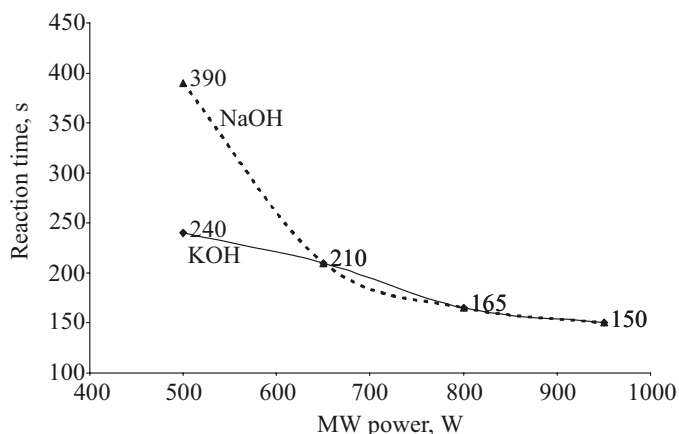h glycerin or DEG solvents (NaOH as a catalyst) showed the better effectiveness of DEG. The reason is probably higher degree of freedom in DEG molecules.

As shown in the Fig. 3, MEA also acts as effective destroying reagent in combination with base catalysts used by us. And also here, as in a case of glycerin, the faster is degradation in the presence of KOH.

In all studied solvolysis systems, the degradation reactions were performed faster in MW assisted processes than in those carried out by conventional heating (Tables 1—3).

T a b l e 2. Comparison of PET depolymerization processes by MW radiation at 650 W and conventional heating at 160 °C in DEG/NaOH system (1 g of PET and 0.5 g of KOH)

Heating method	Reaction time	TPA yield mol %	Unreacted PET mol %
MW	150 s	90.2	0
Thermal	101 min	90.2	0

T a b l e 3. Comparison of PET depolymerization processes by MW radiation at 800 W and conventional heating at 120 °C in MEA/KOH system (1 g of PET and 0.5 g of KOH)

Heating method	Reaction time	TPA yield mol %	Unreacted PET mol %
MW	165 s	90	0
Thermal	21 min	90	0

The next step of work was investigation of the effect of catalyst concentration on the course of the process, in the presence of different solvolysis agents. Typical reactions were performed with use of DEG/NaOH or glycerin/KOH systems at 650 W of MW power (Fig. 4).

Results showed that with increasing concentration of KOH or NaOH the reaction time is decreased and minimized for 1.3 mol L^{-1} of KOH and 1.9 mol L^{-1} of NaOH.

Fig. 2. Reaction times for complete degradation of PET at various MW radiation doses in DEG/NaOH system
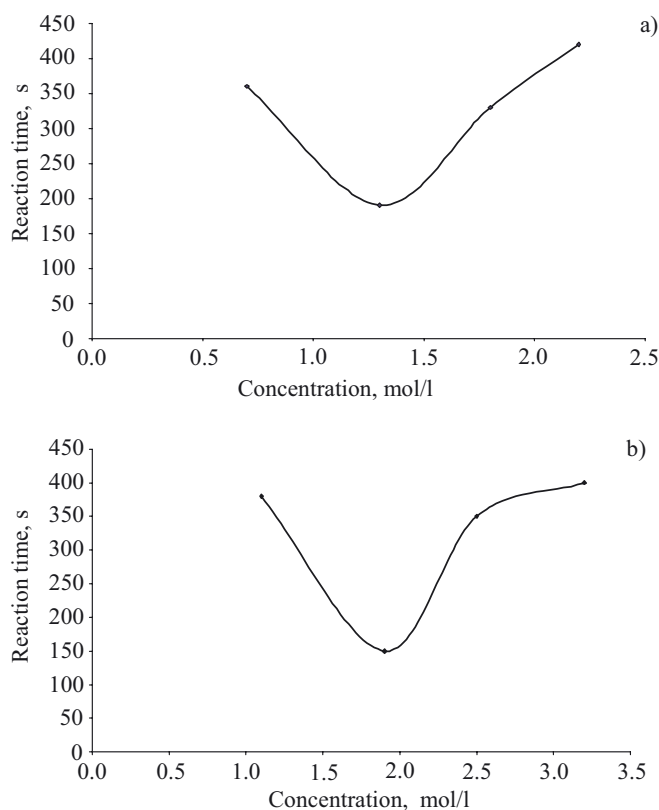
Fig. 4. Effects of NaOH or KOH concentrations on time to complete degradation of PET, in KOH/glycerin (a) and NaOH/DEG (b) systems at 650 W of MW power

The further decrease in reaction rate may be attribute to the increase in viscosity of the solution as well as difficulties in the removal of disodium or dipotassium terephthalate from the flake surface [12, 13].

The results obtained with MEA as solvolysis agent were the same as for glycerin/KOH and DEG/NaOH systems. As shown in Fig. 5, the optimum conditions for complete TPA recovery in this case are *ca.* 1.5 mol L^{-1} of KOH. As for use of glycerin or DEG also here, and for the same reasons, the time required to complete PET degradation increased for larger amounts of KOH.
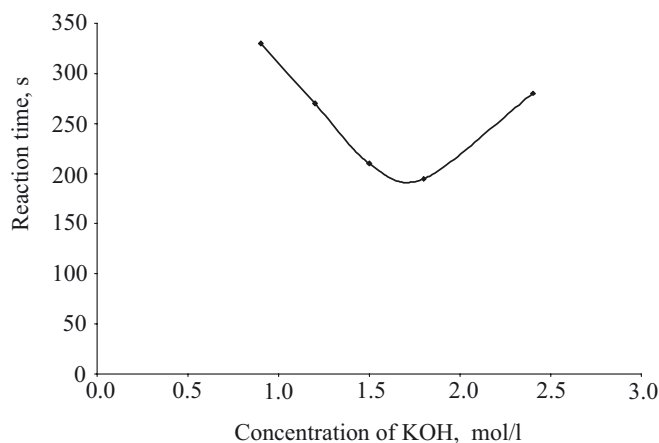

Fig. 5. Effect of KOH concentration on time to complete degradation of PET in MEA at 650 W of MW power

CONCLUSION

Microwave radiation as the energy source in alkali--decomposition of PET resulted in shorter reaction time for complete PET degradation in comparison with conventional heating method. Results showed the efficiency of glycerin, DEG or MEA as destroying agents in combination with sodium or potassium hydroxides as catalysts. The dependence of recycled TPA yield on the catalyst concentration shows the minimal times to complete the degradation correspond to 1.3—1.5 mol L^{-1} of KOH and 1.9 mol L^{-1} of NaOH. KOH appeared to be more efficient catalyst of PET degradation process studied.

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