Effect of quaternary ammonium salt as a phase transfer catalyst for the microwave depolymerization of polyethylene terephthalate waste bottles

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ABSTRACT

Poly(ethylene terephthalate) (PET) obtained from waste bottle product was depolymerized under microwave irradiation in open vessel equipment. PET bottle was shredded and ground to <0.5 mm particle size and subjected to basic hydrolysis to terephthalic acid (TPA) and ethylene glycol using 10% NaOH under the influence of microwave irradiation (200 W) in the presence of quaternary ammonium salt as a phase transfer catalyst (PTC). The effect of irradiation time, base concentration, particle size, PTC quantity, and microwave irradiation power on the extent of depolymerization was investigated. Results show that the optimum conditions to give ~99% of TPA were 10% NaOH, 60 min, 200 W power, and 3% wt./wt. PTC/PET. This process is viable economically and interesting, since that PTC could be recovered and the side products after acidification are glycol and sodium chloride.

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1. Introduction

Polyethylene terephthalate (PET) is one of the versatile engineering plastics that is widely used in manufacturing of packaging containers (bottles, jars, and tubes), semi-rigid sheet for thermoforming (trays and blisters) and high-strength fibers (audio and video tubes) [1–4]. PET production is growing rapidly, and the world's annual consumption amounts to 13 million tons [5].

PET plastic is non-degradable in ecosystem or take a long time to decompose, possibly up to hundreds of years [6]. Therefore, PET waste quantities are increasing dramatically. So PET recycling is very important, firstly, to reduce waste volume and keep the ecosystem and secondly to recover and utilize its starting monomers. Chemical recycling is one of the most important processes leading in total depolymerization of PET to terephthalic acid and ethylene glycol or partial depolymerization to oligomers and other chemical substances. There were several chemical processes for PET depolymerization that have been reported such as hydrolysis, aminolysis, and alcoholysis [7–12]. Most of these reactions need a high reaction temperature and pressure or cost chemicals. Other methods employed different types of catalysts such as metal acetate, titanium phosphate, solid super acid, metal oxide, carbonate, and so on [13–15]. Recently, phase transfer catalyst agents, which facilitate organic reactions in two immiscible phases, were studied to depolymerize PET in an alkaline solution medium [16–23].

Microwave irradiation was also used as a rapid heating method for the synthesis and recycling of plastics and ceramic powders (PVC, PS, PEO, PA, PE, PET, and ABO3) [24–27].

In order to develop a more convenient hydrolytic method for PET, we examined the depolymerization of PET in alkaline solution in the presence of phase transfer catalyst under microwave irradiation technique.

2. Materials and methods

Post consumer soft drink PET bottles were used as starting materials to produce different PET particle sizes (<0.5 to >2 mm), with number-average molecular weight of 30,000 [28] using rotary grinder (FZ 102 microplant grinding machine) and several sieves. The phase transfer catalysts (PTCs), tetrabutyl ammonium iodide (TBAI) (≥98.0%) and standard terephthalic acid (98%) were purchased from Aldrich. Other chemicals used were of reagent grade. Melting point was obtained on a Gallenkamp melting point apparatus. FT-IR spectrums (KBr) were recorded on a Shimadzu 8261 PC spectrophotometer. Elemental analysis (C.H.N) was performed on a Perkin 240 C Elemental Analyzer. Uwave-1000 Microwave Reactor Oven (SINEO Microwave Chemistry Technology Co. Ltd.) was used for the depolymerization process.

2.1. Hydrolytic depolymerization

To study the optimum conditions for the hydrolytic depolymerization of PET, a series of reaction experiments was carried out under microwave irradiation technique. The microwave reactor was a multimode system operating at 2.45 GHz. The reaction

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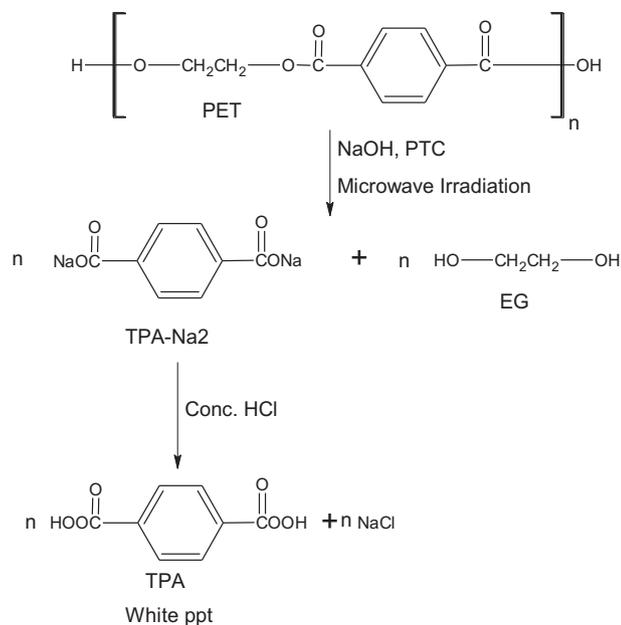
Scheme 1. Hydrolytic depolymerization reaction of PET.

was preceded in a 100 mL Pyrex round-bottom flask equipped with reflux condenser. The reaction was heated only by microwave irradiation and the temperature was monitored along the reaction and evaluated by an infrared detector, which indicated the surface temperature. All reactions were magnetically stirred all along the irradiation to provide a good homogeneity (power and temperature).

The reactions also included the study of the effect of NaOH concentration, percentage of PTC, reaction time, particle size of PET powder and microwave power effects.

2.2. General procedure

To 3 g of grinded PET powder, an aqueous sodium hydroxide solution (50 mL) and an appropriate quantity of PTC were added in a one necked 100 mL round-bottom flask. The reaction was carried out in the microwave reactor with continuous stirring. At the end of the reaction, unreacted residue was filtered, and the filtrate was acidified by conc. HCl to give a solution with white precipitate. The precipitate was washed with water, dried and identified by FT-IR and melting point measurements as terephthalic acid (TPA).

The carboxylic acid concentration in the solid product was determined by potential titration [29]. A total of 25 mL of DMSO was used as the solvent, in which 0.1–0.2 g of solid product was dissolved. The solution was titrated with 0.1 N potassium hydroxide/ethanol solutions at room temperature. The purity of (TPA) was also investigated by FTIR and (C.H.N.) analysis.

3. Results and discussion

Waste PET was depolymerized to disodium terephthalate (TPA-Na$_2$) and ethylene glycol (Scheme 1) by alkaline hydrolysis (NaOH) under microwave irradiation in the presence of phase transfer catalyst. This TPA-Na$_2$ was protonated to terephthalic acid (TPA) by hydrochloric acid.

The above reaction has a solid organic phase (PET) and an aqueous liquid phase (NaOH solution), so the phase transfer catalyst (PTC) works with interfacial mechanism [18]. The first stage includes formation of metal carbanion (MR) at the interface of organic and aqueous phases followed by the extraction of (MR) species from the interface into the organic phase by the action of PTC to produce reactive intermediate (RQ) as shown in Scheme 2.

In this way, the ester linkage in the PET macromolecule became easier to attack by the hydroxyl ion (OH$^-$) and the depolymerization is accelerated (Scheme 3). The terephthalate anion formed returns to the aqueous phase and produce the TPA-Na$_2$ salt. The reaction proceeds until depolymerization completes, while the catalyst remains in the aqueous phase.

It seems that this catalyst plays an important role in the reaction kinetics. The increase in the phase transfer catalyzed reaction rate was related mainly to the greater value of the pre-exponential factor (A) [22]. The purity of TPA formed was confirmed by the FTIR technique. The FTIR spectrum of the TPA product (Fig. 1) shows the same characteristic bands when compared with reference FTIR spectrum of terephthalic acid. The characteristic bands at 2500–3250 cm^{-1}, 1685 cm^{-1} and 1574–1425 cm^{-1} are related to carboxylic group, carbonyl group, and aromatic ring respectively. These results show good agreement with the reference data, indicating that the purity of the product in the mentioned method is acceptable. In addition, the melting point of the obtained TPA was in agreement with that of standard TPA.
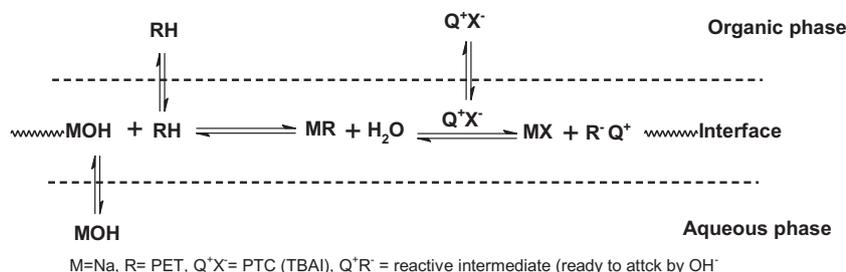
Elemental analysis (C.H.N.) also proved the purity of the obtained TPA. All the element compositions were found to be the same as those of TPA within experimental errors (0.1% for hydrogen and 0.2% for carbon). Moreover, the titration for the solid product showed that the acid concentration of the solid product was also close to the value of TPA, 12.1 mmol/g of TPA. These results indicate that TPA was the solid product obtained after acidification with high purity.
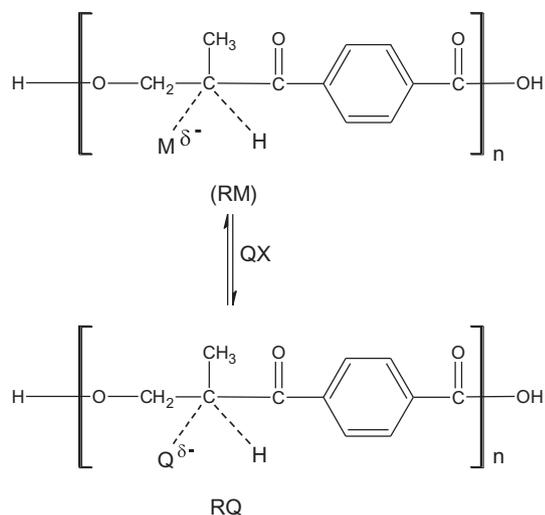
The % yield of TPA was calculated using the formula:

$$\text{TPA yield } (\%) = \frac{\text{Wt. TPA}}{\text{Wt. TPA}_0} \times 100$$

where wt. TPA: weight of TPA produced experimentally from the hydrolytic depolymerization of PET. wt. TPA$_0$: weight of TPA (theoretically) that could be obtained from complete depolymerization of PET. wt. of TPA$_0$ was calculated as follows:

$$\text{wt. TPA}_0 \text{ in PET} = \frac{\text{wt. of PET used}}{\text{Mwt. of PET}} \times \text{Mwt. of TPA} \times \text{No. of repeating units}$$

M=Na, R= PET, Q$^+$X$^-$= PTC (TBAI), Q$^+$R$^-$ = reactive intermediate (ready to attck by OH$^-$

Scheme 2. Interfacial mechanism.

(RM)

QX

RQ

RQ intermediate, ready to attack by hydroxyl ion

Scheme 3. Formation of reactive intermediate (RQ).

$$\text{No. of repeating units} = \frac{\text{Mwt. of PET}}{\text{Mwt. of repeating unit}}$$

The optimum base concentration that gives the highest yield of TPA was investigated using 5, 10 and 15% w/v of NaOH. The highest yield was obtained with 10% w/v NaOH as shown in Fig. 2, above that concentration the yield decreased, which may be due to the reverse reaction toward the formation of ester.

It was also found that as the particle size of ground PET decreased, the rate of depolymerization increased, Fig. 3 illustrates this effect. With a particle size of <0.5 mm the rate is maximum compared to that with a larger particle size (0.5–2 mm and >2 mm). A smaller particle size provides a larger contact surface area, which accelerates the formation of polar reactive intermediate RQ that promotes higher microwave absorption and heat transfer inside the reaction mixture that would accelerate the entire hydrolytic reaction. Therefore, the heating rate, maximal reaction temperature, and mass reduction ratio were all increased. For a smaller particle size, the satisfactory microwave power could be lowered.

The influences of microwave power on hydrolysis reaction were examined and the temperature was monitored along the reaction, as shown in Fig. 4. A great increase in PET conversion with increasing microwave power was observed. At 200 W (90 °C), the PET conversion is only 98% after 1 h. However, under the given conditions, when the power was increased to 400 W (98 °C), this allows a higher level of microwave power to be directly administered to the reaction mixture, the hydrolysis of PET conversion was gradually increased to 100%. Since microwave energy is transferred into the sample much faster than molecular kinetic relaxation occurs, this will increase sample heating rate [25]. The best power that we choose for the optimum condition was 200 W to avoid overheating that could be occurred with a higher microwave power.
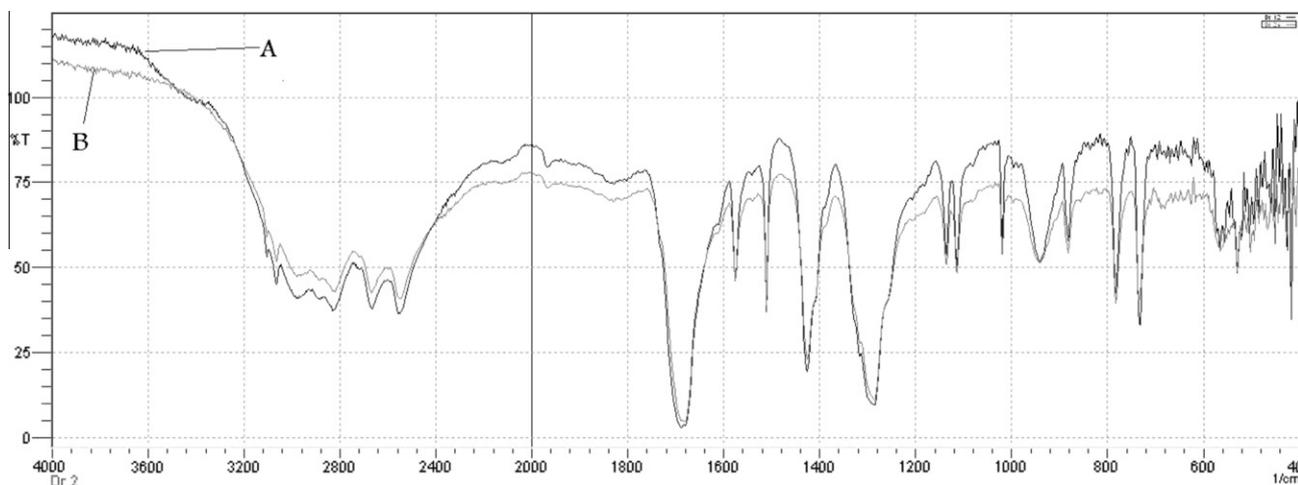

Fig. 1. FT-IR spectra of standard TPA (98%) (A) and TPA obtained from hydrolytic depolymerization reaction (B).
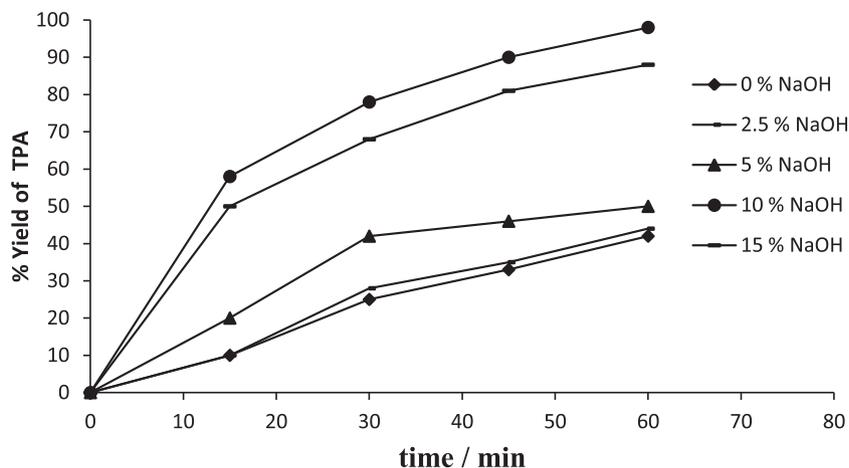

Fig. 2. Effect of NaOH concentration on PET depolymerization using 3% TBAI (wt. TBAI/wt. PET) and 200 W microwave power.
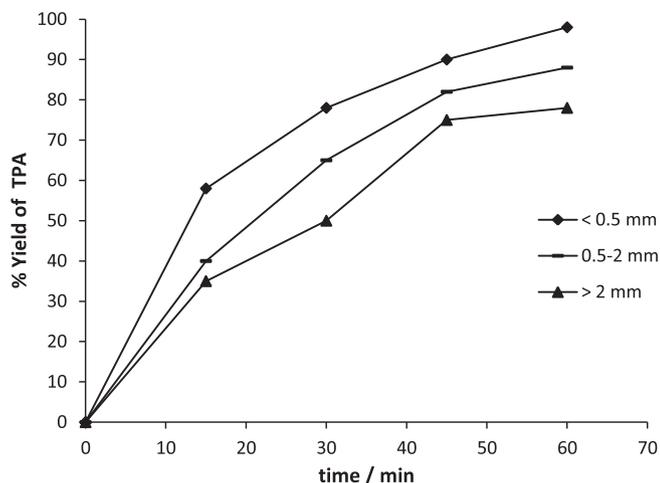
Fig. 3. Effect of PET particle size distribution on PET depolymerization using, 50 mL of 10% NaOH and 200 W microwave power, 3% wt./wt. PTC (wt. TBAI/wt. PET).
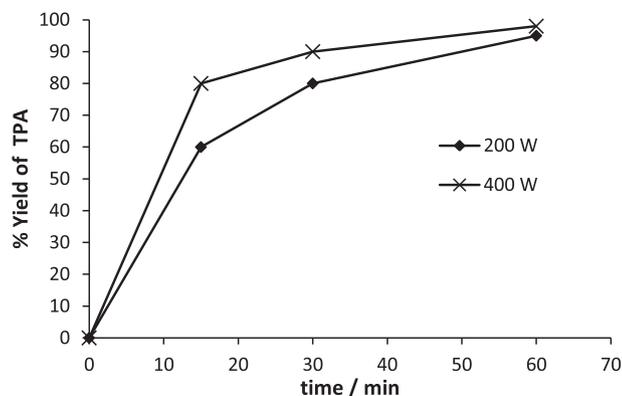

Fig. 4. Effect of microwave power on the TPA% 50 mL NaOH 10% 60 min, time 3 g PET(<0.5 mm particle), and 3% (wt. TBAI/wt. PET).
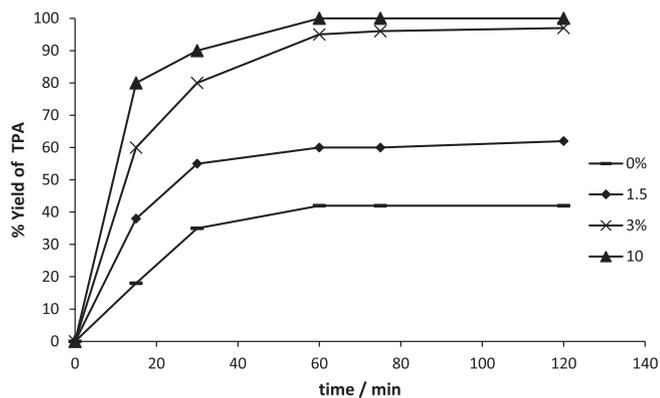

Fig. 5. Effect of TBAI wt.% on the yield TPA% in the product mixture 50 mL of 10% NaOH, 60 min, 3 g PET(<0.5 mm particle size), and 200 W microwave power.

The reaction was examined over time by calculating the TPA wt.% formed to determine the optimum time at which the reaction is almost finished. It was found that the reaction time depends on PTC concentration, as shown in Fig. 5. The higher concentration of PTC will produce more reactive intermediate RQ (Scheme 2), consequently the reaction will be faster.

4. Conclusion

The present work confirms the special efficiency of coupling PTC conditions and MW activation for the aqueous depolymeriza-tion of PET in the presence of NaOH. The process could be described as an ecofriendly method for the recycling of PET.

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