# Hydrolytic Depolymerization of Poly(ethylene terephthalate) Under Microwave Irradiation

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**ABSTRACT:** This article covers the depolymerization of poly(ethylene terephthalate) (PET) under microwave irradiation in neutral water. The reaction was carried out in a sealed reaction vessel in which the pressure (or temperature) was controlled. The hydrolytic product contained terephthalic acid, ethylene glycol, and diethylene glycol characterized by IR spectrometry and gas chromatography. The undepolymerized PET was identified by gel permeation chromatography. Both the yield of terephthalic acid and the degree of PET depolymerization were seriously influenced by pressure (or temperature), the weight ratio of water to PET, and the reaction time. The applied irradiation power had little influence on the degree of PET depolymerization. With a pressure of 20 bar (temperature = 220°C), a reaction time of 90–120 min, and a weight ratio of water to PET of 10:1, the PET resin was depolymerized completely. The molecular weight and the molecular weight distribution indicated that the hydrolytic depolymerization of PET obeyed the regular chain-scission mechanism to some extent. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 719–723, 2005

**Key words:** polyesters; degradation; gel permeation chromatography (GPC)

## INTRODUCTION

The chemical recycling of waste plastics has received much attention by some scientists as a means of obtaining valuable products. The processes for the chemical recycling of waste poly(ethylene terephthalate) (PET) are mainly divided into (l) methanolysis, (2) glycolysis, (3) hydrolysis, (4) supercritical methanolysis, and (5) supercritical hydrolysis. Growing interest has been focused on the process development of the hydrolytic depolymerization of PET, in which terephthalic acid (TPA) and ethylene glycol (EG) are recovered and can be directly used in the synthesis of virgin PET.[1–4]

Microwave irradiation has been successfully applied to a number of classical reactions. The main advantage of microwave irradiation as an energy source in PET solvolysis and polyamide-6 depolymerization is its short reaction time.[5,6] In this study, microwaves were applied to PET hydrolytic depolymerization. There was no catalyst or acid or base added, and there was no need for complex treatment of the products.

## EXPERIMENTAL

### Materials

Pure PET resin was obtained in the form of fiber-grade commercial chips supplied by LiaoYang Petrol Chemical Fiber Co. (LiaoYang City, People's Republic of China). The intrinsic viscosity (IV) of PET was 0.642 dL/g [measured in a 60/40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25°C], corresponding to a viscosity-average molecular weight of 18,912, which was calculated from the following equation: $IV = 7.55 \times 10^{-4} \ M^{0.685}$.[7] There was 0.9% diethylene glycol (DEG) in the resin. The water we used was of high purity and was prepared by third distillation; the other reagents were of analytical grade.

### Hydrolytic depolymerization

The hydrolytic depolymerization experiments were carried out in an ETHOS 900 microwave oven equipped with temperature and pressure sensors that could be inserted directly into the sealed 100-mL polytetrafluoroethylene reaction vessel. A typical sample in the experiments contained 2.0 g of PET chips and 20 mL of distilled water, which were put in the reaction vessel without stirring. In the closed system, the vessel was sealed and the experiment conducted. At the end of the reaction time, the reaction vessels were taken from the oven, and the closed vessels were put in a

cold-water bath to be cooled for about 15 min. The solid product was then separated from the solution by filtration; washed with cold water (0–5°C) to remove any residual water-soluble components, such as EG monomer; then dried at 45°C *in vacuo* to a constant weight; and weighed ($w_1$). The solid was dissolved in a 10% potassium hydroxide solution; TPA dissolved in the solution was separated from the solid remainder of PET by filtration. Sulfuric acid was added to the filtrate, and solid TPA was precipitated and separated again by filtration, washed with water, dried at 45°C *in vacuo* to a constant weight, and weighed ($w_2$). The solid residue was dried to a constant weight ($w_3$) as mentioned previously and then dissolved in methanol to dissolve low molecular esters; the solid was precipitated, separated, and dried as mentioned previously.

### Analysis of the results

The reaction extent was calculated as follows:

Degree of PET depolymerization (%)

$$= \frac{\text{Weight of PET depolymerized to TPA and EG}}{\text{Weight of PET charged}}$$

$$\times 100\% = \frac{w_0 - w_3}{w_0} \times 100\% \quad (1)$$

Yield of TPA (%)

$$= \frac{\text{Weight of the actual TPA monomer}}{\text{Theoretic output}} \times 100\%$$

$$= \frac{w_1 - w_3}{w_{TPA,0}} \times 100\% \quad (2)$$

where $w_0$ and $w_3$ are the initial and the final weights of PET, respectively, and $w_{TPA,0}$ is the theoretical weight of TPA.

### Characterization

The IV and molecular mass of the residue of PET were determined as described previously. Gel permeation chromatography (GPC) (Waters Model Alliance GPC V2000) was used to determine the molecular weight distribution. The sample was dissolved in an *o*-dimethylphenol/chloroform solvent system, a chloroform system, at 40°C.

The solid product of complete hydrolytic depolymerization was TPA, which was characterized by IR spectrometry.

EG that remained in the solution was characterized by gas chromatography (GC). The liquid sample (0.1 $\mu$L) was injected into a capillary gas chromatograph, coupled with an AutoSystem XL chromatographic data processor (GC) (Perkin Elmer Model AutoSystem XL), a column packed with nitroterephthalic acid modified polyethylene glycol; the components were carried by nitrogen at a flow rate of 1 mL/min and detected with a flame ionization detector. The temperatures of the detector and injector compartment were 280 and 290°C, respectively.

## RESULTS AND DISCUSSION

### Effects of the reaction parameters

A series of PET hydrolytic experiments under microwave irradiation were performed to determine the effects of the weight ratio of water to PET, pressure, irradiation time, and applied irradiation power on the degree of depolymerization. The effects of the reaction conditions are shown in Table I.

First, the weight ratio of water to PET was examined. According to the literature, although PET undergoes hydrolytic depolymerization at high temperatures or in supercritical methanol, the degree of PET depolymerization increases with increasing hydrolysis solvent.[1,8] In this reaction, we increased the proportion of water further. The effect of the weight ratio of water to PET on depolymerization at an irradiation power of 600 W, a pressure of 15 bar, and a reaction time of 120 min is shown in Figure 1. With increasing ratio of water to PET, the depolymerization degree of PET increased when the ratio of water to PET was less than 10 and decreased when the ratio was above 10:1. The results indicate that when the reaction time was 120 min, the pressure was 15 bar, the microwave irradiation power was 600 W, and the ratio of water to PET was 10, optimal depolymerization results were obtained. This implies that under the reaction conditions, there existed an optimal weight ratio of water to PET of 10:1 in our experiments.

Pressure has a strong influence on the reaction; the pressure dependence of the degree of hydrolytic depolymerization at an irradiation power of 600 W, a weight ratio of water to PET of 10:1, and a reaction time of 120 min is shown in Figure 2. The change in the degree of hydrolytic depolymerization of PET from 21.56% to complete depolymerization was achieved by an increase in pressure from 10 to 20 bar. When the reaction pressure was lower than 20 bar, even longer reaction times did not result in the complete depolymerization of PET.

Plots of the degree of PET depolymerization versus reaction time at different depolymerization pressures are shown in Figure 3. The depolymerization degree increased slowly with increasing reaction time from the very beginning of the reaction and then increased sharply as the reaction proceeded; finally, it reached an equilibrium state. When the reaction pressure was 15 bar and the reaction time was just over 100 min, the degree of PET depolymerization reached a constant

**TABLE I**
**Experimental Conditions of the Hydrolytic Depolymerization of PET**

| Run | Water/PET | $P$ (bar) | $t$ (min) | Power (W) | Degree of PET depolymerization (%) | TPA yield (%) |
|---|---|---|---|---|---|---|
| 1 | 5 | 15 | 120 | 600 | 75.54 | 75.82 |
| 2 | 8 | 15 | 120 | 600 | 80.24 | 79.15 |
| 3 | 10 | 15 | 120 | 600 | 84.39 | 84.09 |
| 4 | 15 | 15 | 120 | 600 | 72.35 | 73.14 |
| 5 | 20 | 15 | 120 | 600 | 45.18 | 44.78 |
| 6 | 10 | 10 | 120 | 600 | 21.56 | 21.82 |
| 7 | 10 | 13 | 120 | 600 | 34.52 | 34.59 |
| 8 | 10 | 18 | 120 | 600 | 95.42 | 95.40 |
| 9 | 10 | 20 | 120 | 600 | 100.00 | 100.00 |
| 10 | 10 | 15 | 50 | 600 | 2.82 | 2.80 |
| 11 | 10 | 15 | 60 | 600 | 10.47 | 11.04 |
| 12 | 10 | 15 | 70 | 600 | 30.20 | 31.15 |
| 13 | 10 | 15 | 80 | 600 | 45.74 | 44.87 |
| 14 | 10 | 15 | 90 | 600 | 75.31 | 75.69 |
| 15 | 10 | 15 | 100 | 600 | 82.50 | 83.27 |
| 16 | 10 | 15 | 120 | 600 | 84.39 | 84.09 |
| 17 | 10 | 20 | 50 | 600 | 9.64 | 10.15 |
| 18 | 10 | 20 | 60 | 600 | 69.36 | 70.61 |
| 19 | 10 | 20 | 70 | 600 | 93.85 | 94.15 |
| 20 | 10 | 20 | 90 | 600 | 99.03 | 98.94 |
| 21 | 10 | 20 | 120 | 600 | 100.00 | 100.00 |
| 22 | 10 | 15 | 120 | 200 | 84.94 | 84.70 |
| 23 | 10 | 15 | 120 | 400 | 84.33 | 84.00 |
| 24 | 10 | 15 | 120 | 600 | 84.39 | 84.09 |
| 25 | 10 | 15 | 120 | 800 | 84.24 | 83.80 |

$P$ = reaction pressure; $t$ = reaction time.

value. The higher the pressure was, the faster the degree of PET depolymerization increased. When the pressure was 20 bar, the degree of PET depolymerization increased by 84.2% in a reaction time interval of 20 min (from 50 to 70 min); whereas when the pressure was 15 bar, within the same reaction time, the degree of PET depolymerization increased only by 27.4%. To determine the influence of the reaction conditions clearly, a reaction pressure of 15 bar was chosen in our experiments.

The influence of the applied irradiation power on the depolymerization at a pressure of 15 bar, a weight ratio of water to PET of 10:1, and a reaction time of 120 min is summarized in Table I (runs 22–25). The applied irradiation power had little influence on the degree of PET depolymerization. However, the microwave irradiation power influenced the time needed for heating the reactor to the set reaction temperature, as shown in Figure 4. The time needed for heating the reactor to the set reaction temperature decreased with increasing irradiation power from 4.1 min at 200 W to 1.6 min at 800 W. The difference was 2.5 min, compared with the whole reaction time of 120 min; this time difference could be neglected, and it did not have much effect on the degree of PET depolymerization.

## Analyses of the depolymerized product and the depolymerization mechanism

The product of PET depolymerization carried out at a microwave irradiation power of 600 W, a weight ratio
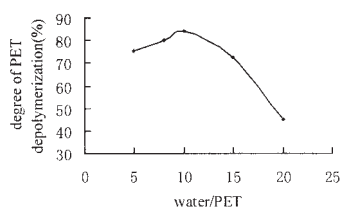


**Figure 1** Effect of the weight ratio of water to PET on the degree of PET depolymerization at a pressure of 15 bar, a microwave irradiation power of 600 W, and a reaction time of 120 min.
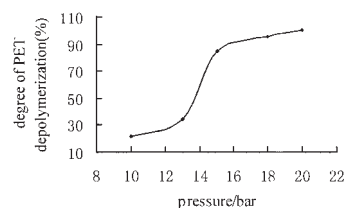


**Figure 2** Effect of the reaction pressure on the degree of PET depolymerization at a microwave irradiation power of 600 W, a weight ratio of water to PET of 10:1, and a reaction time of 120 min.
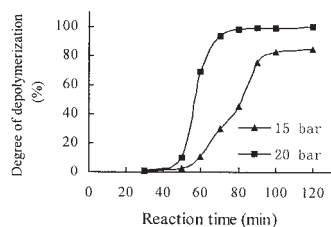
**Figure 3** Effect of the reaction time on the degree of PET depolymerization at a constant pressure, a microwave irradiation power of 600 W, and a weight ratio of water to PET of 10:1.

of water to PET of 10:1, a pressure of 20 bar, and a reaction time of 120 min was analyzed by IR spectrometry, which is shown in Figure 5. The IR spectrum indicates the presence of TPA according to the Sadtler Standard Infrared Grating Spectra (15,694 K). There was a C=O stretching band at 1686.77 cm$^{-1}$ and absorption peaks at 1283.33 and 1423.33 cm$^{-1}$ show to a —COOH group. There was an absorption peak for an —OH group at 2543.1 cm$^{-1}$, and absorption peaks at 1573.52 and 1509.19 cm$^{-1}$ proved the benzene.

The product in the filtrate was analyzed by GC (Fig. 6). The temperature of the column was 100–250°C (20°C/min). The peak at a retention time of 1.6 min was EG, and that at 2.62 min was DEG. A trace amount of DEG was found in the solution. This was due to a 0.9%(wt) concentration of DEG in the PET charge.

The results of the IR and GC spectra indicate that under suitable degradation conditions, the PET resin could be depolymerized to TPA and EG. To determine the nature of the hydrolytic depolymerization mechanism, the concentration of EG in the aqueous phase was monitored by GC for an initial charge ratio of l0 g of water/g of PET. The results show that the bulk of EG monomer appeared relatively late in the reaction, which indicates a random chain scission mechanism according to PET hydrolytic depolymerization at high temperature.

The average molecular weights [number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$)] of the recovered PET of Figure 3 (15 bar)
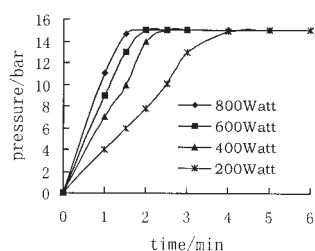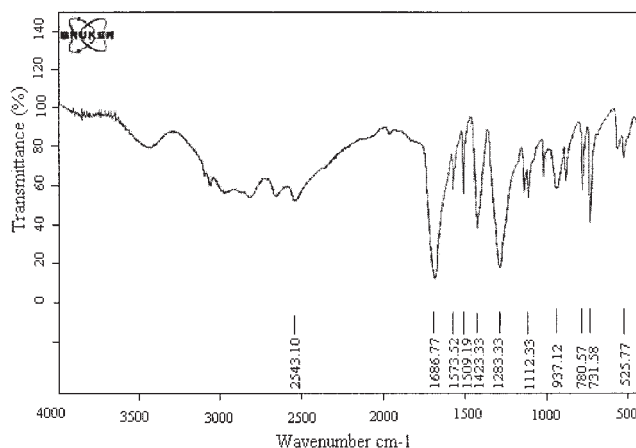


**Figure 5** IR spectrum of the solid product.

were analyzed by GPC, as shown in Figure 7 and Table II. The average molecular weight of the initial PET charged was 14,311, and its $M_w/M_n$ was 1.799 [Fig. 7(a)]. After hydrolysis for 70 min, PET was disintegrated to a powder; after TPA was removed, $M_n$ of the PET residue was 2754, its $M_w/M_n$ was 1.964 [Fig. 7(b)]. As the reaction continued, the molecular weight decreased further. After 90 min, the $M_n$ of the PET residue powder was 1477, its $M_w/M_n$ was 1.645 [Fig. 7(c)]. The random chain-scission mechanism was also mentioned by Kurokawa et al.[9] They believed that methanolysis of PET took place at random positions on the polymer chain. Because as the GPC curves tailed to a low molecular weight, the PET residue showed a broad and multimodal molecular weight distribution, the peaks were assigned to the oligomers formed during the reaction. The GPC curve of Figure 7(c) was also tailed to a low molecular weight,[10] but the molecular weight distribution of the PET residue became sharp and was not a multimodal curve; the



**Figure 4** Pressure versus time of different microwave irradiation powers at the initial heating stage.
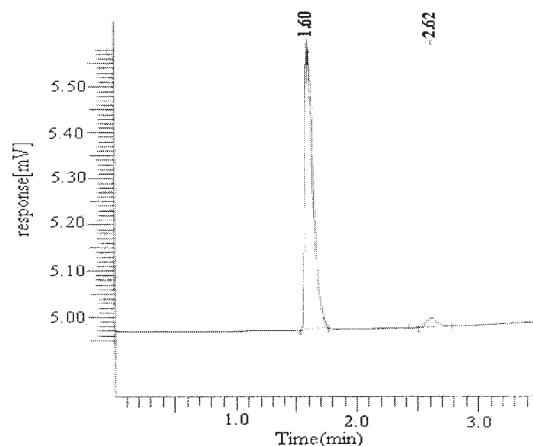


**Figure 6** GC spectrum of the liquid phase at a pressure of 15 bar, a weight ratio of water to PET of 10:1, a microwave irradiation power of 800 W, and a reaction time of 120 min.

many peaks attributed to the oligomers were not observed. So the hydrolytic depolymerization of PET obeyed the regular chain-scission mechanism to some extent.

## CONCLUSIONS

The results of this study show that the use of microwave irradiation as the energy source in PET hydrolytic depolymerization resulted in a short reaction time and a required lower reaction pressure for complete PET depolymerization. Complete depolymerization of PET to its monomer TPA and EG was achieved at a pressure of 20 bar and within 120 min in pure water without any catalyst. The degree of the depolymerization of PET increased with increasing reaction
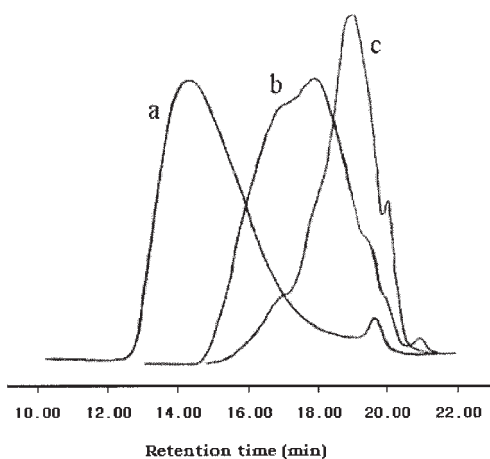
**TABLE II**
**GPC Chromatographic Results for the Solid Residue of PET**

| Sample | $M_n$ | $M_w$ | $M_w/M_n$ | Degree of PET depolymerization (%) |
|--------|-------|-------|-----------|-------------------------------------|
| a | 14,311 | 25,741 | 1.799 | — |
| b | 2,754 | 5,410 | 1.964 | 30.20 |
| c | 1,477 | 2,429 | 1.645 | 75.31 |

pressure (temperature) and reaction time, whereas the microwave irradiation power (from 200 to 800 W) had little influence on it. According to the results of our experiments, the optimal reaction conditions were a reaction time of 120 min, a pressure of 20 bar, and a weight ratio of water to PET of 10:1. The liquid and solid products of the PET depolymerization were characterized by IR spectrometry, GC, and GPC; the hydrolytic depolymerization of PET obeyed the regular chain-scission mechanism to some extent.



**Figure 7** GPC curves of the solid residue of PET at different reaction times at a pressure of 15 bar, a microwave irradiation power of 600 W, and a weight ratio of water to PET of 10:1: (a) PET initially charged, (b) a reaction time of 70 min, and (c) a reaction time of 90 min.

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