

NOTES

Hydrolysis of Waste PET by Sulfuric Acid at 150°C for a Chemical Recycling

INTRODUCTION

Recently, the disposal of waste materials has been the focus of environmental problems familiar to most people, since it is difficult to set up an intermediate treatment plant as an incinerator or the land for reclamation. Plastics contained in waste materials, such as polyethylene terephthalate (PET) bottles have been disposed by an incineration and reclamation in Japan. Also, a high transportation cost and a reduction of lifetime of the land for reclamation are serious social problems due to their large volume. Consequently, the development of a new process is expected to support social recycling for waste PET.

Chemical recycling of waste PET has been performed by methanolysis^{1,2} and glycolysis³⁻⁷ in an excess diols. However, it is said that the cost of PET produced from recycle materials is higher than that using new feeds in polymerization of PET by terephthalic acid (TPA) and ethylene glycol (EG), or dimethyl terephthalate (DMT) and EG. Puztaseri⁸ reported that TPA could be produced by dissolution of PET hydrolysis of PET in ($> 14.5 M$)

sulfuric acid. However, in this process, the recycling of concentrated sulfuric acid is impossible and large amount of sulfuric acid containing EG is disposed of.

In this work, waste PET powder was hydrolyzed to TPA and EG in relatively dilute sulfuric acid ($< 10 M$) and the sulfuric acid can be reused by recovery methods such as dialysis.

EXPERIMENTAL

PET powder of 0.1–0.3 mm was prepared from commercial PET bottles and has a number-average molecular weight of 30000. Then 0.2 g PET powder was put in 30 cm³ of H₂SO₄ in a sealed Pyrex tube and heated to 150°C for 1–6 h in an oven. After the reaction, a mixture of PET residue and TPA deposited was filtrated with a 1G-5 glass filter. TPA was separated as terephthalate from the unreacted PET by dissolving with 12 cm³ of 5 M NH₃. Then, TPA insoluble in acid solutions was precipitated again in the filtrate containing H₂SO₄. The degree of degradation of PET and yield of TPA were determined by weight. The yield of EG was measured by HPLC and the amount of total organic carbon (TOC) in the filtrates.

Journal of Applied Polymer Science, Vol. 52, 1353–1355 (1994)
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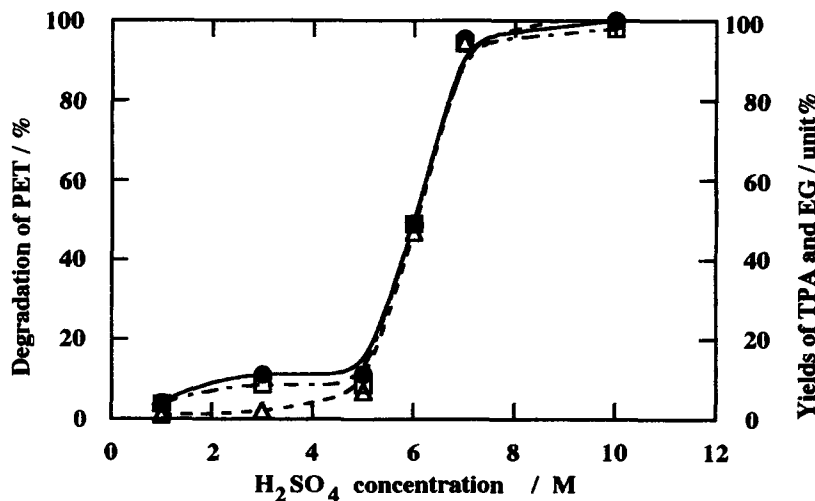


Figure 1 Effect of H₂SO₄ concentration on the degradation of PET, yields of TPA and EG at 150°C for 5 h. (—●—) degradation of PET, (---△---) yield of TPA, and, (---□---) yield of EG.

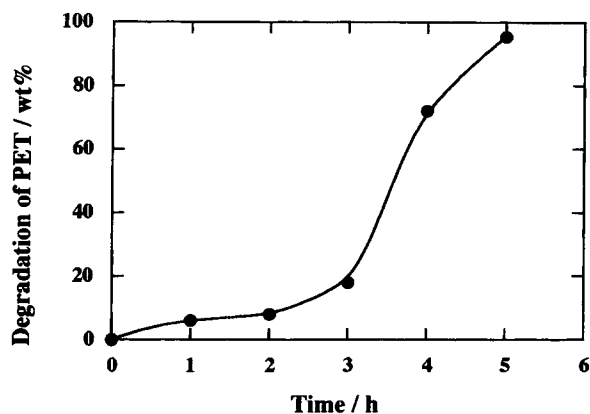


Figure 2 Effect of reaction time on the degradation of PET at 150°C in 7M H₂SO₄.

RESULT AND DISCUSSION

Effect of H₂SO₄ Concentration

Effect of H₂SO₄ concentration on the degradation of PET and yields of TPA and EG at 150°C for 5 h is shown in Figure 1. The degradation of PET and yields of TPA and EG were defined as follows:

Degradation of PET

$$= \frac{(\text{weight of PET before reaction}) - (\text{weight of PET after reaction})}{(\text{weight of PET before reaction})} \times 100 \text{ (wt \%)}$$

Table I Elemental Analysis of TPA (wt %)

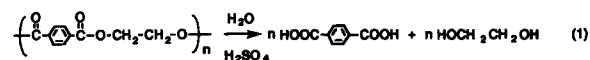
	C	H	O ^a	S
TPA (cal.)	57.83	3.61	38.56	—
TPA (obs.)	57.97	3.59	38.44	0.00

^a Difference.

$$\text{Yield of TPA} = \frac{(\text{moles of produced TPA})}{(\text{moles of TPA units in PET})} \times 100 \text{ (unit \%)}$$

$$\text{Yield of EG} = \frac{(\text{moles of produced EG})}{(\text{moles of EG units in PET})} \times 100 \text{ (unit \%)}$$

The degradation of PET was increased gradually to 5M, then rapidly increased 48.7 wt % at 6M and 95.5 wt % at 7M, and reached 100 wt % at 10M. The yield of TPA was increased linearly to 5M and then rapidly increased to 94.6 unit % at 7M then reached to 100 unit % at 10M similar to the degradation of PET. Also, the yield of EG agreed well with that of TPA. These results indicate that the hydrolysis of PET takes place according to Eq. (1).



Effect of Reaction Time

Effect of the reaction time on the degradation of PET in 7M H₂SO₄ at 150°C is shown in Figure 2. The degradation

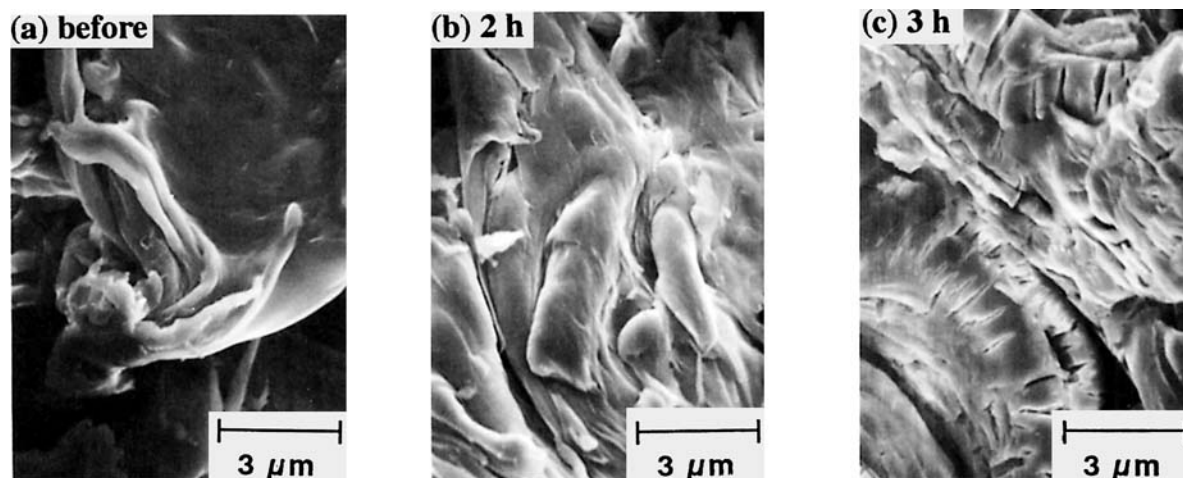


Figure 3 SEM photographs of PET powder at 150°C in 7M H₂SO₄ (a) before reaction, (b) 2 h, and (c) 3 h.

increased with an increase in time and was accelerated longer than 3 h analogously to those in Figure 1. Figure 3 shows SEM microphotographs. No particular change is observed on the PET surface until 2 h, as shown in Figures 3 (a) and (b). However, at 3 h [Fig. 3 (c)] a large number of cracks are observed on the PET surface. Generally, the rate of acid hydrolysis of esters is proportional to the product of the ester, water, and proton concentrations. In this system the ester concentration is equivalent to the surface area of PET powder. Consequently, the acceleration of degradation as Figures 1 and 2 may be brought about due to an increase in the specific surface area of PET by the formation and growth of cracks.

Characterization of Precipitated TPA

The elemental analysis of TPA obtained is shown in Table I. These are the average values in three measurements. The contents of C, H, and O (by difference) in the TPA coincided well with the calculated values, respectively. The purity of TPA produced was 100.2% by base carbon. IR spectra of TPA obtained agreed well with those of reagent-grade TPA and TPA obtained did not contain sulfur (< 0.01 wt %).

This work was supported in part by a grant-in-aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan.

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Received October 28, 1993

Accepted November 30, 1993