

# Chemical Recycling of Polyethylene Terephthalate

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## ABSTRACT

Polyethylene terephthalate (PET) is one of the most important and commercial thermoplastics polyesters which has been in the market since 1977 and it has vastly been used both in industry and household. Through chemical recycling, plastics can be converted into their primary components for use in other chemical processes under especial conditions. Polyethylene terephthalate is a thermoplastic, therefore, recycling by chemical method which converts it into primary components can be achieved. In this study the optimal routes of the existing chemical methods have been chosen. For chemical recycling, acidic hydrolysis is used and PET is converted to terephthalic acid (TPA) and ethylene glycol (EG). Effective factors in the decomposition and the yield such as acid concentration, time, temperature and PET particle size were investigated. Characterization of the products is carried out by FTIR, and the effect of reaction time on PET particles is evaluated by scanning electron microscopy.

**Key Words:** chemical recycling, polyethylene terephthalate, hydrolysis, terephthalic acid, ethylene glycol

## INTRODUCTION

In all industries, there are many wastes or off-grades, which among them the wastes of polymer industries are the most important because of their resistance to biological degradation.

Today, there are many methods for recycling of plastics waste including: mechanical recycling, burning to generate energy, and chemical recycling to convert them into intermediates, or by converting them into the primary component instead of wastes disposal.

Chemical recycling of polyethylene terephthalate (PET) is carried out by other methods including meth-

analysis [1, 2] glycolysis; ammonolysis and hydrolysis [3, 4].

For PET hydrolysis much research has been carried out in acidic environments. Puztaseri [5] studied PET hydrolysis in  $H_2SO_4$  ( $M < 14.5$ ). Sato and Yoshioka [6] also studied hydrolysis under acidic concentration ( $M < 10$ ) conditions. The yield of hydrolysis under this condition is reported up to 100%, but, this result is not always confirmed by reported experiments.

In this article hydrolytic degradations of PET powder, its conversion to terephthalic acid (TPA) and ethylene glycol (EG), and its influencing factors are

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reported.

Degradation is studied under  $H_2SO_4$  (<10M) condition and then the acid can be collected by a method such as dialysis.

## EXPERIMENTAL

### Materials

Virgin PET granules ( $\mu=0.82-0.85$  dL/mg) of Sabic Arab Saudia Co. were used.  $NH_3$  and  $H_2SO_4$  were obtained from Merck Co.

### Equipment

#### FTIR

Collected samples of TPA from hydrolysis were identified by a Philips Analytical PU9800 FTIR spectrometer (Figure 1). The samples' spectra were compared to reference spectra (Merck sample with KBr). As shown in Figure 1, the specific peaks are:  $1687\text{ cm}^{-1}$  for carbonyl group,  $3300-2700\text{ cm}^{-1}$  wide peak for OH<sup>-</sup> group,  $1600\text{ cm}^{-1}$  stretch peak for C=C, and the peak at  $781\text{ cm}^{-1}$  shows *para* position for acidic groups.

#### Scanning Electron Microscopy Study

The degradation rate of hydrolytic surface was traced by using a S-360 Cambridge, scanning electron microscope for 3 different samples (Virgin, after 3 h and after 5 h reaction) and SEMs pictures were obtained.

It was noticed that by increasing the treating time the length and width of the cracks on the PET surface are increased.

### Methods

Virgin PET powder and  $H_2SO_4$  solution in 1:15 ratio were mixed, i.e. 0.2 g powder and 30 mL  $H_2SO_4$  (1–10 M) were placed in a sealed pyrex tubes in the specified temperature ( $130-170\text{ }^\circ\text{C}$ ) at specified time (1–6 h) and the tubes were heated in an oven. After

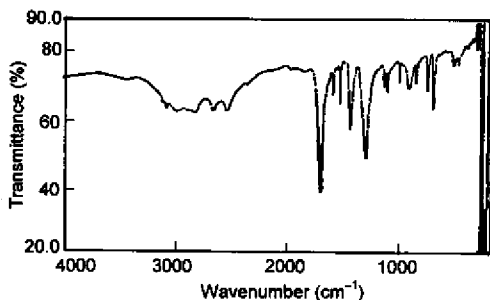


Figure 1. FTIR Spectra of terephthalic acid.

completion of the reaction, TPA and remaining PET mixture were separated from EG and  $H_2SO_4$  solution by a filter glass. TPA as terephthalate salt was separated from PET by ammonia solution of 5M, and then it was precipitated in the acidic environment.

PET segregation ratio and the acid yield were measured by gravimetric methods and were calculated by using the following equation:

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

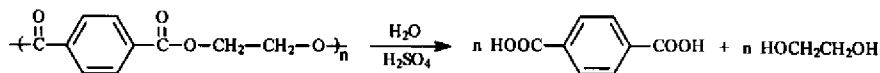
$$\text{Yield of EG} = \frac{\text{EG produced (mol)}}{\text{EG units (mol) in PET}} \times 100 (\text{unit } \%)$$

By comparison of TPA yield in specified acid concentration it was concluded that PET segregation is followed according to Scheme I [6].

## RESULTS AND DISCUSSION

### Acid Concentration Effect

Effect of acid concentration on PET degradation (at  $150\text{ }^\circ\text{C}$ , 5 h, and 0.25 mm particle size) is shown in Figure 2. It can be seen that with increasing acid concentration, degradation does not occur (1.3 % for



Scheme I

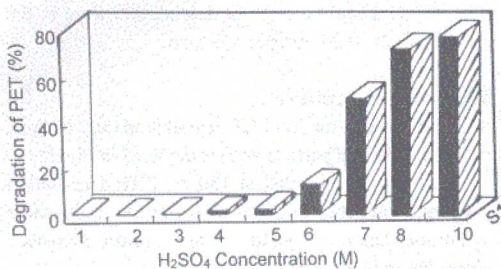


Figure 2. Effect of acid concentration on PET degradation (at 150 °C, 5 h treatment and 0.25 mm particle size).

4 m). At first, degradation is observed in 6M acid concentration (13.5 %), and a significant degradation happens in 7M acid concentration. For 9M acid concentration the degradation yield is about 80%.

#### Time Length Effect

Effect of time on PET degradation (at 150 °C, 7 M H<sub>2</sub>SO<sub>4</sub> and 0.25 mm particle size) is shown in Figure 3. It can be seen that with increasing time reaction, degradation is increased. The trend of increasing is presented in Figure 2.

Effect of time on PET degradation is followed by SEM. Degradation is started by cracking formation on surface particles. Cracks make carbonyl groups of PET in contact with H<sup>+</sup>, and so hydrolysis conditions are achieved. Figures 4a, 4b and 4c show SEM micrograph of the surface of the virgin PET particles, after 3 h and after 5 h treatment, respectively. As it can be seen, by increasing the treatment time the

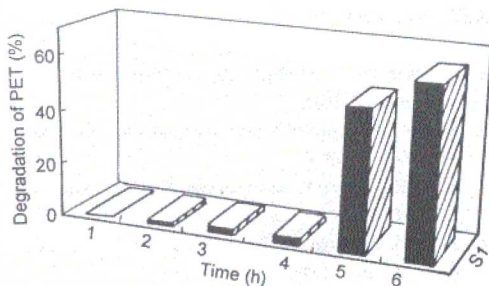


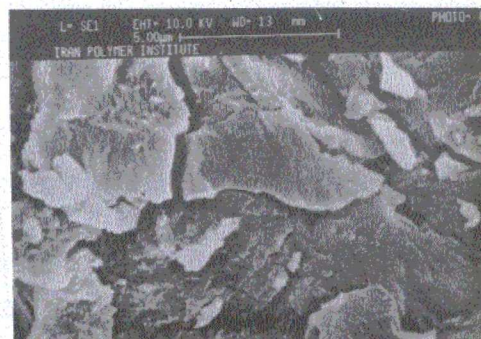
Figure 3. Effect of time duration on PET degradation (at 150 °C, 7 M H<sub>2</sub>SO<sub>4</sub> and 0.25 mm particle size).



(a)



(b)



(c)

Figure 4. SEM Micrograph of (a) virgin PET particle, (b) after 3 h, (C) after 5 h treatment.

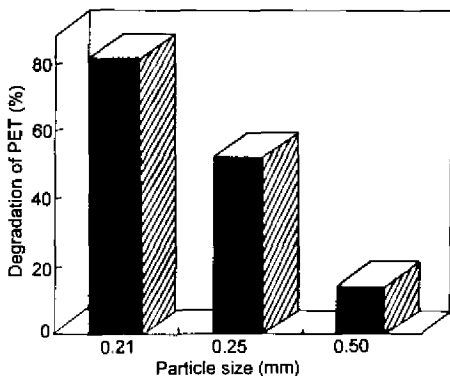


Figure 5. Effect of particle size on PET degradation (at 150 °C, 7 M H<sub>2</sub>SO<sub>4</sub> and 5 h treatment time).

cracks numbers and length of the cracks are increased.

#### Effect of Particle Size

Effect of particle size on PET degradation (at 150 °C, 7 M H<sub>2</sub>SO<sub>4</sub> and 5 h) is shown in Figure 5. As particle size decreased the yield of degradation increased and it confirmed that with greater surface contact of PET particles with H<sup>+</sup> the more hydrolysis occurred. It should be noted that the most important reason for the yield decreasing, compared to Sato's and Yoshioka's [6], is the particle size. In their study all reactions were reported for 0.1–0.3 mm particle size regardless of the weights and size distributions. The results of

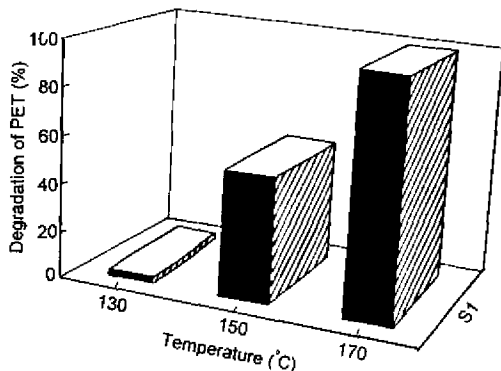


Figure 6. Effect of temperature of PET degradation (at 7 M H<sub>2</sub>SO<sub>4</sub>, 5 h and 0.25 mm particle size).

our study for rapid growth of degradation were in the range of 0.21–0.25 mm particle size.

#### Effect of Temperature

Effect of temperature on PET degradation (at 7 M acid, 5 h with 0.25 mm particle size) is depicted in Figure 6.

It can be seen that at 130 °C, PET degradation reaction, compared to upper temperature, in the same condition, has lower yield. As temperature increased degradation is increased as well.

#### CONCLUSION

Chemical recycling of PET is possible and under certain conditions PET is converted to the terephthalic acid (TPA) and ethylene glycol (EG).

There is no considerable reaction in low acid concentration. It is proposed that 7 M acid to be used, and thus acid to be reconsumed by dialysis.

To make sure that reaction would occur, we propose 5 h duration time for this purpose, because in short period (3 h) there is no sufficient time for degradation. Fine particles are best to achieve for better results in laboratory practice; therefore, we propose 0.2–0.25 mm particle size to be suitable. The main degradation results are based on increasing temperature. At 130 °C and 170 °C the yield is 0% and 100 %, respectively. At temperature range of 130–170 °C degradation rapidly increases.

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