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CHEMICAL RECYCLING OF POLY(ETHYLENE TEREPHTHALATE) USING SULFURIC ACID

Hayat TABEKH,[a] Yahia KOUDSI[a], and Zaki AJJI[b,*]

[a] Faculty of Science, Damascus University, Damascus, Syria
[b] Polymer Technology Division, Department of Radiation Technology, A ECS, P. O. Box 6091, Damascus, Syria

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Poly(ethylene terephthalate) has been hydrolyzed using commercial sulfuric acid produced by the Syrian Chemical Corporation in order to obtain the raw materials. The reaction parameters have been investigated, which affect the hydrolysis conversion such as: acid purity and concentration, reaction time, reaction temperature and PET particle size. The acid concentration plays an important role, the hydrolysis occurs with an acid concentration of 6 M, the reaction conversion increases with increasing the acid concentration until 8.5 M, and then it tends to decrease. The use of commercial sulfuric acids led to higher hydrolysis yield than the pure sulfuric acid. As expected the reaction time leads to higher conversion until achieving the equilibrium. The reaction yield is also increased with increasing the temperature of the oil bath and with decreasing the PET particle size.

INTRODUCTION

Plastics have become common materials of our everyday lives, and many of their properties, such as durability, versatility and light-weight, can be a significant factor in achieving sustainable development. So they are produced in huge amounts, 245 M tone in 2008.[1] Nationwide, six plastics account for over seventy percent of all plastics sales, low density polyethylene, poly(vinyl chloride), high density polyethylene, polypropylene, polystyrene, and poly(ethylene terephthalate).[2] However, plastic applications also contribute to the growing amounts of solid waste generated, as plastic products are often used only once before disposal. The disposal problem is not simply technical, but it also has social, economic and even political aspects.

Poly(ethylene terephthalate) (PET) is a semi-crystalline thermoplastic polyester widely used in the manufacture of apparel fibers, disposable soft-drink bottles, photographic films, etc. It is used largely in the production of textile fibers since mid-1940s.[3] The world production of PET in 2002 was 26 million tons which is expected to rise to 55 million ton in 2010.[4] In 1980s, PET also began to be used popularly for the production of disposable soft-drink bottles with a high growth rate.[5] A serious cause of concern to the environmentalists is the nonbiodegradability of PET in spite of several advantages as the nontoxic nature, durability and crystal clear transparency.[3] PET accounts for more than 8% by weight and 12% by volume of the world's solid waste.[6] Since land filling of such nonbiodegradable waste has severe limitations, chemical recycling is the best possible alternative. The major sources of PET fiber waste generation are the manufacturing waste and the post-consumer waste.[3]

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.[7] Growing interest has been focused on the process development of the hydrolytic depolymerization of PET, in which

* Corresponding author: scientific@aec.org.sy (Z. Ajji)

terephthalic acid (TPA) and ethylene glycol (EG) are recovered and can be directly used in the synthesis of virgin PET or other needed compounds.[8-11] Several researchers tried acidic hydrolysis of PET under various reaction conditions, pressure, temperatures, acid concentration etc.[12-15]

The present work reports on the use of commercial sulfuric acid produced by the Syrian corporation for fertilizer production for the hydrolysis of PET waste under normal pressure; the influence of various reaction parameters has been studied as acid concentration, temperature, reaction time, and the particles size. Also the hydrolysis of pure, molded, and waste PET has been compared. Furthermore, Pure and commercial sulfuric acid have been tested for the hydrolysis reaction.

RESULTS AND DISCUSSIONS

1. Acid concentration effect

Fig. 1 represents the conversion of the PET hydrolysis with respect to sulfuric acid concentration, and the other reaction parameters are constant: reaction time = 5 h; particle size= 0.25 mm; temperature of the oil bath = 170 ^oC. It can be seen that the hydrolysis starts at an acid concentration of 7 moles. Then the degradation increases with increasing the acid concentration until an acid concentration of 8.5 M. Thereafter the reaction conversion decreases due to oxidation of the compounds; the color of the solution becomes dark. The esterfication is an equilibrium reaction, and the concentration of the acid plays an important role to enhance the reaction velocity in both directions. The protonation of the ester group leads to the back reaction according to the chemical kinetics.[17]

The hydrolysis occurs at higher acid concentration compared with published work,[14] where the hydrolysis was performed in sealed Pyrex tubes. The pressure seems to influence the hydrolysis reaction, and a lower acid concentration is needed.

In the next experiments, an acid concentration of 8 moles has been used to avoid the oxidation effect of the concentrated sulfuric acid.

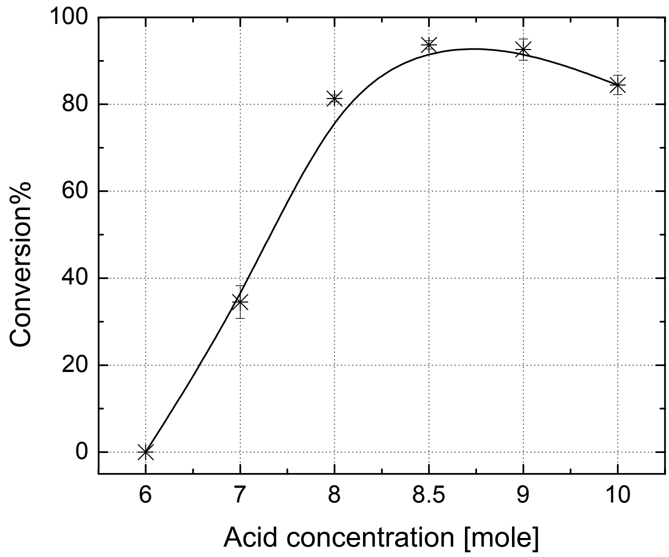

Fig. 1 – The hydrolysis conversion with respect to sulfuric acid concentration; reaction interval = 5 hours; particle size = 0.25 mm; oil bath temperature = 170 ^oC.

2. Effect of reaction time

Fig. 2 shows the conversion of the PET hydrolysis versus the reaction time, while the other reaction parameters are constant: sulfuric acid concentration = 8M; particle size= 0.25 mm; temperature of the oil bath = 170 ^oC. It can be seen that the hydrolysis yield increases with increasing the reaction time, which is also observed in.[14] Almost 10-12 hours are needed to achieve a total conversion.

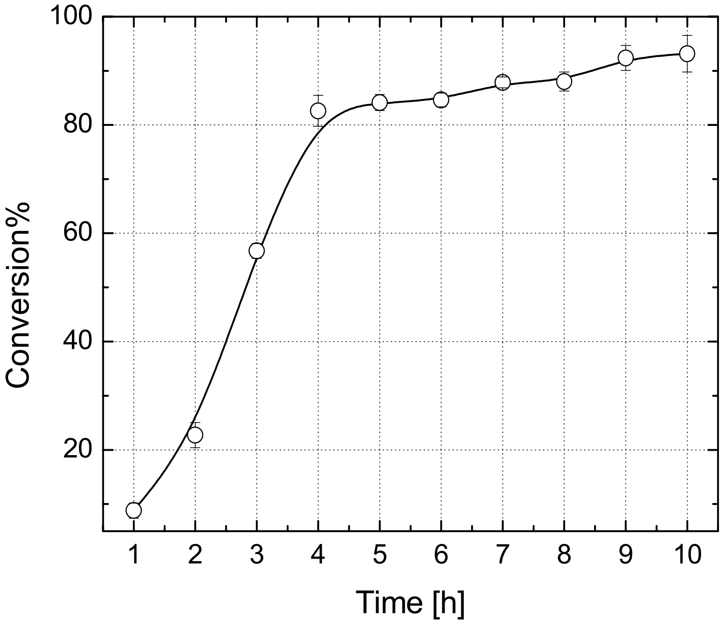

Fig. 2 – The hydrolysis conversion with respect to reaction time; sulfuric acid concentration = 8 M; particle size = 0.25 mm; oil bath temperature = 170 °C.

3. Effect of reaction temperature

The conversion of the PET hydrolysis is illustrated in Fig. 3 with respect to the reaction temperature, and the other reaction parameters are constant: sulfuric acid concentration = 8M; reaction time = 5 h; while particle size = 0.25 mm. The graph shows that the hydrolysis starts with limited conversion at a temperature of 130 °C, and it increases with the increase in the oil bath temperature. It is known from chemical kinetics that reaction velocity doubles when the reaction temperature is increased 10 degrees. The hydrolysis conversion is lower than in [14], which is due to the pressure applied in the published work.

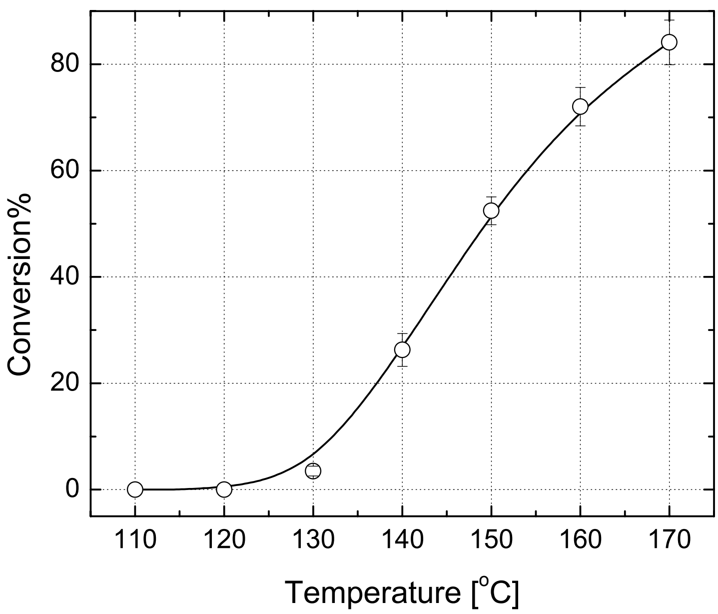

Fig. 3 – The hydrolysis conversion with respect to the temperature of the oil bath; sulfuric acid concentration = 8 M; reaction time = 5 hours; particle size = 0.25 mm; oil bath temperature = 170 °C.

4. Effect of particle size

Fig. 4 illustrates the conversion of the PET hydrolysis versus particle size of PET, while the other reaction parameters are constant: the reaction temperature = 170 ^{o}C; sulfuric acid concentration = 8M; reaction time = 5 h. It can be seen from the graph that the hydrolysis conversion decreases drastically with increasing the particle size of PET. This behaviour can be explained with increased surface area available for the reaction with smaller particle size.

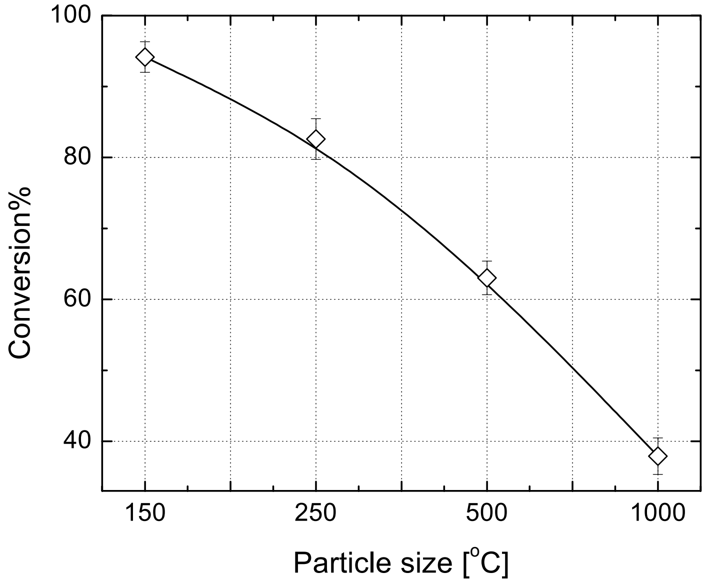

Fig. 4 – The hydrolysis conversion with respect to particle size; sulfuric acid concentration = 8 M; reaction time = 5 hours; oil bath temperature = 170 ^{o}C.

5. Effect of use history

Fig. 5 shows the hydrolysis conversion of pure PET granulates, molded PET, and used PET bottle, and the other reaction parameters are constant: the reaction temperature = 170 ^{o}C; sulfuric acid concentration = 8M; reaction time = 5 h. The graph indicates that there is significant difference between the three different PET types. The thermal molding and the use of PET do not seem to influence the chemical structure of Pet and consequently hydrolysis reaction, conversion.

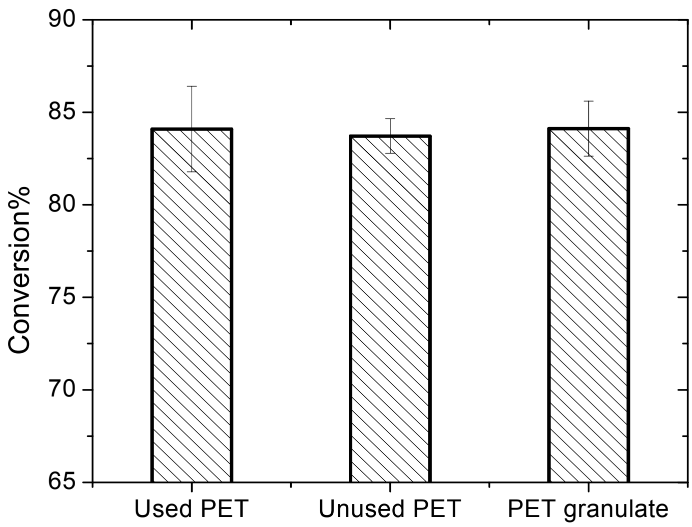

Fig. 5 – The hydrolysis conversion for three different PET type; sulfuric acid concentration = 8 M; reaction time = 5 hours; particle size = 0.25 mm; oil bath temperature = 170 ^{o}C.

6. Effect of acid purity

Fig. 6 represents the conversion of the PET hydrolysis using Syrian commercial sulfuric acid and pure sulfuric acid obtained from Merck, and the other reaction parameters are constant: particle size = 0.25 mm; reaction temperature = 170 °C; sulfuric acid concentration = 8M; reaction time = 5 h. The Syrian commercial sulfuric acid contains several heavy metals. The graph shows a 20% higher conversion using the Syrian commercial acid than the pure acid. The reason for this increase could be due to the presence of heavy metals, which could act as catalyst. Some published works report about using of catalyst in the degradation depolymerization of PET.[18-19]

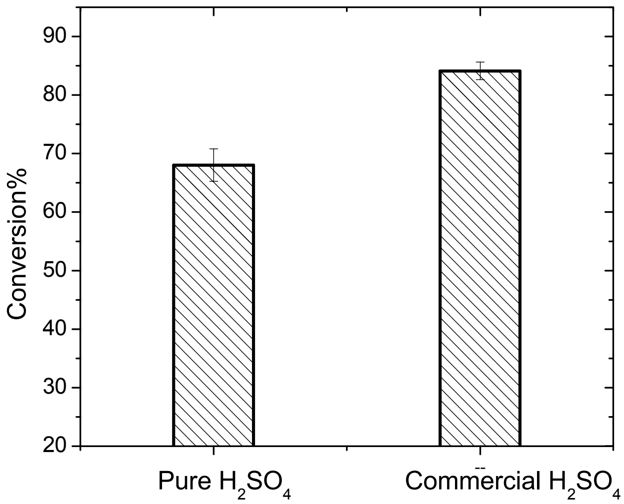

Fig. 6 – The hydrolysis conversion using commercial and pure sulfuric acid; sulfuric acid concentration = 8 M; reaction time = 5 hours; particle size = 0.25 mm; oil bath temperature =170 °C.

EXPERIMENTAL

1. Materials

Powdered virgin PET from Sabic, powdered PET from PET-bottles before using, and powdered wasted PET bottles. Hydrochloric acid; Scharlau Chemie S.A. Barcelona, Spain; Sodium Hydroxide (Merck); commercial sulphuric acid obtained from the Syrian Company for Production of Fertilizers; the quality of the produced commercial sulfuric acid has been studied,[16] and the impurities included in the acid are listed in Table 1.

Table 1

The content of impurities in sulfuric acids

Impurity [mg/kg]	pure acid	commercial acid
Chloride	0.001	3.75
Arsenic	0.0001	0.3
Cadmium	0.0002	0.005
Calcium	0.002	37
Copper	0.0001	0.018
Iron(Fe)	0.001	12
Potassium	0.001	0.045
Magnesium	0.0005	2.8
Manganese	0.0001	0.052
Sodium	0.005	1.8
Nickel	0.0002	0.14
Lead(Pb)	0.0002	0.01
Zinc	0.0005	0.065

2. Methods

PET powder was placed with H_2SO_4 in a flask (2 gr of PET powder and 25 ml H_2SO_4), which is connected with water-cooled condenser. The flask was heated in oil bath (silicon oil) for desired time intervals. After completion of the reaction, TPA and remaining PET mixture were separated from EG and H_2SO_4 solution using a filter glass. TPA was converted into terephthalate salt by reaction with NaOH solution (1 M), and then separated from PET. TPA was then precipitated again in an acidic medium (HCl 15%) and filtered using a filter glass and dried in an oven (50 ^oC). The PET degradation conversion and the acid yield were measured gravimetrically.

CONCLUSIONS

Poly(ethylene terephthalate) has been hydrolyzed using commercial sulfuric acid produced by the Syrian Chemical Corporation in order to obtain raw materials. The reaction parameters have been investigated, which affect the hydrolysis conversion such as: acid purity and concentration, reaction time, reaction temperature and PET particle size. The acid concentration plays an important role, the hydrolysis occurs with an acid concentration of 6 M, the reaction conversion increases with increasing the acid concentration until 8.5 M, and then it tends to decrease. The use of commercial sulfuric acids led to higher hydrolysis yield than the pure sulfuric acid. As expected the reaction time leads to higher conversion until achieving the equilibrium. The reaction yield is also increased with increasing the temperature of the oil bath and with decreasing the PET particle size.

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