ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2013, *58*(11-12), 887-890

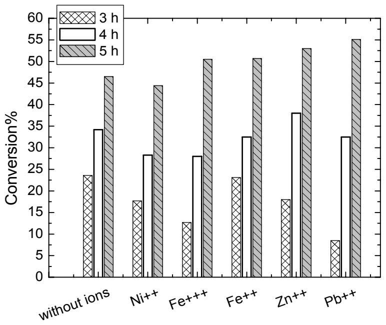
EFFECT OF METAL IONS ON THE CHEMICAL RECYCLING OF POLY(ETHYLENE TEREPHTHALATE) IN SULFURIC ACID

Hayat TABEIKH,[a] M. Hassan Al KURDI,[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

Received August 2, 2013

Poly(ethylene terephthalate) has been hydrolyzed in sulfuric acid using various additives (Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) in order to investigate their influence on the reaction conversion. The addition of 5 μM of the single ions increased the conversion; the addition of 30 μM did not enhance the conversion more than did the addition of 5 μM of metal ions. Iron ions seem to be the best additives which improve the reaction conversion. The use of binary ion mixtures seems to suppress the reaction and the conversion was consequently lower than in the ion free acidic solution. The ternary ion mixtures did not increase the reaction conversion.



INTRODUCTION

The international production of polymers is increasing rapidly in the last decades; it has grown up from about 1.5 million tons in 1950 to about 280 million tons in 2011.[1] The production has increased about 187 times in 60 years. In addition, the synthetic polymers have long life due to their resistance to biodegradation. This aspect has caused a major concern to the environmentalists from the point of view of polymer waste management.[2]

Poly(ethylene terephthalate) (PET) is a semi-crystalline thermoplastic polymer; it is one of the most common polymers, and forms about 18% of world's polymer production,[3] and forms 6.5% of European plastics production.[1] Also PET is used generally in Syria, and its imported amounts have grown up from 15 k tones in 2006 to 66 k tones in 2009.[4] That is because PET can be used in the preparation of a variety of products differing widely in their physical characteristics and hence, their end uses. The varieties of prominence are fibers and filaments, sheets and soft drink bottles.[2]

Recycling of PET does not only serve as a partial solution to the solid-waste problem, but also serves as a source of raw material to some industries and contribute to the conservation of high cost raw petrochemical products and energy which are of great importance in today's world.[3]

PET can be recycled chemically by different methods as hydrolysis,[5] methanolysis, glycolysis,[6-7] and aminolysis.[2] The hydrolysis of PET can be performed in acidic, basic and natural conditions; the acidic hydrolysis using commercial sulfuric acid has around 10% higher conversion than pure sulfuric acid.[8] The presence of metallic ions may be the reason for the difference between the two acids which has raised many questions about their effects on acidic hydrolysis.

The effect of different compounds on the chemical recycling of PET has been studied using different approaches. PET has been depolymerized

---

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

using ethanol amine with sodium acetate and potassium sulphate as catalyst.[2] Ions such as zinc, manganese, cobalt and lead were used as catalyst in depolymerization of PET using ethylene glycol.[7] In addition, PET was hydrolyzed and decarboxylised using a calcium oxide filled column under several thermal conditions, in order to obtain high yields of high purity benzene.[9] Furthermore, metal oxides as $Ca(OH)_2$, NiO, Fe_2O_3 or TiO_2 have shown different effects on the pyrolysis of PET at 700 °C in a helium atmosphere.[10,11]

The present work reports on the influence of various metal ions as additives and their mixtures (Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) on the acidic hydrolysis of PET using pure sulfuric acid; these ions are present in the Syrian commercial sulfuric acid as impurities,[8] which may be used for the recycling of PET.

RESULTS AND DISCUSSION

1. Effect of addition of metal ions

Fig. 1 represents the conversion of the PET acidic hydrolysis by adding 5 or 30 μM of various metallic ions; all other reaction parameters were held constant as: oil bath temperature = 170°C; sulfuric acid concentration = 8 M; reaction time = 5 h; particle size = 0.5 mm. It can be seen that the added ions do have a positive effect on the reaction conversion in general, and the highest yield was obtained by addition of Fe^{2+}. The addition of 30 μM of metal ions does not seem to enhance the reaction conversion more than the addition of 5 μM of metal ions in the all cases beside Fe^{+++}.

2. Effect of metal ions and the reaction time

Fig. 2 represents the conversion of the acidic hydrolysis of PET by addition of the metal ions for reaction times of 3, 4 and 5 hours; the other reaction parameters were held constant: acid concentration was 7M, particle size = 0.5 mm, temperature of the oil bath = 170 °C, and addition of 30 μM of (Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}). It can be seen from Fig. 2 that the hydrolysis conversion increases with the reaction time, which is also observed in the acidic hydrolysis of PET using pure sulfuric acid.[11,12] Furthermore, all ions except Fe^{2+} do not compete with sole acid medium at the beginning of the reaction; for the reaction time of 5 hours the conversion became competitive and higher than that of the sole medium.

3. Effect of varying ions and the acid concentration

Fig. 3 shows the conversion of the acidic hydrolysis of PET using two different acid concentrations and the addition of different metal ions; other reaction parameter were held constant as: Amount of added ions was 30 μM (Fe^{+2}, Fe^{+3}, Ni^{+2}, Pb^{+2}, Zn^{+2}), reaction time = 5 h, particle size= 0.5 mm, temperature of the oil bath = 170 °C. It is obvious that the conversion increases when the acid concentration increases from 7 M to 8M. It can also be said that the presence of the metal ions has a positive influence on the reaction conversion especially when using the higher acid concentration.

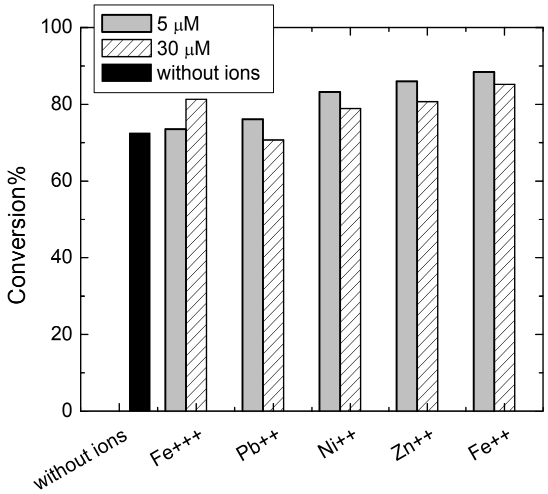


Fig. 1 – Conversion of PET acidic hydrolysis by addition of 5 or 30 μM of metallic ions to the reaction medium; other reaction parameters were held constant: oil bath temperature = 170 °C; sulfuric acid concentration = 8 M; reaction time = 5 h; particle size = 0.5 mm.

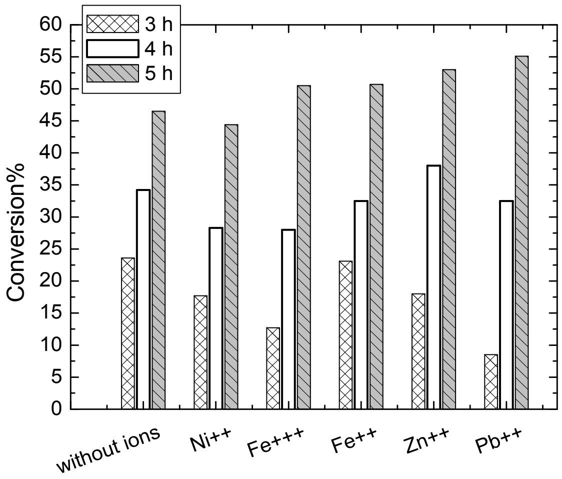


Fig. 2 – Effect of metal ions on the acidic hydrolysis of PET during 3, 4 and 5 hours.

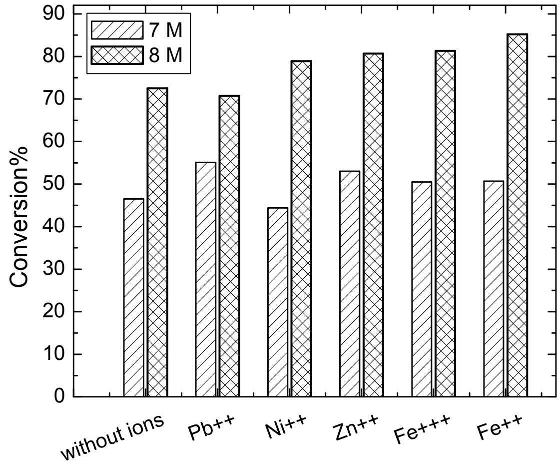


Fig. 3 – Conversion of the acidic hydrolysis of PET for two different acid concentrations and different metal ions; Amount of added ions was 30 μM (Fe^{+2}, Fe^{+3}, Ni^{+2}, Pb^{+2}, Zn^{+2}), reaction time = 5 h, particle size= 0.5 mm, temperature of the oil bath = 170 °C.

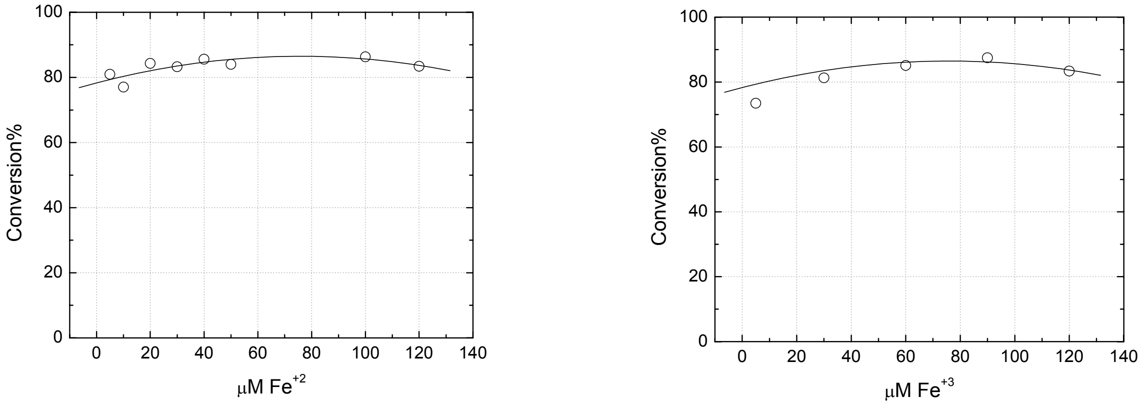


Fig. 4 – Conversion of the acidic hydrolysis of PET by varying the concentrations of Fe^{2+} and Fe^{3+}; reaction time = 5 h; particle size = 0.5 mm; acid concentration= 8M; temperature of the oil bath = 170 °C.

4. Effect of increasing [Fe^{2+}] and [Fe^{3+}]

Fig. 4 represents the conversion of the acidic hydrolysis of PET by addition of Fe^{2+} or Fe^{3+} as a catalyst with regard to metal ion concentration; other reaction parameters constant: reaction time = 5 h; particle size = 0.5 mm; sulfuric acid concentration = 8M; temperature of the oil bath = 170 $^{\circ}$C. The graphs show that increasing [Fe^{2+}] and [Fe^{3+}] amounts leads to a slight increase achieving a flat maximum at about the addition of 60 µM of both iron species.

5. Effect of ions synergism

Table 1 presents the conversion of the acidic hydrolysis of PET in presence of single metal ions and their mixtures; the reaction parameters were held constant: oil bath temperature = 170°C; sulfuric acid concentration =8M; reaction time = 5 h; particle size = 0.5 mm, and concentration of ions: 30 µM. It can be seen that addition of iron ions in both oxidation levels leads to the highest conversion. Addition of Fe^{3+} combined with other metal ions as binary mixtures has decreased the reaction conversion except the addition of Ni^{2+} which does not show any difference at all. Ternary mixture of Pb^{2+} with Fe^{3+} combined with further metal ions showed a negative effect on hydrolysis except with Zn^{2+}.

Table 1

Acidic hydrolysis of PET in presence of ion mixtures; reaction parameters were: oil bath temperature = 170°C; sulfuric acid concentration =8M; reaction time = 5 h; particle size = 0.5 mm, and concentration of ions: 30 µM

Single ion	Conversion%	Binary ion mixture	Conversion%	Ternary ion mixture	Conversion%
Fe^{+3}	81				
Pb^{+2}	70.7	Fe^{+3} + Pb^{+2}	66.6		
Zn^{+2}	80.7	Fe^{+3} + Zn^{+2}	71.8	Fe^{+3} + Pb^{+2} + Zn^{+2}	83.4
Fe^{+2}	85.2	Fe^{+3} + Fe^{+2}	78.3	Fe^{+3} + Pb^{+2} + Fe^{+2}	76.8
Ni^{+2}	78.9	Fe^{+3} + Ni^{+2}	81	Fe^{+3} + Pb^{+2} + Ni^{+2}	78.6

EXPERIMENTAL

1. Materials

PET powder was obtained from SABIC; sulfuric acid was received from Panreac, Spain; sodium hydroxide and the metal salts were obtained from Merck, Germany; Metal nitrate and Ferrous(II) sulfate, were used to obtain the ions Fe^{+2}, Fe^{+3}, Ni^{+2}, Pb^{+2}, Zn^{+2}.

2. Methods

0.01 molar solutions of the metal salts have been prepared to adjust the required concentration of added metal ions. Various volumes of the metal solutions and the needed concentrated sulfuric acid were poured into a flask and distilled water was then added to obtain a total volume of 25 ml with the desired concentration of the acid (8 molar) and the metal ions. 2 grams of PET powder was transferred into the flask, which is connected to water-cooled condenser. The flask was heated in oil bath (silicon oil) for desired time intervals. After completion of the reaction, terephthalic acid (TPA) and remaining PET mixture were separated from ethylene glycol (EG) and H_2SO_4 solution using a glass filter. 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 glass filter and dried in an oven (50 $^{\circ}$C). The PET degradation conversion and the acid yield were measured gravimetrically.

CONCLUSIONS

Various metal ions (Fe^{2+}, Fe^{3+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) were used to enhance the acidic hydrolysis of poly(ethylene terephthalate) using sulfuric acid. The use of single ions increased the reaction conversion, both Fe^{2+} and Fe^{3+} gave the best results.

The reaction conversion increased with respect to the reaction time also by using the metal ions.

Binary ion mixtures decreased the hydrolysis conversion compared with the ion free acidic solution. The ternary ion mixtures did not enhance the reaction conversion significantly.

Acknowledgements: The authors would like to thank Prof. I. Othman (D.G. of AECS) for his encouragement.

REFERENCES

1. Association of Plastics Manufacturers (Plastics Europe), Plastics – the facts 2012 an analysis of European plastics production, demand and waste data for 2011, *Plastics Europe*, association of plastics manufacturers, **2012**.
2. S.R. Shukla and A. M. Harad, *Polym. Degrad. Stab.*, **2006**, *91*, 1850.
3. M. Kathalewara, N. Dhopatkara, B. Pacharanea, A. Sabnisa, P. Rautb, V. Bhaveb, *Prog. in Org. Coat.*, **2012,** 2948.
4. Foreign Trade, *Central Bureau of Statistics in Syria*, council of ministers, **2011** tab. 9.
5. O. Sato, K. Arai, M. Shirai, *Catalysis Today*, **2006**, *111*, 297.
6. S.H. Mansour, N.E. Ikladious, *Poly. Test.*, **2002**, *21*, 497.
7. M. Ghaemy, K. Mossaddegh, *Polym. Degrad. Stab.*, **2005**, *90*, 570.
8. H. Tabeikh, Y. Koudsi and Z. Ajji, *Rev. Roum. Chim.*, **2012**, *57*(12), 1029.
9. G. Grause, T. Handa, T. Kameda, T. Mizoguchi, T. Yoshioka, *Chem. Eng. J.*, **2011,** *166*, 523.
10. T. Yoshioka, T. Handa , G. Grause, Z. Lei, H. Inomata, T. Mizoguchi, *J. Anal. Appl. Pyrol.*, **2005**, *73*, 139.
11. G. Grause, W. Kaminsky, G. Fahrbach, *Polym. Degrad. Stab.*, **2004**, *85*, 571.
12. M. Mehrabzadeh, S. T. Shodjaei, M. Khosravi, *Iran. Polym. J.*, **2000,** *9*, 37.