Hayat TABEIKH, M. Hassan Al KURDI, Zaki AJJI*
Department of Chemistry, Faculty of Science, Damascus University, Damascus, Syria
*Polymer Technology Division, Department of Radiation Technology, Damascus, Syria

Effect of Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+} ions on the chemical recycling of poly(ethylene terephthalate) in sulphuric acid

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Summary

Poly(ethylene terephthalate) has been hydrolyzed in sulphuric acid using various additives (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}) in order to investigate their influence on the reaction conversion. The addition of 5 μM of the single ions does not seem to increase the conversion significantly, but the addition of 30 μM does enhance the conversion compared with 5 μM. Cd^{2+} and Al^{3+} ions seem to be the best additives which improve the reaction conversion obviously. The increase in the acid concentration leads to increase in the hydrolysis conversion. The addition of iron ions to the studied ions seems to suppress the reaction in some cases (Cr^{3+}, Cu^{2+}, Co^{2+}) and the conversion was consequently lower than in the ion free acidic solution. Using binary mixture of iron ions with Cd^{2+} and Al^{3+} does not show a significant increase in the conversion compared with the use of single ions.

KEY WORDS:
hydrolysis
metal ions
poly(ethylene terephthalate)
recycling
sulphuric acid

KLJUČNE RIJEČI:
hidroliza
metalni ioni
poli(etilen-tereftalat)
recikliranje
sumporna kiselina

Učinak iona Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+} na kemijsko recikliranje poli(etilen-tereftalata) u sumpornoj kiselini

Sažetak

Poli(etilen-tereftalat) hidroliziran je u sumpornoj kiselini uz različite aditive (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}) kako bi se istražio njihov utjecaj na reakcijsku konverziju. Dodavanje 5 μM pojedinačnih iona ne povećava znatno konverziju. S druge strane dodavanje 30 μM poboljšava konverziju u usporedbi s 5 μM. Čini se da su ioni Cd^{2+} i Al^{3+} najbolji aditivi, koji očito poboljšavaju reakcijsku konverziju. Povećanje koncentracije kiseline ima za posljedicu povećanje konverzije hidrolize. Dodavanje iona željeza proučavanim ionima usporava reakciju u nekim slučajevima (Cr^{3+}, Cu^{2+}, Co^{2+}), stoga je konverzija bila niža nego u otopini kiseline bez iona. Uporaba binarne mješavine iona željeza s Cd^{2+} i Al^{3+} ne pokazuje znatno povećanje konverzije u usporedbi s uporabom pojedinačnih iona.

Introduction

Poly(ethylene terephthalate) (PET) was introduced to consumers as a plastic bottle for soft drinks in the 1970s. PET quickly gained acceptance among bottlers and consumers. Since it was lightweight, economical and shatterproof, PET plastic is now used as a packaging material for a whole range of consumer products in addition to carbonated beverages. These bottles and containers are used to package such consumer products as spring water, juice, food and household cleaners.[1] It accounted for 6.3% of imported plastics to Syria in 1997,[2] and 6.5% of the European plastics production in 2012.[3]

Recycling of PET does not only serve as a partial solution to the solid-waste problem, but it also serves as a source of raw material to some industries and contributes to the conservation of both high-cost raw petrochemical products and energy which are of great importance in today's world.[4] Depolymerizing PET to yield monomers as its raw materials has been gaining greater interest as ideal means of recycling. PET can be depolymerized by different methods such as hydrolysis,[5,6] methanolysis, glycolysis[7,8] and aminolysis.[9,10] Also, PET could be hydrolysed in acidic, basic and natural conditions.[11-12] Acid hydrolysis is performed most frequently using concentrated sulphuric, nitric or phosphoric acid. To avoid high pressures and temperatures in the reaction vessel, a concentrated sulphuric acid (>14.5 M) has been proposed.[13] However, the process proves very costly due to the need to recycle large amounts of concentrated H_2SO_4 and the purification of EG from the sulphuric acid. An acid hydrolysis of waste PET powder in relatively dilute sulphuric acid (<10 M) and the reuse of the sulphuric acid by recovery methods such as dialysis has also been proposed.[14] However, this requires longer reaction time (5 h) and increasing the reaction temperature (150°C). Mehrabzadeh *et al.* reported about optimal reaction conditions.[15] Another approach described a process for the depolymerization of PET powder from waste bottles using nitric acid (7–13 M) at 70–100°C for 72 h.[16]

The effects of many metallic compounds on PET chemical recycling have been studied. PET has been depolymerized by ethanol amine with sodium acetate and potassium sulphate as catalyst.[9] Also, the ions of zinc, manganese, cobalt and lead were used as catalysts in depolymerization of PET by ethylene glycol.[8] In addition, PET was hydrolyzed and decarboxylised using calcium oxide filled column under several thermal conditions, in order to obtain high yields of high purity benzene.[17] Furthermore, metal oxides such as CaO, NiO, Fe_2O_3 or TiO_2 have shown different effects on the pyrolysis of PET at 700ºC in helium atmosphere,[18] and NiO, Fe_2O_3 or TiO_2 have also effected as catalysts of transition metal oxides which have reduced the content of TA in oligomers to 8%, in a temperature range between 400 and 500°C.[19]

In previous work, the use of commercial sulphuric acid has given around 10% higher conversion ratio than pure sulphuric acid.[20] The presence of metal ions causes the main difference between the two acids. Thus, the present work reports on the influence of various metal ions and their mixtures (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}) as additives on the acidic hydrolysis of PET using pure sulphuric acid; these ions are present in the Syrian commercial sulphuric acid as impurities,[20] and may allow

the use of the commercial sulphuric acid instead of the pure one for the recycling of PET.

Experimental

Materials

PET powder was obtained from SABIC; sulphuric acid was received from Panreac, Spain (concentration 95–98%; impurities: Cu, Pb, Ni = 0.0005%; As, Fe = 0.0001%); sodium hydroxide and the metal salts were obtained from Merck, Germany; Metal nitrate was used to obtain ions Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+} Fe^{3+}.

Methods

PET powder was placed with H_2SO_4 into a flask, which was connected to a water-cooled condenser; in each experiment 2 g of PET powder and 25 ml H_2SO_4 were used. The flask was heated in an oil bath for desired time intervals. After completion of the reaction, terephthalic acid (TPA) and the 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°C). The PET degradation conversion and the acid yield were measured gravimetrically.

Results and Discussions

Effect of adding metal ions

Figure 1 represents the conversion of the PET acidic hydrolysis by addition of 5 or 30 μM of various single metallic ions, where other reaction parameters were held constant as: oil path temperature - 170°C; sulphuric 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 Al^{3+} (Figure 1). The addition of 30 μM of metal ions seems to enhance the reaction conversion more than the addition of 5 μM of metal ions in most cases.

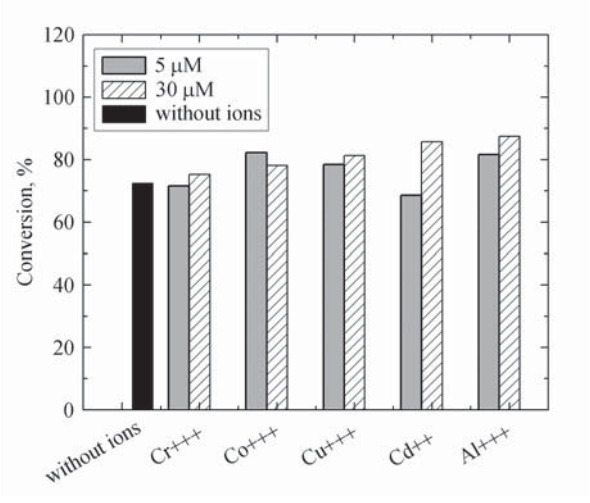

FIGURE 1 –Conversion of PET acidic hydrolysis by addition of 5 or 30 μM of metallic ions to the reaction medium; other reaction parameters were held constant: oil path temperature - 170°C; sulphuric acid concentration - 8 M; reaction time - 5 h; particle size - 0.5 mm.

Effect of metal ions and the reaction time

Figure 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; other reaction parameters were held constant: acid concentration was 7 M, particle size = 0.5 mm, temperature of the oil bath = 170°C, and addition of 30 μM of (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}). It can be seen that the hydrolysis conversion increases with the reaction time in general, which is also observed in the acidic hydrolysis of PET using sulphuric acid.[21] Furthermore, all studied ions except Cr^{3+} do compete with the sole acid medium, and show higher reaction conversion.

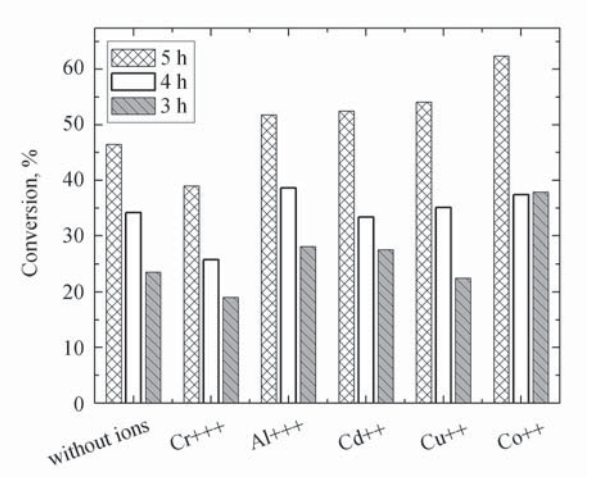

FIGURE 2 – Effect of metal ions on the acidic hydrolysis of PET during 3, 4 and 5 hours in presence of various metal ions (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+})

Effect of varying ions and the acid concentration

Figure 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 (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}), reaction time - 5 h, particle size - 0.5 mm, oil bath temperature - 170°C. An enormous increase in the conversion can be observed as the acid concentration increases from 7 to 8 M. This can be explained with higher protonation ability with increased acid concentration in the solution.

It can also be noticed that the presence of metal ions has a positive effect on the conversion especially using the higher acid concentration. Cd^{2+} and Al^{3+} seem to have the highest results in the used metal group.

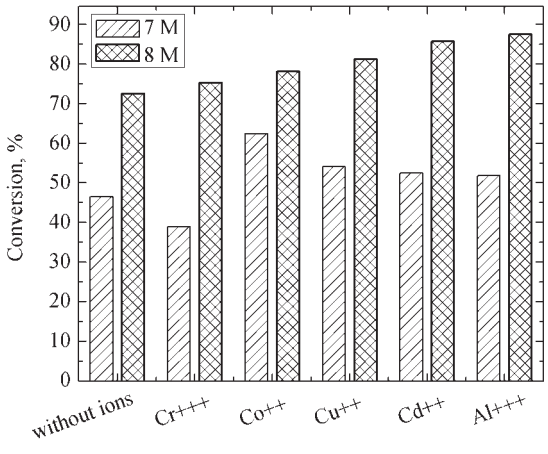

FIGURE 3 – Conversion of the acidic hydrolysis of PET for two different acid concentrations and different metal ions; the amount of added ions was 30 μM (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}), reaction time - 5 h, particle size - 0.5 mm, temperature of the oil bath - 170°C

Effect of increasing Cd^{2+} and Al^{3+} concentrations

Figure 4 represents the conversion of the acidic hydrolysis of PET by addition of Cd^{2+} and Al^{3+} as a catalyst with regard to metal ion concentration; other reaction parameters constant: reaction time - 5 h; particle size - 0.5 mm; sulphuric acid concentration - 8 M; temperature of the oil bath - 170°C. The graphs show that increasing the concentration of Cd^{2+} and Al^{3+} ions leads to an increase in the reaction conversion until the addition of 30 μM of both metal species and then decreases. The presence of metal ions up to some extent might support the protonation of ester group.

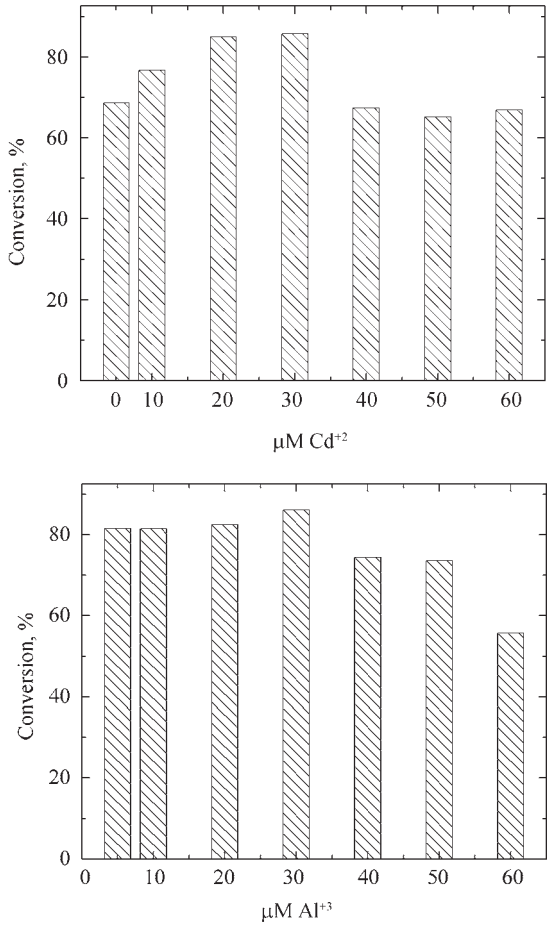

FIGURE 4 – Conversion of the acidic hydrolysis of PET by varying the concentrations of Cd^{2+} and Al^{3+}; reaction time - 5 h; particle size - 0.5 mm; sulphuric acid concentration - 8 M; temperature of the oil bath - 170°C

Effect of ions synergism

In the previous work the addition of Fe^{3+} showed a very high increase in the reaction conversion.[21] Thus, the addition of Fe^{3+} combined with Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+} has been investigated. Figure 5 presents the conversion of the acidic hydrolysis of PET in the presence of single metal ions and binary mixtures of iron ions with the studied ones; the reaction parameters were held constant: oil path temperature - 170°C; sulphuric acid concentration -8 M; reaction time - 5 h; particle size - 0.5 mm, and concentration of ions - 30 μM. It can be seen that the combination of Fe^{3+} with other metal ions as binary mixtures has almost decreased the reaction conversion.

Conclusion

Various metal ions (Cd^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Co^{2+}) were used to investigate their influence on the reaction conversion of the hydrolysis of poly(ethylene terephthalate) using sulphuric acid. The addition of 30 μM of the single ions increased the reaction conversion clearly, where Cd^{2+} and Al^{3+} gave the highest values. The reaction conversion also increased with increasing the reaction time and the acid concentration.

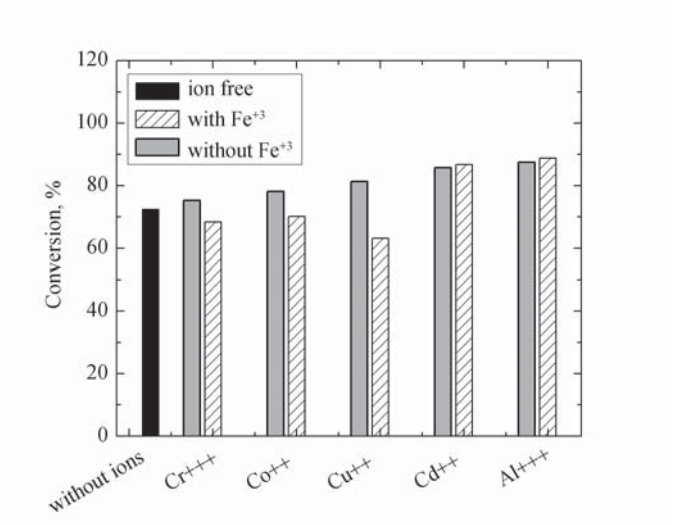

FIGURE 5 – Acidic hydrolysis of PET in presence of ion mixtures; reaction parameters were: oil path temperature - 170°C; sulphuric acid concentration -8 M; reaction time - 5 h; particle size - 0.5 mm, and concentration of ions - 30 μM

Binary ion mixtures of iron and the above mentioned ions decreased hydrolysis conversion in some cases (Cr^{3+}, Cu^{2+}, Co^{2+}); binary mixture of iron ions with Cd^{2+} and Al^{3+} does not show a significant increase in the conversion compared with the use of single ions. Ternary ion mixtures of the studied ions and iron and lead ions did not improve the reaction conversion significantly.

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Contact

Zaki Ajji
Polymer Technology Division, Department of Radiation Technology
A ECS, P. O. Box 6091, Damascus, Syria
E-mail: ascientific@aec.org.sy

Andreas Schötz

Abmusterung von Spritzgießwerkzeugen Strukturierte und analytische Vorgehenweise

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Sadržaj: *Vorwort; Informationen zum Buchaufbau; Einführung; Informationsbeschaffung und Vorbereitung der Abmusterung; Werkuezg rüsten; Grundeinstellung der Schließeinheit; Grundeinstellung der Plastifiziereinheit; Füllstudie; Nachdruck und Werkzeugzuhaltekraft; Ambusterungsanalyse der Grundeinstellung; Optimiterung der Grundeinstellung; Dokumentation der Werkzeugabmusterung; Kurz-Meeting und Maßnahmenfestlegung; Folgeabmusterung (Iterationsshilfe) oder Freigabe; Stichwortverzeichnis.*

Projekt razvoja i proizvodnje kalupa za injekcijsko prešanje u pravilu je uvijek na kritičnom putu terminskog plana projekta razvoja i proizvodnje bilo kojega polimernog otpreska. Konstruktori kalupa i alatničari stoga su pod velikim vremenskim pritiskom. U trenutku kada je kalup načinjen, slijedi još dodatna faza: provjera, odnosno ispitivanje udovoljava li načinjeni kalup zahtjevima na polimerni proizvod. Bez dovoljno iskustva i znanja zaposlenih na aktivnosti iz te faze proizvodnje kalupa vrlo se često upravo u tom trenutku počinje gubiti mnogo vremena (posljedično i novca te energije) kako bi se raznim zahvatima optimirala uporaba izrađenoga kalupa.

Osnovna namjena knjige je pružiti čitatelju bolje razumijevanje standardiziranoga, strukturiranog i sistematiziranog pristupa u procesu ispitivanja kalupa i probne proizvodnje injekcijskim prešanjem. Vremenski pritisak pri provedbi tih faza provjere kalupa neupitno je velik i stoga sve aktivnosti treba provoditi korektno, a posebice ih je važno dokumentirati. Činjenica je kako se mnoge aktivnosti pri ispitivanju kalupa zaboravljaju ili čak ignoriraju, što prije svega dovodi do nepotrebnog produljenja ispitivanja kalupa ili čak donošenja pogrešnih zaključaka. U kasnijoj serijskoj proizvodnji takvi propusti također mogu dovesti do ozbiljnijih teškoća. Sljedeći ozbiljan problem je i nedostatak dokumentacije o identificiranim i uklonjenim greškama na kalupima, kao i nedostatak međusobne komunikacije svih relevantnih sudionika te faze razvoja kalupa za injekcijsko prešanje. Kao posljedica, u praksi se pri provjeri kalupa, zbog nedostatka sistematiziranih teškoća i načina njihova rješavanja, vrlo često provodi velik broj iteracija prije negoli kalup udovolji postavljenim zahtjevima. A često izmjene temeljene na metodi pokušaja i pogreške mogu dovesti i do pogoršanja postignutih rezultata.

Autor knjige tom problemu posvećuje veliku pozornost te svim fazama ispitivanja kalupa (od načina montaže na ubrizgavalicu nadalje) pristupa strukturirano i sistematizirano, uzimajući u obzir komponente kao što su vrijeme, energija, dokumentacija, komunikacija, računalne analize (računalna simulacija injekcijskog prešanja), zatim optimalne parametre prerade, optimiranje čitavog ciklusa injekcijskog prešanja itd. Velikim brojem praktičnih primjera, savjeta, potrebnih informacija autor upućuje sve uključene čimbenike kako u što kraćem roku završiti ispitivanje kalupa i pripremiti ga za serijsku proizvodnju.

Knjiga je prije svega namijenjena prerađivačima, odnosno stručnjacima koji često ispituju nove kalupe za injekcijsko prešanje polimera, no slična načela mogu se primijeniti i kod tlačnog lijevanja metala. Osim za tu primarnu skupinu čitatelja, knjiga je vrlo vrijedan alat i za konstruktore, alatničare, prerađivače te za akademsku zajednicu kako bi se što bolje informirali o vrlo osjetljivoj fazi ispitivanja kalupa.

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