

Promotional Effect of Copper (II) Chloride on the Degradation of Poly(ethylene terephthalate)

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Promotional effect of CuCl_2 on the degradation of various PET samples was studied in a quartz reactor at atmospheric pressure by batch operation. Copper (II) chloride was found to be an effective additive for enhancing the degradation ability of these PET samples. The percentage weight loss of these samples degraded over such an additive was in the order: fiber grade powders > wasted water bottle flakes > bottle grade pellets. The methods of mixing PET sample and additive affect the extent of degradation of PET. For most cases, impregnation method showed higher degradation ability than physical mixing. The effect of other factors, degradation temperature and degradation time, on the extent of degradation of PET when copper (II) chloride was used as an additive was also investigated. The results showed the degradation over this additive could be carried out at a lower temperature and faster rate to achieve the same degree of degradation as that of without additive at higher temperature. Pyrolyzer GC-MS analyses showed that the gaseous products distribution of PET samples degraded with or without copper (II) chloride were little different. But the relative abundance of each component in the gaseous product was significantly changed.

Introduction

PET is one of the most popular plastics and widely used in the manufacture of various kinds of packaging, especially for bottles, containers, and jars [1]. Such post-consumer PET products cause a problem due to its substantial volume fraction and its poor biodegradability and photodegradability. It is important and necessary to recycle or to treat the post-consumer PET products because of both environmental protection and economic benefits. Methods of recycling waste PET products include physical [2-4] and chemical [5-7] ways. Degradation is one of the useful processes among chemical methods. Especially, adding a suitable catalyst or additive to the waste products may lower the required degradation temperature, shorten the degradation time, increase the degradation ability of plastics, reduce the proportion of solid residue in final products, and/or narrow the product distribution. In this study, we report the results of degradation of different PET samples, which were degraded over copper (II) chloride and some other active compounds found in our previous study. The effect of

degradation conditions, as well as the analyses and comparisons of gaseous products of PET samples degraded with or without the copper (II) chloride was also investigated.

Experimental

Three kinds of PET samples were used as reactants in this study, fiber-grade powders (sample A), bottle-grade pellets (sample B), and flakes cut from a used colorless mineral water bottle (sample C). A detail description about the degradation process can be found in our previous paper [8]. The degradation gaseous products were analyzed by using a pyrolyzer-GC-MS instrument system.

Results and discussions

Table 1 shows the effect of additives on the percentage weight loss of PET (X) by physical mixing PET sample and additive. The X values demonstrated, except for copper (II) chloride, no one could effectively enhance the extent of degradation of all PET samples. The extent of degradation of these samples with copper (II) chloride was in the order: sample A > sample C > sample B. Values in parentheses in Table 1 also shows the effect of additives on the percentage weight loss of PET using another contact method - impregnation. The results in this case were similar to previous one, i.e. copper (II) chloride was the only additive showing the ability to aid the degradation of PET samples and the order of extent of degradation was still the same for these three samples. Comparing these two cases, it was found impregnation method led to a higher value of X, no matter what kind of samples.

The dependence of percentage weight loss of PET on degradation temperature is illustrated in Table 2. Data demonstrate that the degradation of PET without adding copper (II) chloride at any reaction temperature is substantially lower than that of PET with this additive, especially at lower temperature. The results suggest that degradation of PET over copper (II) chloride can be carried out at a lower temperature to achieve the same degree of degradation as that of without additive at higher temperature. The degradation time dependence of the percentage weight loss of PET without and with copper (II) chloride is shown in Figure 1. The tendencies of weight change for these three kinds of samples under two different kinds of degradation processes were almost the same. The weight loss for each sample reached the maximum value approximately within five to seven hours. The extents of degradation for fiber grade powders are always greater than the other two kinds of samples, which are nearly equal.

The samples used in gaseous product analysis for the degradation reactions were undertaken at the apparatus of pyrolyzer-GC-MS. The analysis was done on sample A degraded without and with copper (II) chloride, which were mixed through impregnation and physical methods. The name of main products for these three processes is listed in Table 3.

Numbers are given in each peak on the table and its correspondence pyrogram to identify every gaseous product. The peaks were numbered as N1, N2, etc on the table, which represent new-formed products only when PET degraded with copper (II) chloride. A complete result of the analysis is also given in Table 3. The relative concentration of each product among total gaseous products could be used as a method to observe the change of product distribution. The peak No.1 was chosen as a base for the comparison due to its large quantity and the possible deviation may be reduced. The data in the parenthesis on the Table 3 were the ratio of the height of each peak to that of peak No.1. The alteration of the relative abundance of every component is more obviously than that of product distribution. The main difference between them is that the relative abundance of each component among gaseous products changed significantly. The copper (II) chloride additive can not significantly alter or narrow down the product distribution but has an ability to promote the degradability of PET resin. The mechanism about the promotion effect of copper (II) chloride on the degradation of PET for this study should be further studied.

Conclusions

Copper (II) chloride is an effective additive, which can substantially enhance the extent of degradation of PET. The percentage weight loss of fiber-grade powders is found to be the greatest one of the three samples tested. Impregnation method has a better ability of degradation than by physical mixing method. From a comparison of the pyrograms, the gaseous products are similar for degradation with or without additive. The relative abundance of each component in the gaseous product streams is significantly changed.

Acknowledgement

Financial support from the National Science Council of the Republic of China under Contract No. NSC87-2214-E-131-001 is gratefully acknowledged.

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Table 1 Effect of additive on weight loss of different PET samples degradation ^{a)}

additive	weight loss (%)		
	A	B	C
CuCl ₂	27.8(40.5)	19.0(24.8)	21.9(26.1)
MgCl ₂	21.4(31.0)	10.8(10.2)	10.3(14.1)
Sb ₂ O ₃	12.5(14.6)	7.8(6.6)	9.9(6.5)
Zn(OAc) ₂	10.1(16.1)	11.2(11.3)	8.1(13.6)
Sn(OAc) ₂	13.0(17.8)	8.8(5.3)	7.5(9.6)
-	10.5	10.2	9.6

a) 400 °C, 1 hr, 100 mL N₂/min, weight ratio of additive/PET sample = 1/10, physical mixing

b) values in parentheses are impregnation

Table 2. Effect of temperature on weight loss of PET ^{a)} samples

T (°C)	weight loss(%)		
	A	B	C
350	5.5(1.1)	4.5(1.0)	5.1(1.0)
400	40.5(10.3)	24.8(10.2)	26.1(9.6)
450	89.5(75.0)	86.5(74.3)	88.7(72.8)
500	90.8(80.5)	90.6(81.8)	91.0(82.2)

a) 1 hr, 100 mL N₂/min, weight ratio of CuCl₂/PET sample = 1/10, impregnation method

b) values in parentheses are without CuCl₂

Table 3 Gaseous product distributions for the degradation of PET at 445 °C for 6 sec

peak no.	Compound	Sample A		
		thermal	impreg	phymix
1	CO, CO ₂ , C ₂ H ₂ , C ₂ H ₄	S(1.00)	S(1.00)	S(1.00)
2	acetaldehyde	S(0.93)	S(0.81)	S(0.84)
N1	chloroacetaldehyde	-	W(0.13)	W(0.29)
3	benzene	W(0.20)	W(0.13)	trace
4	toluene	W(0.23)	trace	W(0.11)

N2	tetrachloroethene	-	trace	trace
N3	benzoyl chloride	-	trace	trace
5	vinyl benzoate	S(0.87)	M(0.61)	M(0.50)
6	benzoic acid	M(0.67)	M(0.41)	M(0.53)
7	p-vinyl acetophenone	M(0.30)	trace	W(0.26)
N4	2-chloroethyl benzoate	-	S(1.74)	S(1.92)
8	X1	M(0.37)	-	M(0.34)
N5	pentachlorobenzene	-	trace	W(0.18)
9	divinyl terephthalate	S(2.13)	S(1.05)	S(0.63)
N6	chlorobenzoic acid	-	W(0.16)	S(1.32)
10	ethyl vinyl terephthalate	M(0.43)	-	W(0.21)
11	X2	S(2.27)	S(2.90)	S(2.74)
12	X3	S(0.77)	M(0.39)	S(1.53)
13	X4	M(0.30)	W(0.19)	W(0.26)
14	ethylene dibenzoate	S(2.90)	M(0.42)	S(0.82)

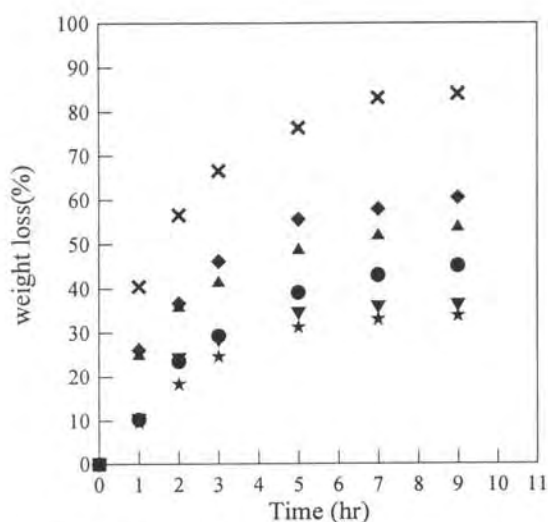


Figure 1 Effect of degradation time on the weight loss of PET with (x:A, ◆:B, ▲:C) and without (●:A, ▼:B, ★:C) CuCl₂ at 400 °C