Depolymerization of Poly(ethylene terephthalate) with Catalyst Under Microwave Radiation

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Received 7 February 2007; accepted 4 December 2007
DOI 10.1002/app.28187
Published online 17 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Grain poly(ethylene terephthalate) (PET) was depolymerized in pure water in the presence of different catalysts. The product quantity of bis(2-hydroxy ethylene) terephthalate (BHET) and glycol obtained was different from the one without catalysts; especially, using zinc acetate as catalyst, the product obtained was in its pure form with sufficiently high yields. Meanwhile, the depolymerization rate nearly reached to 100%. The purified product was characterized by IR spectroscopy. The depolymerization process of PET reported here was economically viable for the high yields of BHET and glycol. Among all the catalysts used in the reaction, zinc acetate was testified as the most effective one, and the optimal dosage of zinc acetate was 0.4% of the feedstock PET. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1298–1301, 2008

Key words: polyesters; degradation; catalysts

INTRODUCTION

Catalytic depolymerization of poly(ethylene terephthalate) (PET) has been studied and used in practice for depolymerization efficiency.[1–4] In our previous work, microwave was applied to PET hydrolytic depolymerization in neutral water, and the hydrolytic product contained terephthalic acid (TPA), ethylene glycol (EG), and diethylene glycol (DEG).[5] In this article, the depolymerization reaction of PET under microwave radiation in the presence of different catalysts were investigated, especially zinc acetate was studied systematically.

EXPERIMENTAL

Chemicals

Pure PET grain was obtained in the form of fiber-grade commercial chips supplied by LiaoYang Petrol Chemical Fiber Corp. (LiaoYang City, PRC). The intrinsic viscosity [η] of PET was 0.621 dL/g [measured in a 60/40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25°C, corresponding to a number-average molecular weight of 25,703 and a weight-average molecular weight of 38,905, which was calculated from the following equation: $[\eta] = 3.72 \times 10^{-4} \overline{M_n}^{0.73}$, $[\eta] = 4.68 \times 10^{-4} \overline{M_w}^{0.68}$.[6–8] There was about 0.9% DEG in the PET grain. The water we used was of high purity and was prepared by third distillation.

Some compounds were used as catalysts in the depolymerization reaction, including $InCl_3{\cdot}4H_2O$, $NiCl_2$, $CoCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}_4H_2O$, $Na_2C_2O_4$, CH_3COOK, $Zn(CH_3COO)_2$, $Mn(CH_3COO)_2$, and all were of analytical grade without further purification.

Catalytic depolymerization

The depolymerization experiments were carried out in a microwave system (CEM Discover) equipped with fiber optic temperature control system and direct pressure control system, which can automatically detect accurate temperature and pressure, respectively. Precisely weighed PET grain (w_1), relevant catalyst, and 20 mL distilled water were put in a 80-mL pyrexglass cup, which were then put into the microwave reaction system. In the closed system, the vessel was sealed tightly and the experiment conducted without stirring under projected conditions shown in the computer connected.

At the end of the experiment, the reaction vessel was cooled for 20 min under sealed conditions, and then taken out of the microwave system. The solid product was separated from the solution by

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Contract grant sponsor: National Natural Science Foundation of China (NSFC); contract grant number: 20474043.
Contract grant sponsor: Zhejiang Province Natural Science Foundation of China (ZJNSF); contract grant number: Y506016.

Journal of Applied Polymer Science, Vol. 109, 1298–1301 (2008)

filtration, washed with distilled water to remove some residual water-soluble components, still washed with 0.5 mol/L sodium hydroxide solution to remove the TPA covered on the surface of the solid product, at last washed with distilled water until the pH value reaches 7, and then dried at 80°C in vacuum oven to a constant weight and weighted (w_2). The reaction extent was calculated as follows:

$$\text{Depolymerization rate of PET}(\%) = \frac{\text{weight of PET charged} - \text{remained solid product}}{\text{weight of PET charged}} \times 100 = \frac{w_1 - w_2}{w_1} \times 100$$

where the w_1 is the initial weight of PET and w_2 is the weight of remained solid product.

RESULTS AND DISCUSSION

Depolymerization of PET in the presence of catalysts

The catalytic depolymerization reaction proceeded under the optimal experiment conditions obtained from a series of hydrolytic experiments, among which the temperature is 220°C, pressure is 200 psi, microwave power is 260 W, reaction time is 210 min, and weight ratio of water to PET is 10/1.

As shown in Table I and Figure 1, the depolymerization rate in the presence of different catalysts with the two different quantity changed dramatically from the one without catalyst, and furthermore, it can be seen that zinc acetate was the best one in the eight types of catalysts used, and using 0.43% was the better one of the two different quantity; however, the other catalysts used were not ideal with either of the two quantity, which showed that different catalysts with corresponding quantity had different effects on the depolymerization reaction. For each catalyst, the quantity also had obvious effect on the results.

TABLE I
Effect of Different Catalysts on the Depolymerization Rate of PET

Catalyst	Depolymerization rate of PET (%)	
	0.23% of PET	0.43% of PET
–	65.63	65.63
$InCl_3 \cdot 4H_2O$	59.49	52.44
$NiCl_2$	56.52	58.62
$CoCl_2 \cdot 6H_2O$	54.53	65.22
$MnCl_2 \cdot 4H_2O$	49.92	59.03
$Na_2C_2O_4$	55.68	55.63
CH_3COOK	64.88	49.63
$Zn(CH_3COO)_2$	69.50	75.91
$Mn(CH_3COO)_2$	63.87	63.80

Reaction temperature: 220°C; reaction pressure: 200 psi; reaction time: 210 min; reaction power: 260 W; weight ratio of water/PET: 10/1.

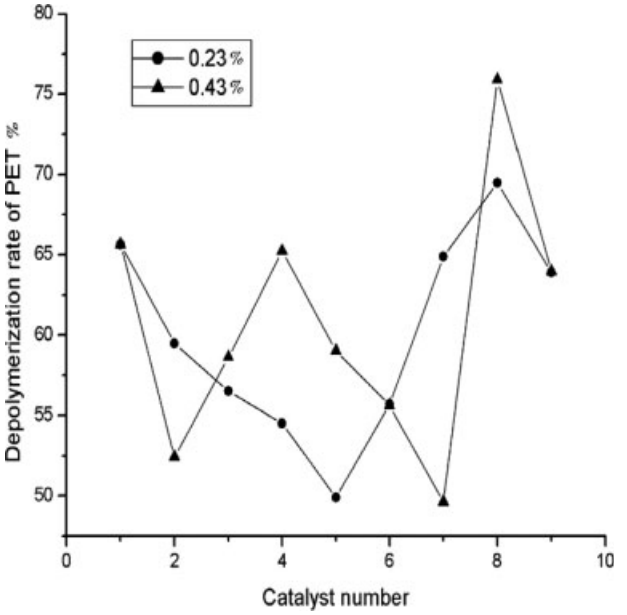

Figure 1 The effect of different catalysts on the depolymerization rate of PET with the two different quantity.

Based on the results in Table I, further research was done to study the effect of the four better catalysts in different quantity on the depolymerization rate of PET. It could be seen from Table II and Figure 2 that zinc acetate had prominent catalytic activity on the depolymerization reaction, and the depolymerization rate could be improved from 65.63% to 89.20% by 23.57%, compared with the noncatalytic one. The optimal usage of zinc acetate was 0.4% of feedstock PET. The depolymerization rate with the other three catalysts also changed greatly, but no matter in which quantity, the depolymerization rate hardly reached 65.63%, and contrarily nearly all the depolymerization rate fell dramatically. The results concluded were not coincident with the ones reported,[1,2,4] maybe partly because of the acceleration of microwave radiation heating, the self-catalytic of EG (produced), and the solvents used. The reason also may be that the microwave radiation changed the catalytic mechanism, which will be studied in the following work.

Depolymerization of PET in the presence of zinc acetate under different temperature

The depolymerization rate of PET in the presence of zinc acetate with time was investigated in details for its catalytic effects. As shown in Table III and Figure 3, a series of experiments were done in different

TABLE II
Effect of Four Preferable Catalysts on the Depolymerization Rate of PET

Weight ratio of catalyst/PET (%)	Depolymerization rate of PET(%)			
	Manganese acetate	Zinc acetate	Potassium acetate	Sodium oxalate
0.00	65.63	65.63	65.63	65.63
0.05	47.00	64.25	62.35	42.16
0.10	43.47	61.13	58.76	43.81
0.15	52.48	68.11	57.14	47.73
0.20	51.99	69.27	56.41	55.68
0.30	54.26	71.48	54.71	56.11
0.34	55.21	76.79	53.19	57.67
0.40	55.43	89.20	52.47	58.06
0.43	56.79	75.91	51.13	55.63
0.60	65.37	68.01	50.87	53.42
1.05	58.44	60.02	49.91	47.96
1.55	57.32	59.64	55.07	38.12
3.05	47.71	59.51	55.26	40.82
4.50	54.22	58.22	49.74	48.32

Reaction temperature: 220°C; reaction pressure: 200 psi; reaction time: 210 min; reaction power: 260 W; weight ration of water/PET: 10/1.

temperature to study the depolymerization process. It could be seen that time and temperature took important part in the depolymerization process when the usage of catalyst and the other reaction conditions were the same. When the reaction time increased from 90 to 240 min, the depolymerization rate of PET increased from 1.23% to 14.19% by 12.96% at 180°C, from 8.13% to 54.46% by 46.33% at 190°C and from 17.89% to 91.23% by 73.34% at 220°C. Furthermore, it was shown that the depolymerization rate increased more greatly at 220°C than at the other two temperatures, and the depolymerization rate began to increase slowly when the reaction time exceeded 210 min. So we considered that 220°C and 210 min were the prominent catalytic reaction conditions with zinc acetate. It could be further concluded that only at proper temperature and time did the catalysts were activated effectively in this reaction, whereas beyond the range, there was no obvious superiority for the catalyst.

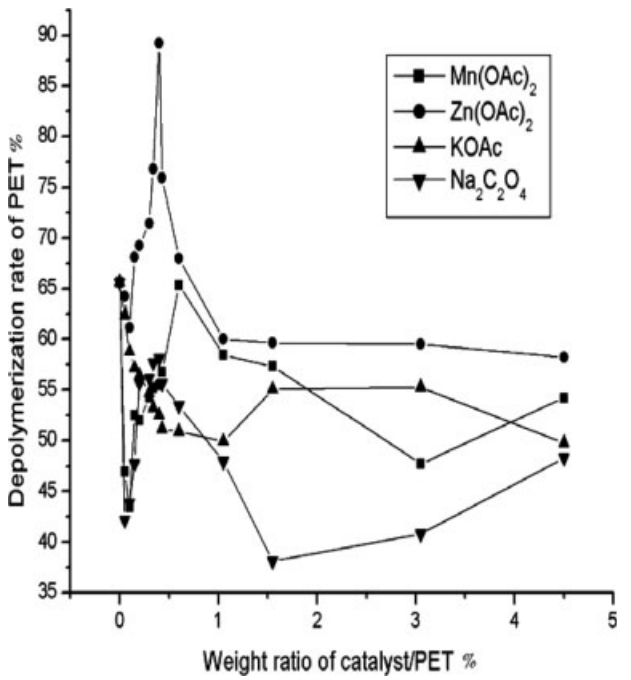

Figure 2 The effect of quantity on the depolymerization rate of PET with the four prominent catalysts.

CONCLUSIONS

A series of experiments were done to study the effects of catalysts on the depolymerization reaction. As shown earlier, zinc acetate was demonstrated as the best one of the eight types of catalysts used, which could improve the depolymerization rate by

TABLE III
Effect of Different Temperature on the Depolymerization Rate of PET in the Presence of Zinc Acetate with Time

Time (min)	Depolymerization rate of PET (%)		
	180°C	190°C	220°C
90	1.23	8.13	17.89
120	4.36	13.78	31.15
150	6.71	17.58	41.15
180	8.89	30.70	56.72
210	9.89	48.85	89.12
240	14.19	54.46	91.23

Reaction temperature: 220°C; reaction pressure: 200 psi; reaction power: 260 W; weight ratio of water/PET: 10/1; weight ratio of zinc acetate/PET: 0.4%.

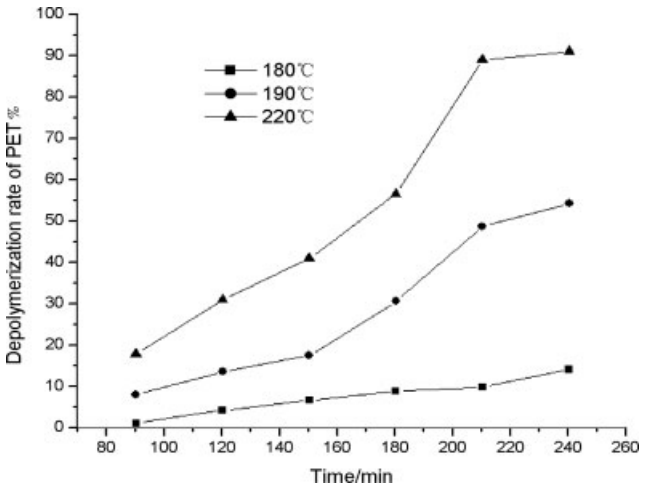

Figure 3 The effect of quantity on the depolymerization rate of PET with zinc acetate.

25.6% compared with the noncatalytic one. The optimal catalyst-to-PET weight ratio was 0.4%, and the optimal reaction conditions were as follows: reaction temperature, 220°C; pressure, 200 psi; microwave power, 260 W; time, 210 min; and weight ratio of water to PET, 10/1.

Note

80 mL Pressure Vessel Accessory of CEM Discover was provided by CEM Corporation in 2004. Designed pressure limit: 500 psi; operating pressure limit: 200 psi; maximum temperature: 220 Centigrade.

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