

Catalysis Investigation of PET Depolymerization Under Metal Oxides by Microwave Irradiation

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ABSTRACT: Grain poly(ethylene terephthalate) (PET) was depolymerized in pure water by different metal oxides, respectively. The catalytic hydrolysis product of terephthalic acid (TPA) obtained was the same with the no catalytic reaction. The depolymerization rate of PET was seriously influenced of the reaction time and temperature. Especially using stannous oxides as catalyst, with a reaction time of 210 min, a temperature of 200°C and a pressure of 200 psi, the depolymerization rate of PET

increased from 59.3 to 90.9% compared with the no catalytic reaction. The morphology of the solid residue indicated that the depolymerization took place on the external surface of the PET grain in the presence of stannous oxide. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3155–3159, 2010

Key words: hydrolysis; catalysts; metal oxide; microwave irradiation

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a widely used polyester material, which is extensively applied in the production of fibers, films, and containers. With increasing PET consumption, disposal of PET wastes turned to be an environmental problem.¹ Hydrolysis was one of the effective methods for chemical recycling of waste PET. This process has been proposed to recover the monomers of terephthalic acid and ethylene glycol which can be used as feedstock for synthesis of original PET.² Sulfuric acid, nitric acid, and alkaline hydroxides have been used to catalyze the hydrolysis with high conversion of the PET, but it also brought corrosion and pollution problem.^{3–5} Several researchers studied the neutral hydrolysis of PET, but they usually ran in high temperature 200~300°C and pressure 1~4 MPa.^{6,7}

In our previous work, microwaves irradiation used as an energy source was applied to PET hydrolytic depolymerization in pure water.⁸ In pure water medium, it is important that the suitable catalytic systems was selected and prepared to realize low pressure depolymerization of PET and to explicit the relationship between catalyzing mechanism of non-

random chain scission depolymerization and catalysts under microwave irradiation, and the catalysis of PET depolymerization under zinc acetate had been studied by us.⁹ In this article, the depolymerization reaction of PET under microwave radiation in the presence of different metal oxides were investigated, especially stannous oxide was studied systematically.

EXPERIMENTAL

Materials

Pure PET resin was obtained in the form of fiber-grade commercial chips supplied by LiaoYang Petrol Chemical Fiber Corp. (LiaoYang City, PRC). The intrinsic viscosity (IV) of PET was 0.642 dL/g [measured in a 60/40 (w/w) phenol/1,1,2,2-tetrachloroethane solution at 25°C], corresponding to a viscosity-average molecular weight of 18,912, which was calculated from the following equation: $IV = 7.55 \times 10^{-4} M^{0.685}$.¹⁰ There was 0.9% diethylene glycol (DEG) in the resin. The water used was of high purity and was prepared by third distillation. All chemicals used were of reagent grade (MgO, Fe₂O₃, Gr₂O₃, ZnO, SnO, Sb₂O₃, Cu₂O, TiO₂, and MnO₂).

Hydrolytic depolymerization

The hydrolytic depolymerization experiments were carried out in a microwave oven (CEM Discover) equipped with temperature and pressure sensors that could be inserted directly into a sealed 80-mL

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TABLE I
Effect of Different Metal Oxides on the Depolymerization Rate of PET

Metal oxides	No cat.	MgO	Fe ₂ O ₃	Gr ₂ O ₃	ZnO	SnO	Sb ₂ O ₃	Cu ₂ O	TiO ₂	MnO ₂
Depolymerization rate of PET	59.3	81.6	77.7	75.9	84.4	90.9	79.3	65.8	75.4	79.3

Reaction temperature: 200°C; reaction time: 210 min; weight ratio of metal oxide/PET: 0.5%; reaction power: 250 W; weight ratio of water/PET: 10/1.

pyrexglass cup. A typical sample in the experiments contained w_1 of PET grain, metal oxide and 20 mL of distilled water, which were put in the reaction vessel without stirring. In the closed system, the vessel was sealed and the experiment conducted.

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 then separated from the solution by filtration, washed with distilled water to remove some residues, further washed with 0.5 mol L sodium hydroxide solution to remove the terephthalic acid (TPA) covered on the surface of the solid product, at last washed with distilled water until the pH value reached 7, and then dried at 80°C in vacuum oven to a constant weight and weighted w_2 .

Analysis of the results

The reaction extent was calculated as follows:

$$\text{PET depolymerization rate(\%)} = \frac{\text{Weight of PET depolymerized to TPA and EG}}{\text{Weight of PET charged}} \times 100\% = \frac{w_1 - w_2}{w_1} \times 100\% \quad (1)$$

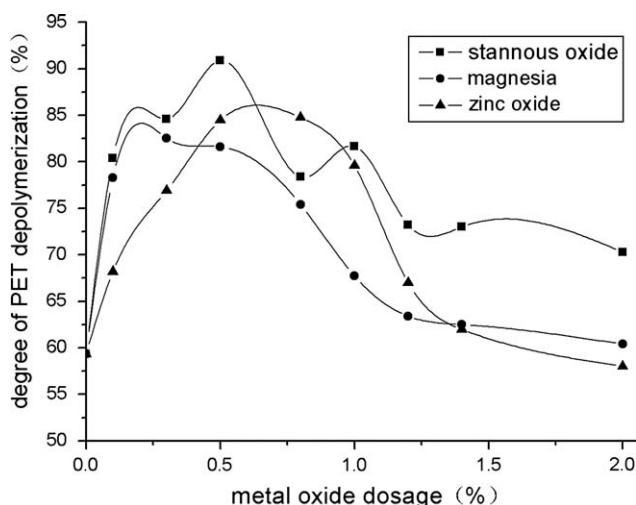


Figure 1 Effect of quantity on the depolymerization rate of PET with the three preferable catalysts.

where w_1 and w_2 are the initial and the final weights of PET, respectively.

RESULT AND DISCUSSION

Depolymerization of PET in the presence of different metal oxides

In the present work, variety metal oxides were used to study the depolymerization reaction process under the optimal conditions obtained from a series of hydrolytic experiments, among which the temperature is 200°C, microwave power is 250 W, reaction time is 210 min and weight ratio of water to PET is 10/1.^{8,9}

As shown in Table I, the depolymerization rate in the presence of different metal oxide catalysts increased dramatically compared with the one without catalyst, and different catalysts had different effects on the depolymerization reaction. Furthermore, it can be seen that magnesia, zinc oxide, and stannous oxide had better catalytic effect than other catalysts in the reaction when the other reaction conditions were the same.

Based on the results of Table I, further research was done to study the effects of the three better catalysts in different quantity on the depolymerization rate of PET. It could be seen from Figure 1 that with

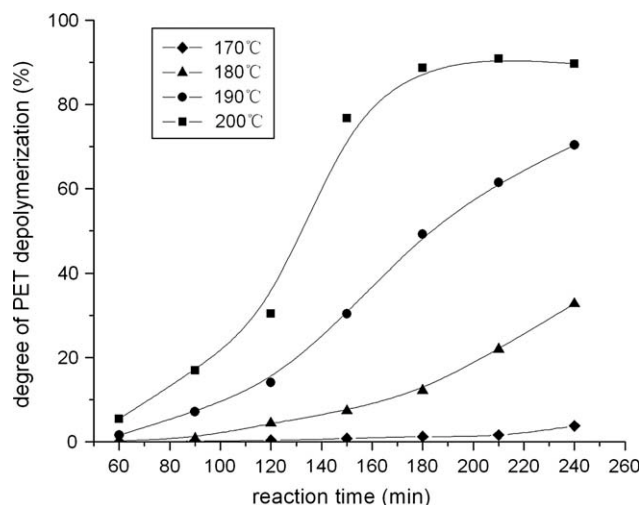


Figure 2 Effect of reaction time on the depolymerization rate of PET in the presence of stannous oxide with different temperature.

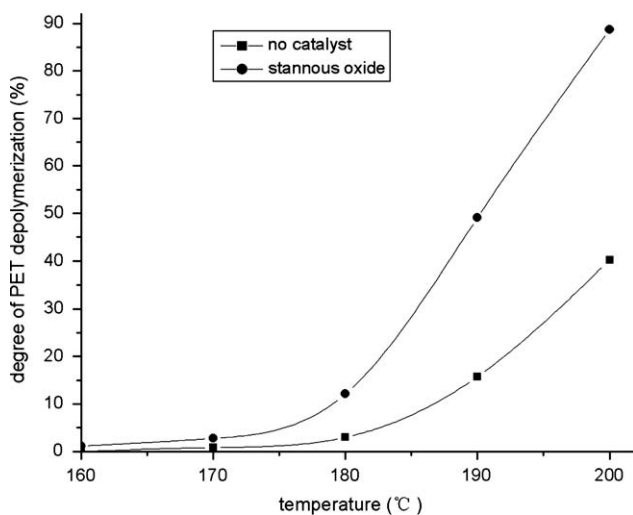


Figure 3 Effect of reaction temperature on the depolymerization rate of PET at a reaction time of 180 min and the weight ratio of water to PET of 10/1.

the increasing of the catalysts quantity the depolymerization rate of PET increases first and decreases afterward. With increasing quantity of stannous oxide, the depolymerization rate of PET increased from 59.3 to 90.9%, when the quantity of the stannous oxide was less than 0.5% of feedstock PET, and decreased when the quantity was above. Furthermore, the depolymerization rate with the other two catalysts also changed greatly and improved to 82.5 and 84.8%, respectively, when using 0.3% magnesia and 0.8% zinc oxide. The results concluded that the three catalysts had prominent catalytic activity on the depolymerization reaction in certain conditions, and the optimal usage of catalysts was 0.3~0.8%.

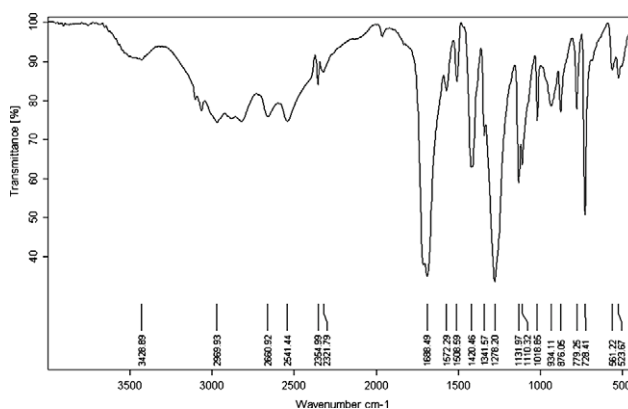


Figure 4 IR spectrum of the solid product.

Depolymerization of PET in the presence of stannous oxide

The depolymerization rate of PET in the presence of stannous oxide with time was investigated in detail for its catalytic effects. As shown in Figure 2, a series of experiments were done in different temperature to study the depolymerization process. It could be seen that the depolymerization rate of PET increased slowly with increasing reaction time from the beginning of the reaction and then increased sharply as the reaction proceeded. When the reaction time increased from 90 to 180 min, the depolymerization rate of PET increased from 16.9 to 88.7% by 71.8% at 200°C, and with the time proceeded to 210 min, the reaction trend to equilibrium. When the reaction temperature was 170°C, the depolymerization rate increased very slowly, it only increased to 1.5% even though the reaction time exceeded 210 min. So we considered that 200°C and 210 min were the

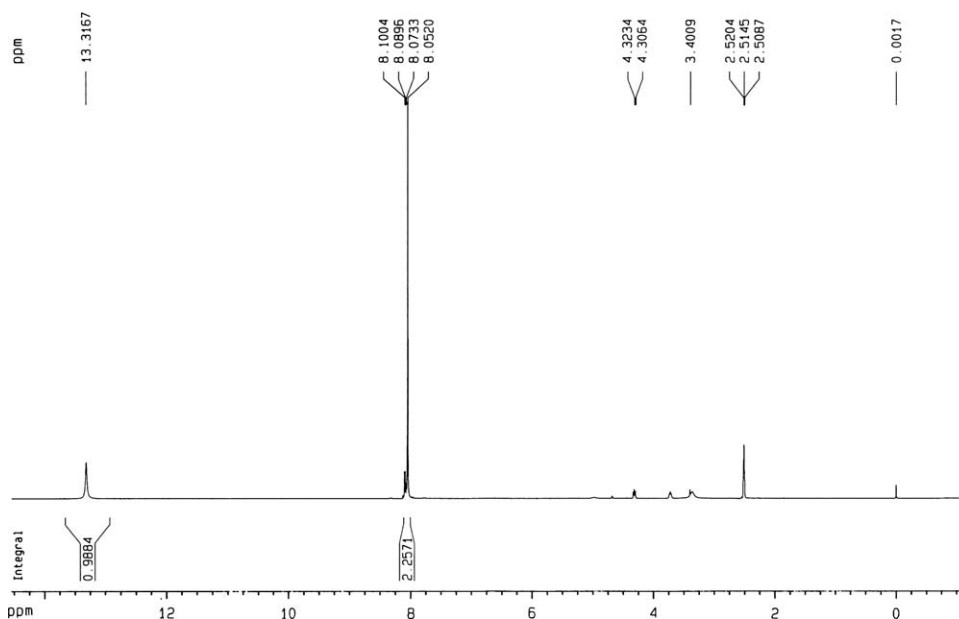


Figure 5 ¹H-NMR spectrum of the solid product.

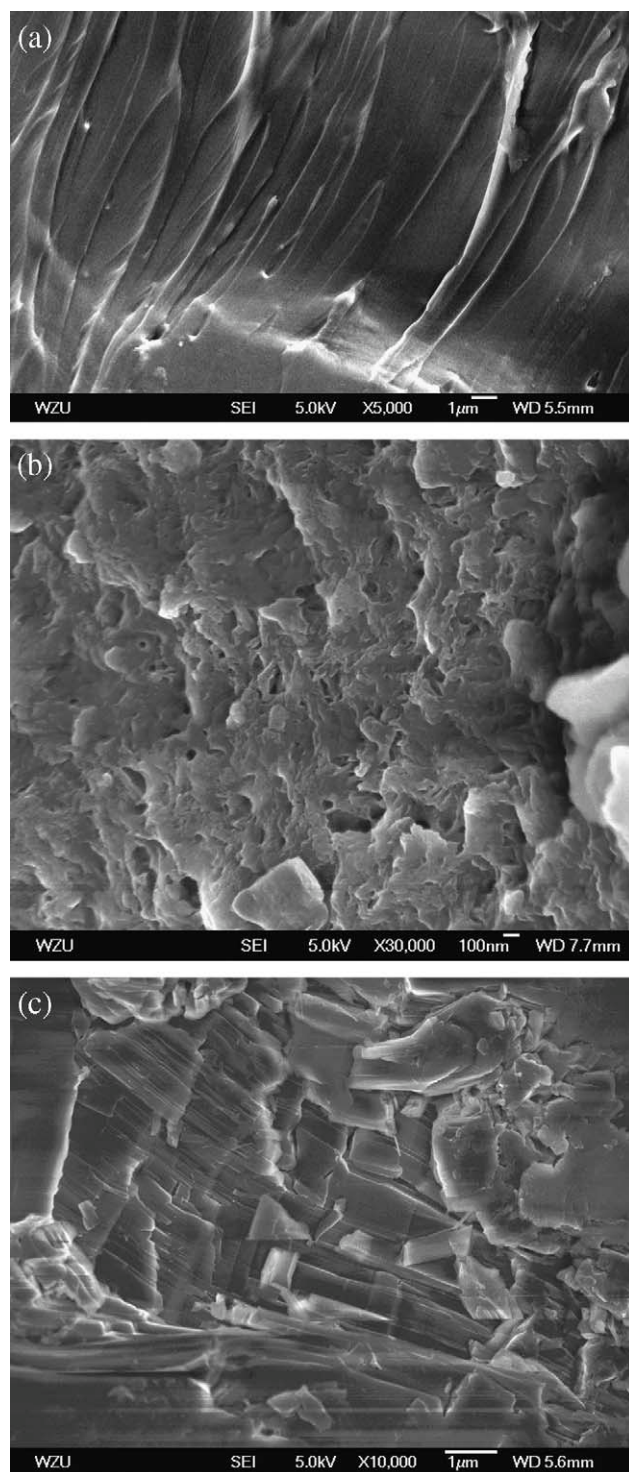


Figure 6 Scanning electron microscopy (SEM) photographs of (a) original PET; (b) the solid residue without catalyst; (c) the solid residue in present of stannous oxide.

prominent catalytic reaction conditions with stannous oxide. It could be further concluded that only at proper temperature and time did the catalysts activate effectively in this reaction, beyond the range, there was no obvious superiority for the catalyst.

Plots of the depolymerization rate of PET versus reaction temperature under stannous oxide and no catalyst were shown in Figure 3. It could be seen that when the reaction temperature was 160°C, the depolymerization rate of PET was almost 0. Therefore, we considered that the reaction could not be carried out at this temperature whether using stannous oxide as catalyst or not. The depolymerization rate of PET in the presence of stannous oxide increased by 1.9% at 170°C, 9.1% at 180°C, 33.4% at 190°C, 48.5% at 200°C compared with noncatalytic reaction. It showed that the catalytic effect of stannous oxide was greatly influenced by the reaction temperature, and with temperature increasing the catalytic effect of stannous oxide were improved.

Analyses of the depolymerized product and the depolymerization mechanism

The solid product of PET depolymerization carried out at a temperature of 200°C, a reaction time of 210 min, and in the presence of 0.5% stannous oxide was analyzed by FTIR and H-NMR, which were shown in Figures 4 and 5, respectively. The IR spectrum indicated the presence of TPA according to the Sadtler Standard Infrared Grating Spectra (15,694 K). It could be seen from the Figure 4 that the spectrograph contained peaks at about 1572, 1508, and 1420 cm^{-1} indicating the framework vibration of benzene, and peaks at 876, 779, and 728 cm^{-1} show the bending band of C—H in the benzene framework. The peak 1688 cm^{-1} show the presence of C=O stretching band, and the peak 1420 cm^{-1} show at the bending band of —CH₂— as well. The absorption peak at 1278, 1131, 1110, and 1018 cm^{-1} show the stretching band of C—O. The IR spectrum indicated that in the presence of stannous oxide the PET resin could be depolymerized to TPA. This conclusion was also supported by the results obtained from H-NMR.

It could be seen from H-NMR spectrum in Figure 5 that the signal at δ 8.10 ppm indicated the presence of the four aromatic protons of terephthalic residue and the signal at δ 13.3 ppm were characteristic of the carboxyl protons COOH. The weak signal between δ 3.4 and δ 4.3 ppm might be related to the very small amounts of protons of impurity. The result of H-NMR spectrum confirmed that the main solid product of PET depolymerization was TPA in the presence of stannous oxide. This result was coincident with the PET hydrolysis in pure water by Liu, et al.,⁸ and the PET depolymerization in the presence of zinc acetate by Li et al.⁹ It indicated that the catalyst just accelerated the reaction process without changing the main product of the reaction. In other words, the main solid product was exclusive in the present of stannous oxide as catalyst.

The morphology of the solid residue was observed by SEM, as shown in Figure 6. The morphology of original PET appeared as a tough and compact material [Fig. 6(a)]. After hydrolysis without catalyst for 210 min at 200°C, the solid residue of PET became rough and brittle, obviously pore and crack were observed inside PET grain [Fig. 6(b)]. The formation of pore and crack might be due to the swelling of PET in noncrystal part in the microwave irradiation. The pore and crack increased the effective reaction surface which accelerated the rate of hydrolysis. In the case of stannous oxide as catalyst, the solid residue of PET became brittle but the residue PET grain appears as lamellar crystal, and no pore and crack were observed inside PET grain [Fig. 6(c)]. This suggested that the depolymerization of PET in the presence of stannous oxide as catalyst occurred on the external surface of the PET grain, and the PET grain were lamellar depolymerized. Therefore, the reaction mechanism of PET depolymerization was changed by the catalyst of stannous oxide. The catalytic mechanism of PET depolymerization will be studied in the following work.

CONCLUSIONS

A series of experiments were done to study the effect of metal oxides catalysts on the depolymerization reaction. Stannous oxide was found to be the most effective catalyst among metal oxides used, which can improve the depolymerization rate by

31.6% compared with the noncatalytic reaction. The optimal dosage of stannous oxide was 0.5% of the feedstock PET, the optimal reaction conditions were a reaction time of 210 min, a temperature of 200°C. The results of FTIR and H-NMR spectra confirmed that the main solid product of PET depolymerization was terephthalic acid (TPA) in the presence of stannous oxide. The reaction mechanism of PET depolymerization was changed by the catalyst of stannous oxide.

Some research works about catalyzing mechanisms of other catalytic systems (such as zinc acetate, and sulfate) will be carried out for perfecting the catalytic researches to PET depolymerization under microwave irradiation.

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