

· 绿色化学与技术专栏 ·

Methanolysis of Poly(ethylene terephthalate) in Supercritical Phase

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Abstract: The depolymerization of poly(ethylene terephthalate, PET) in supercritical methanol is studied using a stainless stirred autoclave at temperature of 255~260 °C, pressure of 8.5~14.0 MPa, and methanol/PET weight ratio of 3~8. Under the optimal conditions, the PET is depolymerized completely to its monomers in 60 min. The main products of the reaction are dimethyl terephthalate and ethylene glycol. There are still some small amounts of byproducts, such as methyl-(2-hydroxyethyl) terephthalate, bis(hydroxyethyl) terephthalate, dimers and oligomers. Reversed-phase high performance liquid chromatography and gas chromatography are used to analyze solid products and liquid products respectively. The results of depolymerization show that the yield of dimethyl terephthalate and the degree of PET depolymerization are dependent on the reaction temperature, weight ratio of methanol to PET and reaction time. But the reaction pressure has little influence on the depolymerization as long as methanol is in supercritical state.

Key words: polyethylene terephthalate (PET); methanolysis; chemical recycling; supercritical fluid; depolymerization

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1 INTRODUCTION

Poly(ethylene terephthalate), commonly known as PET polyester, is extensively used for making synthetic fibers and package containers. The volume of PET consumed is rising by year, and thus the chemical recycling and reuse of waste PET are drawing much attention for the preservation of resources and the protection of environment. Through chemical recycling, waste PET is depolymerized into its valuable monomers such as dimethyl terephthalate (DMT), bis(hydroxyethyl) terephthalate (BHET) and terephthalic acid (TPA), which can be reused as feedstock for synthesizing new polyesters or polyols^[1].

There are several routes to depolymerize PET polyester into its monomers: alcoholysis with liquid methanol^[2] or ethylene glycol^[3, 4], hydrolysis^[5, 6] with alkali or acid solution or even with supercritical water^[7]. All of these routes have both advantages and disadvantages. The alcoholysis can be carried out under mild reaction temperature and pressure, but the rate of reaction is very low. It takes 6~8 h to depolymerize completely, and some metal acetate catalysts are required to

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accelerate the reaction. The process of hydrolysis with alkali or acid may cause corrosion to reactor and pollution to environment. Although hydrolysis with supercritical water proceeds at high reaction rate, the reaction conditions are very severe ($T_c=374.15^\circ\text{C}$, $p_c=22.0\text{ MPa}$), and it is adverse to operate.

In this work, depolymerization of PET polyester with supercritical methanol is carried out with absence of any catalysts. The influences of reaction pressure, weight ratio of methanol to PET and reaction time on the degree of PET decomposition and yield of products are investigated. Reversed-phase high performance liquid chromatography (RP-HPLC) is used to analyze the solid products, and the liquid products of the reaction system are analyzed by gas chromatography (GC).

2 EXPERIMENTAL

PET chips of 2~3 mm size with intrinsic viscosity of 0.661 were obtained from Liaoyang Petrochemical Company (China). Methanol and other reagents were analytical grade and used without further purification.

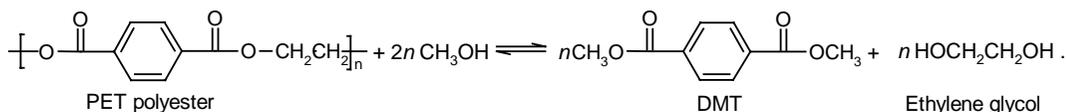
Experimental investigation was conducted at 255~260 $^\circ\text{C}$, 8.5~14.0 MPa. A certain weight ratio of methanol and PET (3~8) were loaded in a 150 ml autoclave. Before heating, the reactor was flushed with N_2 or Ar to remove the air in the reactor for avoiding oxidation of PET and depolymerization products. Then the autoclave was heated with electric heating collar. It will take about 15 min to raise the temperature and the pressure of reaction system to the desired values. The pressure of reaction system was dependent on the amount of methanol charged and the methanolysis temperature. Normally 50~85 ml of methanol is loaded. The heating process has negligible influence on the results of methanolysis, because the rate of methanolysis with absence of catalyst is very low under normal state. By blank test, we found that there were only about 2.0% (ω) ester linkages being broken during the heating interval before reaching the required temperature, while the content of DMT monomer in the solid product was found to be less than 0.2% (ω). So the initial degree of PET depolymerization is counted as 2.0% other than zero. After a specified time interval at reaction conditions, the autoclave was removed from the heating collar and quickly cooled with frigid water. The temperature of reaction system was dropped to 100 $^\circ\text{C}$ in 1~2 min. After the temperature of reaction system falling to room temperature, the autoclave was opened and the mixed products were obtained.

After decomposition, the mixture was separated into solid and liquid phases by filtration. The solid products mainly containing DMT and small amount of BHET, methyl-(2-hydroxyethyl) terephthalate (MHET), oligomers^[8], were analyzed by RP-HPLC^[9]. RP-HPLC analysis was carried out using a Shimadzu LC-3A high performance chromatograph equipped with a reversed-phase Zorbax-C₈ (4.6 mm \times 250 mm) and a SPD-1 ultraviolet detector set at 254 nm. The quantitative analysis of these components in the solid products used an inner unitary method. The procedure of analysis was as follows: 20~40 mg/L sample solution for analysis was prepared by dissolving certain amount of depolymerization product in a 70:30 (V/V) methanol/water solution^[9], which was also used as mobile phase with the flow rate of 1 ml/min. The column was at room temperature. The

filtrate containing ethylene glycol and the unreacted methanol was analyzed with GC, equipped with 2 m stainless column packed with PEG-20M. The temperature of the column, detector and injector port were 160, 200, 200°C respectively. Hydrogen was used as carrier gas with the flow rate of 30 ml/min, and the components of liquid products were detected by a flame ionization detector.

3 RESULTS AND DISCUSSION

With the assumption that supercritical methanolysis has the same reaction mechanism with that of normal methanolysis, two ester-linkages are broken by two methanol molecules to produce an ethylene glycol molecule and a DMT molecule as the following reaction:



The degree of PET depolymerization can be evaluated by the yield of EG. The yields of DMT and EG monomers are defined respectively as follows:

$$\text{Yield of EG (\%)} = \frac{\text{Weight of EG in liquid product} \times 100\%}{\text{Theoretic output of EG}},$$

$$\text{Yield of EG (\%)} = \frac{\text{Weight of DMT in solid product} \times 100\%}{\text{Theoretic output of DMT}}.$$

The reactions with different depolymerization time were investigated at 260°C and 11.0 MPa, and the weight ratio (methanol to PET) of 6:1. Figures 1 and 2 show the degree of PET depolymerization and the yield of DMT monomer respectively. More than 95% PET is depolymerized within 30 min, while the yield of DMT monomer reaches up to 90%. After having reacted for 60 min, PET is almost depolymerized completely, and the yield of DMT monomer exceeds 95%. During the reaction, some byproducts such as BHET and MHET are formed. Figure 3 displays the change of the yields of BHET and MHET versus reaction time. Figure 4 shows the yield of dimers and oligomers in the depolymerization product. It is obvious that the yields of all these byproducts rapidly decrease with the increase of reaction time.

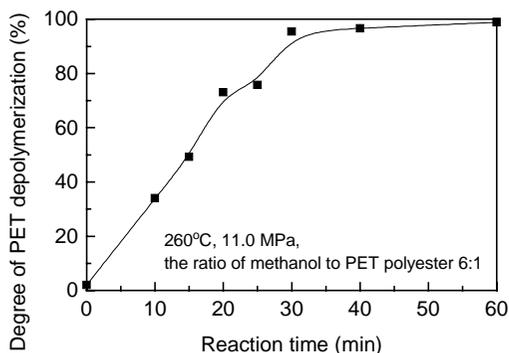


Fig.1 Effect of reaction time on the depolymerization degree of PET

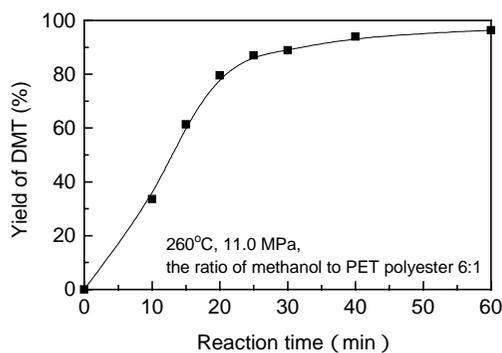


Fig.2 Effect of reaction time on the yield of DMT

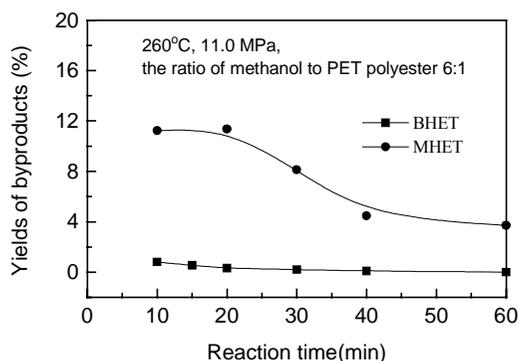


Fig.3 Effect of reaction time on the yield of byproducts

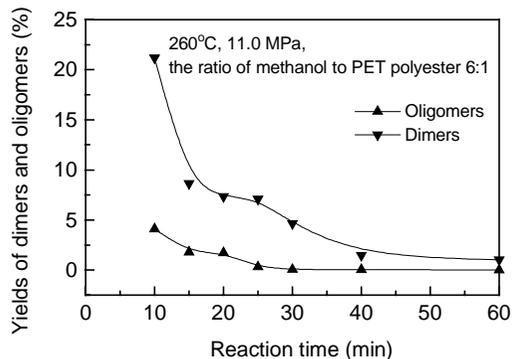


Fig.4 Effect of reaction time on the yields of dimers and oligomers

The influences of pressure and weight ratio of methanol to PET on the reaction were also investigated. The effects of the weight ratio of methanol to PET on the degree of PET depolymerization and the yield of DMT at 255°C, 10.0 MPa and with the reaction interval of 20 min are listed in Table 1. It shows that the degree of PET depolymerization rise with the increase of the weight ratio of methanol to PET. The effect of the reaction pressure on the degree of PET depolymerization at 255°C, methanol/PET=4 and with the reaction interval of 20 min is listed in Table 2. It indicates that the pressure of the reaction system has little influence on the depolymerization degree of PET, when the temperature and pressure of reaction are above the critical point of methanol (239.2°C, 8.09 MPa).

Table 1 The effect of ratio of methanol to PET on the depolymerization of PET (255°C, 10.0 MPa, 20 min)

Weight ratio of methanol to PET	8	6	4	3
PET depolymerization (%)	79.3	72.7	63.5	26.6
The yield of DMT (%)	76.5	67.2	59.1	20.7

Table 2 The effect of pressure of reaction on the depolymerization of PET (255°C, methanol/PET=4, 20 min)

Pressure (MPa)	9.0	10.0	11.0	12.0
PET depolymerization (%)	63.0	63.5	64.1	64.4

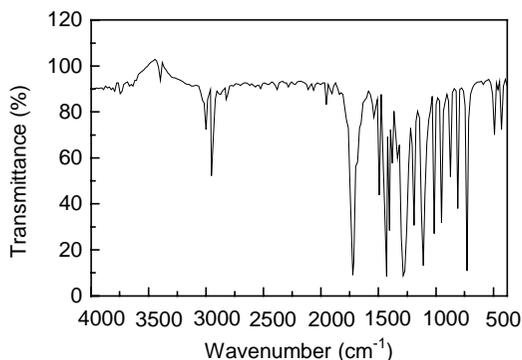


Fig.5 IR spectrum of the purified sample

In addition, in order to remove the byproducts and impurities and extract the DMT monomer, the solid product from depolymerization of 60 min at 260°C and 11.0 MPa with the methanol/PET=6 was washed with methanol. The obtained sample has a melting point at 141~142°C in coincidence with that of pure DMT. The DMT purity of the sample is >98%. Figure 5 shows IR spectrum of the sample. The absorption bands at

3000~2800, 1750, and 1100 cm^{-1} are assigned to C—H, C=O and C—O stretching vibrations, respectively. This result agrees with the standard spectrum of DMT^[10].

4 CONCLUSION

PET polyester is depolymerized quickly and completely into its constituent monomers (DMT and EG) in supercritical methanol within 60 min at 260°C and 11.0 MPa. The purity of DMT in the solid product is >95%, and with further purification, the purity of DMT could be over 98%. The yield of DMT and the degree of PET depolymerization increase with the increase of the ratio of methanol to PET and the reaction time, while the depolymerization pressure has little influence on both of them under the supercritical state of methanol.

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