

MWD Analysis in Decomposition of PET in Supercritical Methanol

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Polyethylene terephthalate (PET) is decomposed to its monomers, dimethyl terephthalate (DMT) and ethylene glycol (EG), by solvolysis (methanolysis) in supercritical methanol. The reaction conditions were reaction time ; 2-120 min, temperature ; 573-623 K, and pressure ; 20 MPa. The reaction products were analyzed with size exclusion chromatography and gas chromatography-mass spectrometry. The molecular weight distribution of the products was obtained as a function of reaction time. The DMT yield was largest of about 80 mol% at 573 K and 120 min. A peaks corresponding to methyl 2-hydroxyethyl terephthalate, which is 1:1 monomer of DMT and EG, was also observed. The greatest yield of EG was about 60 mol% at 573 K in 60 min. In the conditions of this study, both monomers were obtained efficiently when decomposed at 573 K and 20 MPa.

Introduction

Disposal and recycling of waste plastics have become a serious problem. Decomposition of plastics with supercritical fluids has been focused, because of the environmental friendly nature of the fluids. Plastics are decomposed in supercritical fluids quickly by solvolysis (hydrolysis, alcoholysis) or pyrolysis. Condensation polymers having ether linkage, ester linkage, and acid amide linkage are easily decomposed to its monomers by solvolysis in supercritical water or supercritical methanol. The chemical recycling by depolymerization of polyethylene terephthalate (PET), which is an abundantly used condensation polymer, is most required.

Various methods, such as methanolysis in liquid methanol, glycolysis in liquid ethylene glycol, ester exchange, and hydrolysis under the existence of alkali, have been developed in commercial or pilot-scale. However, these methods have problems, such as the use of catalyst and long reaction time. Reactions under supercritical condition have been studied to solve these problems. Hydrolysis in supercritical water ($T_c=647.3$ K, $P_c=22.0$ MPa) [1,2] or methanolysis in supercritical methanol ($T_c=512.6$ K, $P_c=8.09$ MPa) [3,4]

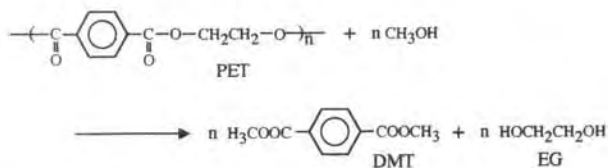


Figure 1 The decomposition reaction formula of PET in supercritical methanol

has been studied for PET decomposition. PET is decomposed to dimethyl terephthalate (DMT) and ethylene glycol (EG) by solvolysis in supercritical methanol as shown in Fig. 1.

In this work, we investigated the depolymerization of PET to its monomers in supercritical methanol. Evolution of molecular weight distribution (MWD) of polymer, oligomer, and monomers and concentration of the products and by-products were measured as a function of reaction time. The influence of the reaction temperature upon the decomposition of PET was studied in the temperature range of 573 K to 623 K.

Experiments

A batch reactor made of stainless steel with the volume of about 5.4 cm³ was used. PET of about 0.3 g and adequate amount of methanol to attain desired pressure were charged into the reactor and the air in the reactor was replaced with N₂ gas. The amount of methanol was calculated by using the Peng-Robinson's equation of state to get the pressure of 20 MPa. The experiments were carried out at the reaction temperature ranged from 573 K to 623 K and the estimated pressure of 20 MPa for 2 to 120 min. The reaction was started by immersing the reactor in the melting salt bath preheated to the reaction temperature. After a certain time from 2 to 120 min, the reactor was cooled quickly in a water bath. The reaction products were analyzed by two kinds of method. All the decomposition products were dissolved in hexafluoro isopropanol (HFIP) and analyzed by size exclusion chromatography (SEC) (Tosoh, TSKgel Super HM-M) using HFIP as a mobile phase with UV detector. GC-MS was used to identify low molecular weight components. On the other hand, the decomposition products were filtrated with water and analyzed for EG related components by reversed phase chromatography (RPLC) (Waters, 5C18-MS) using water as a mobile phase with RI detector.

The PET used was DIANITE PA-500 (Mitsubishi Rayon Co., Ltd.) and its m.p. was 255 °C. Methanol (Wako Pure Chemical Industries Ltd.) with 99.8 % in purity was dehydrated.

Results and Discussions

Figure 2 shows MWD obtained from SEC elution curve of decomposition products. MWD for reaction products of 5 and 60 min reaction at 573 K and 20 MPa are shown in comparison with original PET. With increase in reaction time, molecular weight was reduced. PET with molecular weight of about 47,000 (polymerization degree : 240~250) was decomposed to oligomer with the

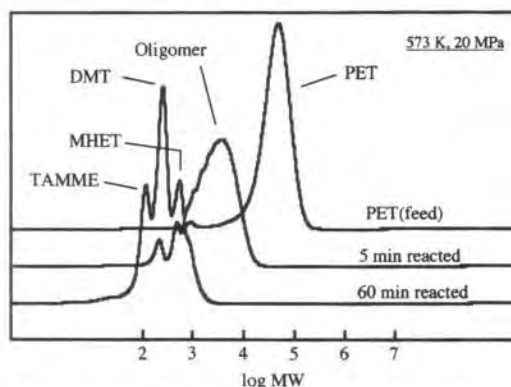


Figure 2 SEC/UV(286.6 nm) measurement of molecular weight distribution for decomposition products

molecular weight of 3,000 (polymerization degree : 15) in 5 min. The DMT peak was also observed. When the reaction time was 60 min, PET was completely decomposed to its monomers, whose three peaks were observed in the elution curve. These peaks were identified its to DMT, methyl 2-hydroxyethyl terephthalate (MHET), which is 1:1 monomer of DMT and EG, and terephthalic acid monomethyl ester (TAMME). The existence of TAMME suggests the progress of a side reaction.

Figures 3 and 4 show change of the yields of each component as a function of the reaction time at 573 K and 603 K, respectively. The yields of each component were evaluated by the following equations.

$$\begin{aligned} \text{Yield of product (mol\%)} \\ = \frac{\text{moles of product obtained by SEC or RPLC analysis}}{\text{moles of PET units}} \times 100 \end{aligned} \quad (1)$$

The yields of DMT and EG increased with the reaction time. The production rates of DMT and EG were larger at higher temperature. However at higher temperature of 603 K, the increase of monomer yield stopped at earlier reaction time than at lower temperature of 573 K. The yield at 573 K was larger than the yield at 603 K for both monomers. The largest yield of DMT was about 80 % at 573 K and 120 min. MHET yield was highest when the reaction time was 30 min at both reaction temperatures, and then the MHET yield decreased. There was a remarkable difference with temperature in terms of the yield of EG. The yield of EG was about 40 % after 30 min at 603 K compared with about 60 % after 60 min at 573 K. A little amount DEG dimerized from EG was also observed up to 2.5 %. Low yields of DMT and EG were owing to the progress of side reaction to MHET, TAMME, and DEG. However, all the polymer and oligomer were completely converted to its monomers and the other components in 60 min.

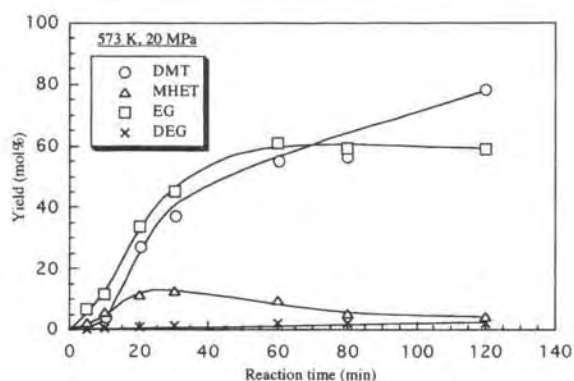


Figure 3 The yields of each component (573 K, 20 MPa)

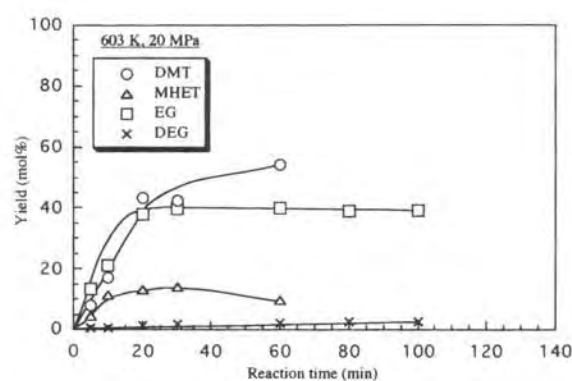


Figure 4 The yields of each component (603 K, 20 MPa)

When the reaction was carried out at 623 K, the color of reaction products was dark brown and it became darker as the reaction time was longer than 20 min. Consequently, the experiments at 623 K couldn't carry out and we found that condition over 623 K (in case at 20 MPa) was not suitable for the decomposition of PET. The results of experiments at 623 K up to 10 min were similar to those at 603 K. In the conditions of this study, both monomers were efficiently obtained when decomposed at 573 K and 20 MPa. The yield of EG was much higher than that for the reaction in supercritical water [1,2].

Figure 5 shows the reaction scheme of PET decomposition in supercritical methanol. PET is depolymerized by random scission to oligomer, and then DMT, EG, and MHET are produced by end scission. Produced MHET reacts further with methanol to produce DMT and EG. Dimerization of EG occurs to produce DEG. Some of TAMME may be produced from MHET by using H₂O produced by the side reaction from EG to DEG.

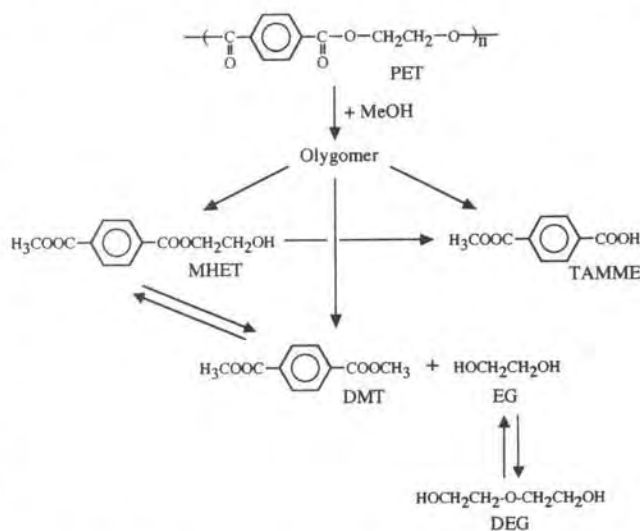


Figure 5 The reaction scheme of PET decomposition in supercritical methanol

Conclusions

The decomposition behavior of PET in supercritical methanol was observed by means of SEC elution curves, MWD, and the variations of yields of each products. The influence of reaction temperature was observed. Conversion to the monomers was most efficient at lower reaction temperature of 573 K. Both DMT and EG monomers and MHET were recovered effectively and the side reactions were substantially low in comparison with reaction in supercritical water.

References

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