

DEPOLYMERIZATION OF POLYETHYLENE TEREPHTHALATE TO MONOMERS WITH SUPERCRITICAL METHANOL

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Introduction

The chemical recycling of plastic waste has been receiving much attention in recent years from the viewpoint of the preservation of natural resources and environmental protection of the earth. In recycling, waste plastics are depolymerized to the constituent monomers or oligomers such as fuel oil. Several different types of chemical treatment have to be developed to deal with the many kinds of commercial plastics (Datye *et al.*, 1984a).

Polyethylene terephthalate (PET), which is a condensation polymer widely used for containers and textile fibers, is a suitable polymer for chemical recycling because it is relatively easy to recover alone; the purity of the polymer is very high, almost 100%; and the calorific value in combustion is low. In 1995, Japan produced 142,000 tons of PET bottles for drinking, which will have to be recycled from 1997, and reused only 2,600 tons (1.8%) as textile fibers or goods of low value.

There are several techniques proposed to depolymerize PET into its monomers: alcoholysis with liquid methanol (Grunschke *et al.*, 1968) or liquid ethylene glycol (Baliga and Wong, 1989), hydrolysis with alkaline solution (Datye and Vaidya, 1984b) or supercritical water (Sato *et al.*, 1995), and transesterification (Delattre *et al.*, 1979). Each technique has both advantages and disadvantages. The conventional two kinds of alcoholyses have the advantages that they have a relatively mild depolymerization temperature and pressure and can recover both monomers almost completely. On the other hand, there are several disadvantages, among them the rate of decomposition of the PET is very low and a catalyst such as zinc acetate is required to accelerate the

reaction. Hydrolytic depolymerization with supercritical water is an attractive method in that a very high reaction rate can be realized without any catalyst. But the decomposition condition is quite severe, that is, the reaction temperature and pressure are around 673 K and 30 MPa, and the ethylene glycol produced disappears through acidic decomposition in the presence of terephthalic acid produced in supercritical water.

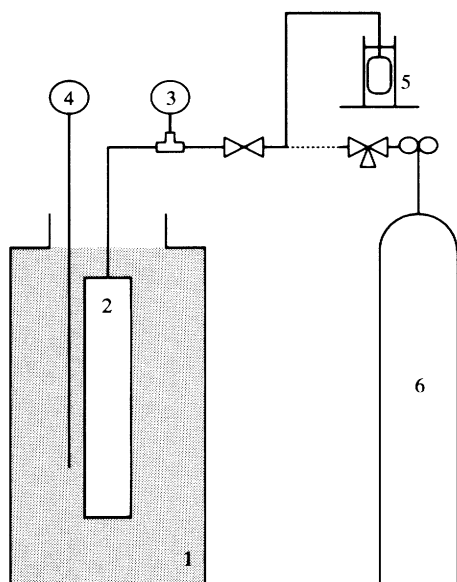
In this work, we investigated the possibility of depolymerization of PET to its monomers with supercritical methanol and checked the pressure dependence on the yield of the decomposition product under constant temperature conditions.

1. Experimental Apparatus and Procedure

A batch-type reactor was used for all methanolysis experiments. The experimental apparatus is shown in Fig. 1. The reactor (2) was made of 316 stainless steel and the inner volume was about 0.02 dm³. The reaction pressure was monitored using a Bourdon pressure gauge (3) attached on the upper line of the reactor. The reaction temperature was considered to be equal to the temperature of a fluidized sand bath (1), which was measured with a K-type thermocouple (4). The influence of the condensation of the methanol in the tube connecting to the pressure gauge, which was outside of the fluidized sand bath, was negligible because the inner volume of the tube, 0.0009 dm³, was much smaller than that of the reactor of 0.02 dm³ volume.

The experimental procedure was as follows. 0.5 g of PET and 0.002–0.015 dm³ of methanol were charged into the reactor and the air inside the reactor was replaced with argon gas of atmospheric pressure to avoid the oxidation of the PET by the air. The reaction pressure was controlled by adjusting the amount of the methanol charged into the reactor.

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1: Fluidized sand bath; 2: Reactor; 3: Pressure gauge; 4: Thermometer; 5: Gas-sampling bag; 6: Ar gas cylinder

Fig. 1 Apparatus for depolymerization of plastics

Then the reactor was put into the fluidized sand bath controlled at the reaction temperature. It took about 5 min for the reactor to reach a given reaction temperature and pressure. After keeping the reactor at a reaction temperature for a set time interval, the reactor was taken out of the sand bath and cooled quickly in water to stop the reaction as soon as possible. It took less than 30 seconds to decrease the temperature of the reactor below 373 K. The gaseous product was collected into a sampling bag (5) to measure the volume and analyze the composition using GC-TCD. The reactor was subsequently opened and the liquid and solid products were taken from the reactor.

The reaction products of the liquid and solid states were analyzed according to the procedure shown in Fig. 2. The product contained the monomers of dimethyl terephthalate (DMT) and ethylene glycol (EG), oligomers linking some units of the monomers, unreacted PET and methanol. In this work the oligomer was defined as the product which was hydrolyzed with NaOH solution to terephthalic acid (TA) and ethylene glycol. In the

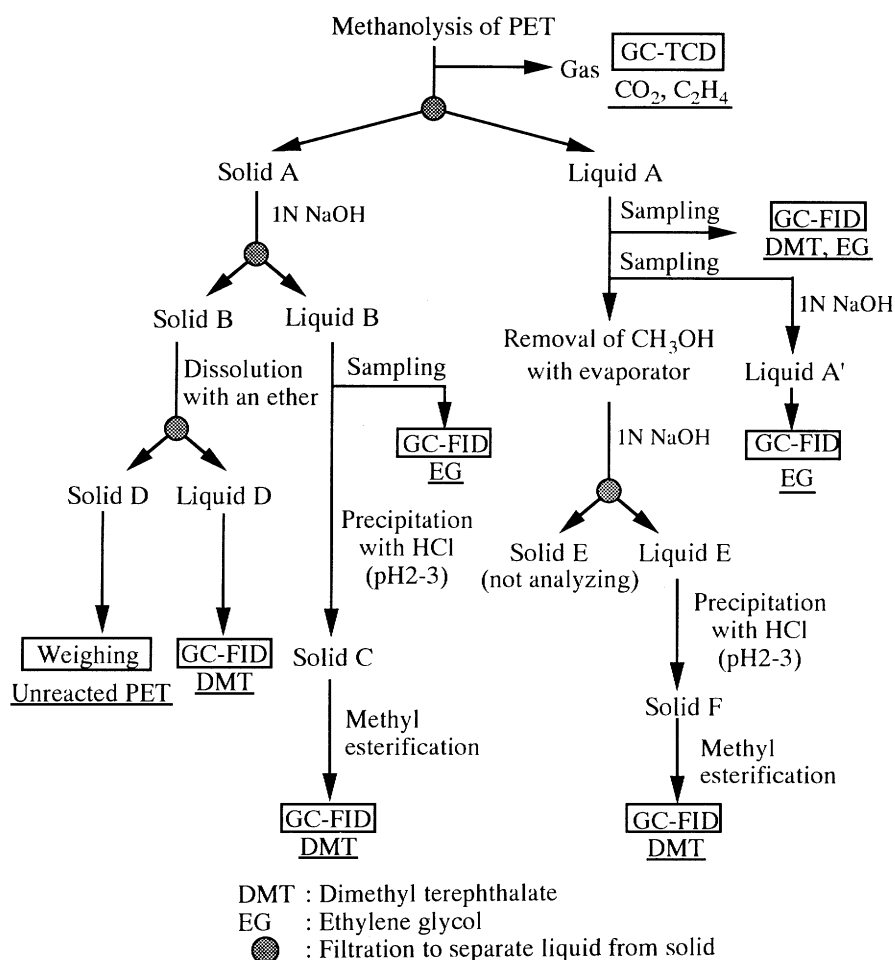


Fig. 2 Analytical procedure of decomposition product of PET

first step, the product was separated into solid (called solid A) and liquid (liquid A) phases using filtration. The solid A contained the DMT monomer and the oligomer, which were not dissolved in liquid A owing to the solubility limitation, and the unreacted PET. The liquid A contained the EG monomer, a part of the DMT monomer and the oligomer.

Each component in solid A was analyzed as follows. After the removal of methanol by heating at 323 K in an air bath, the oligomer was decomposed with 1N NaOH aqueous solution to disodium terephthalate (NaTA) and EG. The solution was filtered to a solid B and a liquid B. Diethyl ether was added into the solid B and, after a while, the filtration was carried out to separate a solid D and a liquid D. The solid D was the unreacted PET and was weighed using a balance after drying at 323 K. The DMT in the liquid D, which was a monomer produced from PET, was analyzed with GC-FID. The liquid B contained NaTA and EG obtained from the oligomer decomposition. The EG was analyzed by GC-FID. The NaTA was precipitated from the liquid B by adding HCl aqueous solution and separated with filtration. The solid was the TA and called solid C. Solid C was esterified with methanol and determined by GC-FID. Each component in liquid A was analyzed in the same manner as that in solid A according to the procedure in Fig. 2.

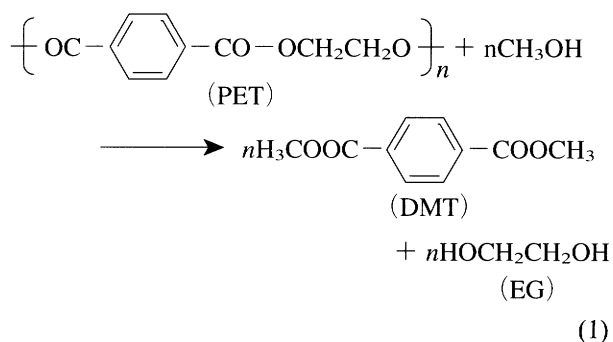
Finally the unreacted PET was recovered as solid D, the DMT monomer as liquids A and D, the EG monomer as liquid A, the DMT component in the oligomer as solids C and F, and the EG component in the oligomer as liquid B and the difference of the amount of the EG in liquid A from that in liquid A'.

The accuracies of the measurement of the reaction temperature and pressure were 1 K and 0.2 MPa, respectively. The gas chromatograph was calibrated by injecting various amounts of pure components and analyzed in the range where the peak area was linear with the sample volumes. The analytical accuracy of GC was $\pm 1.0\%$.

The methanol was supplied by Wako Pure Chemical Industries, Ltd. and its purity was higher than 99.8%. It was dehydrated by molecular sieves for at least a day before all experiments. The PET was provided by Aldrich Chemical Co., and its IV was 0.59.

2. Results and Discussion

Assuming that the methanolysis of the PET using the supercritical methanol proceeds under the same reaction mechanism as that using the liquid methanol, an ester linkage in the PET is cloven by a methanol molecule in supercritical state as shown below:



Each chain scission uses a methanol molecule and creates the end groups of a methyl ester and ethylene glycol. The critical properties of methanol are $T_c=512.3$ K, $p_c=8.09$ MPa and $\rho_c=0.272$ g/cm³ (Reid *et al.*, 1987).

The volume of the gaseous product was less than 0.00001 dm³ and negligibly small. Secondary decomposition of the produced monomers was avoided because of the low depolymerization temperature of 573 K. Most of the decomposition products existed as a liquid or solid state. The degree, selectivity and yield of the PET decomposition were evaluated by the quantities defined by

$$\text{Remaining rate of PET (\%)} = \frac{\text{grams of an unreacted PET} \times 100}{\text{grams of a charged PET}} \quad (2)$$

$$\text{DMT yield of monomer (\%)} = \frac{\text{moles of a produced DMT monomer} \times 8 \times 100}{\text{grams of a charged PET} / (\text{formula weight of a repeating segment of PET}) \times 10}$$

$$\text{EG yield of monomer (\%)} = \frac{\text{moles of a produced EG monomer} \times 2 \times 100}{\text{grams of a charged PET} / (\text{formula weight of a repeating segment of PET}) \times 10}$$

where the formula weight of a repeating segment of the PET is 192.2. The yield of the monomers was defined based on the number of the carbon atoms in the repeating segment of the PET and in the monomers. There were 10 carbon atoms in the PET segment, 8 carbon atoms in the DMT monomer, and 2 carbon atoms in the EG monomer. The EG or DMT yield of the oligomer was defined by equations similar to the monomers given in Eq. (2), where the moles of a specific monomer produced were replaced by the moles of a specific component (EG or DMT) obtained from decomposition of the oligomer. When the PET was decomposed to the monomers completely, the maximum EG yield of the monomer

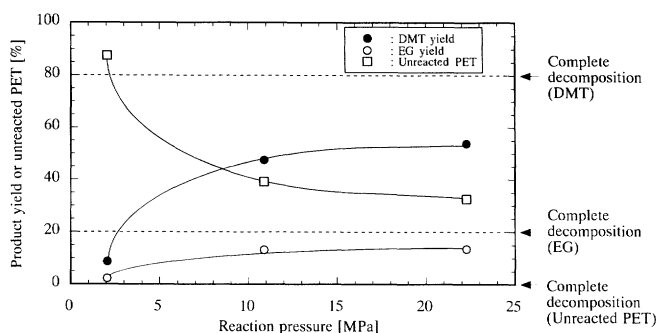


Fig. 3 Effect of reaction pressure on yields of decomposition products (Reaction temp. = 573 K, time = 10 min)

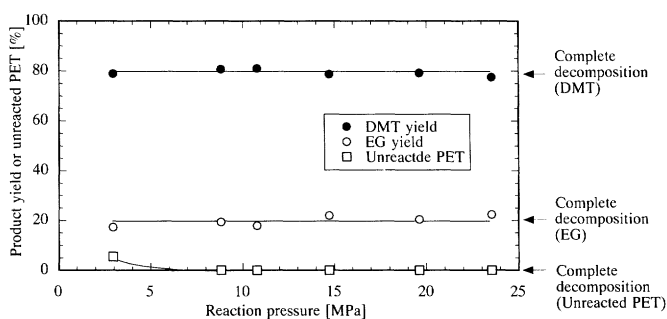


Fig. 4 Effect of reaction pressure on yields of decomposition products (Reaction temp. = 573 K, time = 30 min)

was 20% and the maximum DMT yield of the monomer was 80%.

We investigated the experimental condition of the complete decomposition of the PET with supercritical methanol. In Figs. 3 and 4, the yield of the decomposition products means the sum of the monomer and the same component in the oligomers. Most of the oligomers were 4-methoxy carbonyl benzoic acid-2-hydroxyethyl ($\text{CH}_3\text{COO}-\text{C}_6\text{H}_4-\text{COOCH}_2-\text{CH}_2\text{OH}$), which can be also chemically recycled as a raw material of the PET. **Figure 3** shows the effect of the reaction pressure on the yields of the decomposition products at 573 K and 10 min of the reaction time. About 90% of the PET did not decompose at 2 MPa in a low pressure region, but the decomposition proceeded gradually as the reaction pressure increased. The remaining rate of the PET was about 35% at 22 MPa in the high pressure region. **Figure 4** shows the influence of the reaction pressure on the yields of the decomposition products, where the reaction time was extended to 30 min under the same temperature conditions as that used in Fig. 3. The PET was depolymerized by 95% at 3 MPa and decomposed completely above 8 MPa. Most of the DMT and EG were recovered as either monomers or oligomers, and no secondary decomposition of the

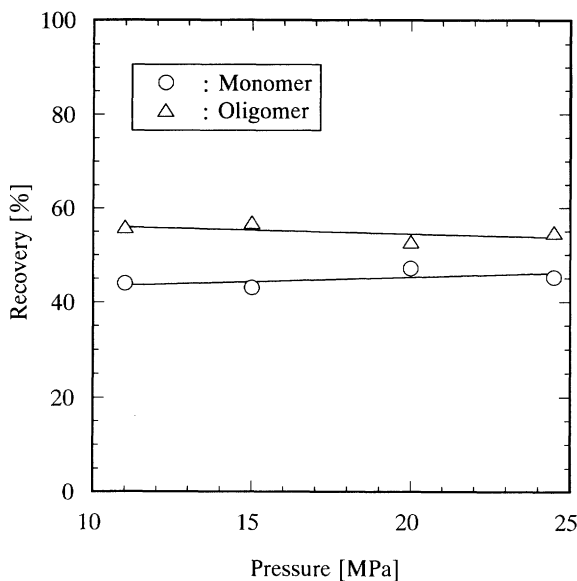


Fig. 5 Pressure dependence of recovery of monomer and oligomer of dimethyl terephthalate in PET (Reaction temp. = 573 K, time = 30 min)

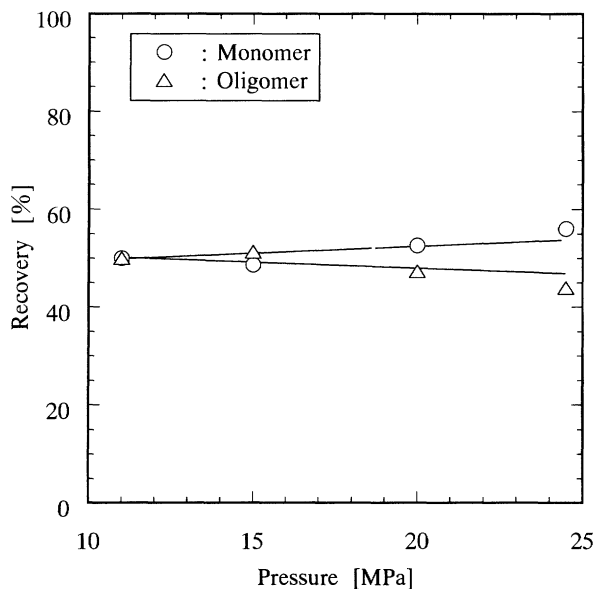


Fig. 6 Pressure dependence of recovery of monomer and oligomer of ethylene glycol in PET (Reaction temp. = 573 K, time = 30 min)

monomers occurred during the experiment.

Under the pressure conditions where the PET was converted completely to monomers and oligomers at 573 K and 30 min of reaction time, the amounts of the monomers and oligomers were determined according to the analytical procedure given in Fig. 2. **Figure 5** shows the pressure dependence of the recovery of the DMT in the monomer and oligomer. The ratio of the DMT monomer to the DMT

oligomers was almost constant between 40 and 50% over the pressures studied in this work. For the EG component, the ratio was also between 50 – 55% as shown in **Fig. 6** and the pressure dependence was small in the same manner as the DMT was. Furthermore, as the ratio of the moles of the DMT to EG monomers produced was almost unity, the oligomer consisted of the same number of DMT and EG molecules. This fact agreed with the GC-MS result that most of the oligomers were 4-methoxy carboxyl benzoic acid-2-hydroxy ethyl, which was 1 : 1 ester of DMT and EG.

Conclusion

PET was depolymerized to its constituent monomers of dimethyl terephthalate and ethylene glycol with the supercritical methanol at a temperature of 573 K and pressures from 2 to 23 MPa. Supercritical methanol was an excellent solvent and decomposed the PET to the monomers completely and rapidly. The decomposition rate was much higher

than that using liquid methanol, which is employed in conventional recovery methods.

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