

Determination of the proportion between hydrolysis and pyrolysis during poly(ethylene terephthalate) degradation in ^{18}O -labeled steam

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Abstract

Poly(ethylene terephthalate) (PET) was decomposed in ^{18}O -labeled steam atmosphere in order to determine the proportions of pyrolysis and hydrolysis, producing labeled and unlabeled terephthalic acid (TPA). It was clear that 13% of ester bonds were hydrolyzed at 400 °C at 25 vol% steam concentration, which fractions were improved with steam concentration increase, resulting in 29% at 75 vol%. In addition, apparent activation energy was determined between 0 vol% and 75 vol% steam concentrations from thermogravimetric analysis, which values decreased from 199 kJ mol⁻¹ at pyrolysis condition to 132 kJ mol⁻¹ at 75 vol%. The results implied that pyrolysis was dominant over hydrolysis at 400 °C since steam mainly reacted on the PET surface.

Keywords: PET, isotopic label, kinetics, proportion

1. Introduction

Thermal degradation is one method for conversion of plastics into monomers, which is less affected by impurities. Poly(ethylene terephthalate) (PET) is also thermally decomposed into terephthalic acid (TPA), which production is accelerated in team atmosphere [1]. The recovered TPA is used as a monomer for PET synthesis or converted into benzene in the presence of CaO [2]. However, PET is decomposed in steam at higher temperatures by both pyrolysis and hydrolysis. Therefore, the degradation mechanism in steam atmosphere should be revealed in order to estimate the exact yields or determine the suitable operating conditions.

In this study, the proportions of pyrolysis and hydrolysis in the steam degradation of PET using ^{18}O -labeled water (H_2^{18}O) were determined. In addition, apparent activation energy for each condition was analyzed using thermogravimetric analysis (TGA).

2. Materials and Methods

Crushed PET bottles (200 mg, <250 μm) were filled into a perforated quartz holder, which was suspended outside of the heating zone in the tube reactor. The 10% H_2^{18}O steam mixed with ion-exchanged water was generated from steam generator heated by an electric furnace. When the experimental conditions were achieved (400 °C, total of helium and steam gas flow of 300 ml min⁻¹, 0, 25, 50, 75 or 100 vol% steam concentration), the sample holder was introduced into the heating zone. The temperature was kept for 30 min. Produced TPA was recovered and esterified with diazomethane, forming dimethyl terephthalate (DMT) without removing the ^{18}O labeled isotope. The DMT was analyzed using gas chromatography-mass spectrometry (GC-MS), the proportions of pyrolysis and hydrolysis

were determined from distribution of labeled and unlabeled DMT.

In order to determine the apparent activation energy for each steam concentration (0, 25, 50 and 75 vol%), a 10 mg PET particle was decomposed between 350 °C and 390 °C using TGA.

3. Result and discussion

The MS spectrum of labeled and unlabeled DMT obtained from hydrolysis of H_2^{18}O containing steam and ion-exchanged water are summarized in Fig. 1. It can be distinguished that the one ($m/z = 196$) or two ($m/z = 198$) ester bonds were hydrolyzed in the presence of H_2^{18}O steam.

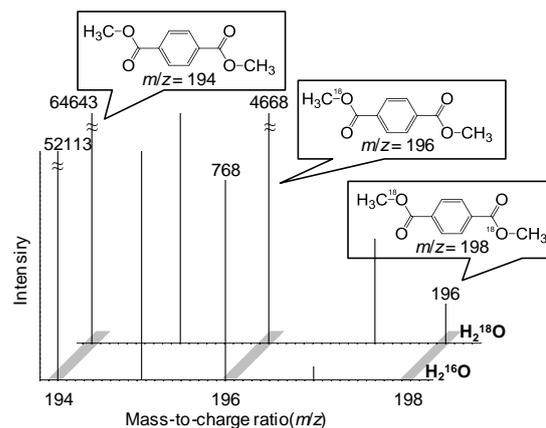


Fig.1 MS spectrum of DMT produced by steam decomposition using ion-exchange water and ^{18}O -isotope-labeled water.

The proportions of pyrolysis and hydrolysis of PET degradation for each steam concentration were shown in Fig. 2. The hydrolysis fraction was 13% at 25 vol% of steam, which was promoted with increasing steam concentration, resulting in 29% at 75 vol%. However,

hydrolysis fractions between 75 vol% and 100 vol% were similar, probably as a result of mass transport phenomena, well known in combustion processes. As the reactive gas approached the substrate, gas product was formed, which moved in a countercurrent with the reactive gas and limited its presence at the surface of the substrate. As a consequence, the hydrolysis rate was limited by the access of steam, which was controlled by the gas product evolution. Pyrolysis therefore remained dominant at all steam concentrations at this temperature. The exchange of ^{18}O -labeled hydroxyl groups between TPA and steam, and vice versa, was not observed when unlabeled TPA was exposed to ^{18}O -labeled steam. Exchange of hydroxyl groups during contact with the condensed water phase can also be excluded because of the low reactivity of the acid under the conditions used[3].

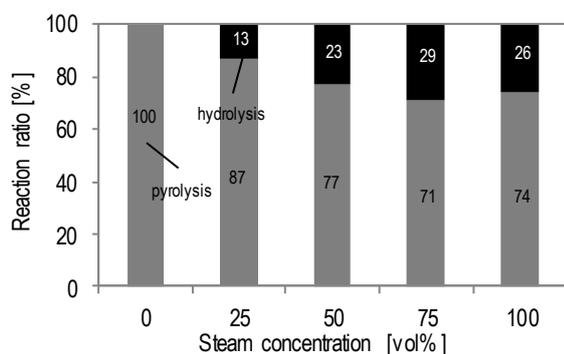


Fig.2 Selectivity of hydrolysis and pyrolysis in steam decomposition of PET at 400 °C and various steam concentrations.

The apparent activation energy for each steam concentration was determined from the Arrhenius plot (eq. 2). The highest correlated reaction model $g(\alpha)$ was selected from Table 2 in Grause *et al.* [4] and reaction constant k_{app} , calculated using eq.1.

$$\frac{d\alpha}{dt} = k_{app} \cdot g(\alpha) \quad (1)$$

$$k_{app} = A \cdot \exp\left(\frac{E_{app}}{RT}\right) \quad (2)$$

where, α : decomposition rate [-], t : time [min], k_{app} : apparent reaction constant [min^{-1}], $g(\alpha)$: reaction model, A : frequency factor [min^{-1}], E_{app} : apparent activation energy [kJ mol^{-1}], R : gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T : temperature [K]

Activation energy was decreased with steam concentration increase, resulting in 199, 190, 137 and 132 kJ mol^{-1} at 0, 25, 50 and 75 vol% steam concentration, respectively. E_{app} decreased drastically between 25 and 50 vol%. The same tendency was observed for the hydrolysis ratio shown in Figure 2.

The reaction mechanism of pyrolysis and hydrolysis in steam decomposition of PET is shown in Fig.3. PET was hydrolyzed by contacting steam, therefore hydrolysis might have progressed only at the PET surface. In contrast, the driving force of pyrolysis was only heat,

hence PET was pyrolyzed anywhere. In addition, it was confirmed that TPA did not decompose under the conditions used.

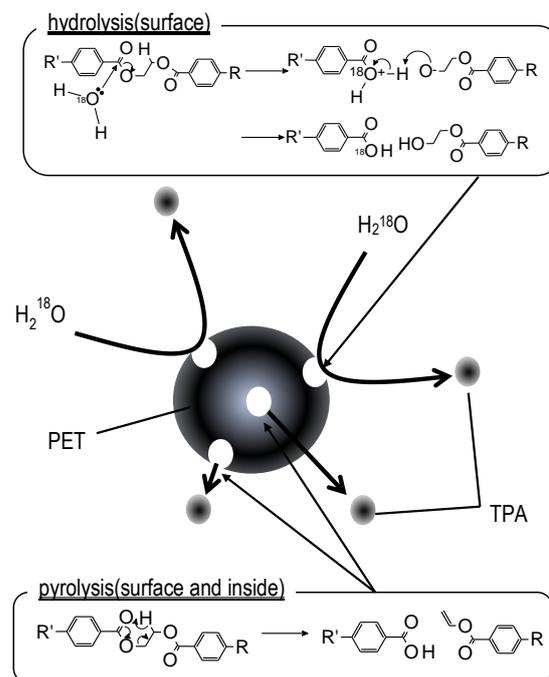


Fig.3 Reaction mechanism of hydrolysis(surface) and pyrolysis(surface and bulk) in steam decomposition of PET using ^{18}O - isotope-labeled water.

4. Conclusion

In this study, the proportions of pyrolysis and hydrolysis during steam decomposition of PET were determined using ^{18}O -labeled water. Additionally, apparent activation energies for each steam concentration were also determined. Both approaches, ^{18}O -labeling and TGA, displayed similar results. Higher steam concentrations caused little changes in the activation energy and hydrolysis rate, supporting the assumption that hydrolysis occurred preferentially at the PET surface. The combination of TGA and atom labeling has proven to be a useful approach in kinetic studies and might be applicable to other condensation polymers.

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