

Kinetic analysis of the thermal decomposition of polyesters by simultaneous TG–DTA/FT-IR

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Abstract

The thermal decompositions of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) were measured by a simultaneous TG–DTA/FT-IR system. Two kinds of data, FT-IR spectra and the specific gas profiles (SGP), were collected as a function of temperature, in addition to the TG–DTA data. Evolved gas analysis was carried out in terms of specific gas profiles (SGP) at the specific absorption band. Kinetic analysis was performed on both the TG and SGP curves obtained at various heating rates, and the activation energy estimated from the TG curves was in agreement with that obtained from the SGP curves of the aromatic esters of PBT. In the case of PET, the activation energy obtained from the TG curves was an average of that calculated from the SGP curves for the aromatic esters and carbon dioxide.

INTRODUCTION

Recently, combined techniques of thermogravimetry (TG)/Fourier transform infrared absorption spectrometry (FT-IR) and TG/mass spectrometry (MS) have been applied to detect not only the thermal decomposition of samples but also the gases evolved from samples in real time [1–5]. Simultaneous TG–DTA/FT-IR has been used to analyze the products of volatilization from various samples [3, 5–7]. We have reported the thermal decomposition processes of polyesters [8–10] and other engineering plastics [11] using the simultaneous TG–DTA/FT-IR system. During the initial stage of decomposition, the evolved gases from poly(ethylene terephthalate) (PET) are mainly benzoic acid, carbon dioxide and carbon monoxide, while those from poly(butylene terephthalate) (PBT) are terephthalic acid esters and benzoic acid esters [8, 9].

Kinetic analyses have been reported in the thermal degradation studies

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of polymers by many researchers. However, only a few polymeric samples are suitable for analysis of the kinetics of their thermal decomposition using the Ozawa method [12]. The thermal degradations of nylon-6 [12] and poly(methyl methacrylate) [13] in a vacuum have been well characterized. The thermal decomposition of both of these materials is due to random scission of the main chain. In our previous paper [9], the thermal decomposition mechanisms of PET and PBT were proposed from their simultaneous TG–DTA/FT-IR measurements. Random main-chain scission occurred from the initial stage in the case of PET. However, the ester linkage of PBT was cleaved selectively.

In this study, a kinetic analysis of the thermal decomposition mechanism of polyesters, with both TG and FT-IR data obtained at various heating rates, is discussed.

EXPERIMENTAL

Two commercial-grade polyesters poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) supplied from Polyplastics Co. Ltd., Shizuoka, Japan, were used in this experiment.

A Seiko thermal analysis system SSC 5200H model with the Seiko thermogravimetry/differential thermal analysis module TG/DTA220 was connected to a Bio-Rad FTS40 Fourier transform infrared spectrometer using the Bio-Rad TGA/IR interface to create an integrated simultaneous TG–DTA/FT-IR system. The simultaneous TG–DTA/FT-IR system is as previously reported [8].

TG–DTA/FT-IR measurements were carried out using samples of about 5 mg in platinum sample containers at various heating rates from 5 to 20 K min⁻¹ under a dry nitrogen gas flow of 200 cm³ min⁻¹. The evolved gases were introduced into a gas cell in the TG–DTA/FT-IR interface from the furnace tube of the TG–DTA instrument via a heated transfer line which was maintained at 553 K [8, 9]. FT-IR spectroscopic data were collected at 8 cm⁻¹ resolution, corresponding to 2 scans per spectrum, which provided a time resolution of approximately 1.7 s. The collected spectra were identified by referring to the EPA vapor-phase library supplied by the Bio-Rad FT-IR spectra data base, as described previously [8, 10].

RESULTS AND DISCUSSION

Two kinds of data, FT-IR spectra and the specific gas profiles, were obtained from the simultaneous TG–DTA/FT-IR measurement. The FT-IR spectra were collected as a function of temperature along with the TG–DTA data. During the qualitative analysis, the spectrum at a given temperature and the difference spectrum at different temperatures were identified by referencing the library. The target spectra selected from the

library search gave the types of evolved gases and additives. The specific gas profiles (SGP), FT-IR spectra obtained for spectral windows of limited wavenumber range, were collected as a function of temperature, and provided a quantitative analysis of the evolved gases. The kinetic analysis was performed for both the TG and SGP curves obtained at various heating rates.

Many methods have been proposed for obtaining the kinetic parameters from TG data. The rate of decomposition is described by the relationship

$$-dW/dt = A \exp(-\Delta E^*/RT)W^n \quad (1)$$

where W is the fractional residual weight of the sample, R , t and T are the gas constant, time and absolute temperature, respectively, A , is the pre-exponential factor, ΔE^* the activation energy, and n the order of the reaction. According to Ozawa [12], kinetic parameters can be obtained from this equation from TG measurements carried out at different heating rate because

$$\log(dT/dt)_1 + 0.4567(\Delta E^*/RT_1) = \log(dT/dt)_2 + 0.4567(\Delta E^*/RT_2) \quad (2)$$

where $(dT/dt)_i$ is the i th heating rate. Plots of $\log(dT/dt)_i$ versus the reciprocal absolute temperature at a given fractional conversion give a straight line, and the activation energy of decomposition is obtained from the slope.

Figure 1 shows the relationship between $\log(dT/dt)_i$ and the reciprocal temperature at various stages of PET weight loss. From 1% weight loss to 80% weight loss, the linear relationships have the same slopes. This suggests that the thermal decomposition process of PET might be explained

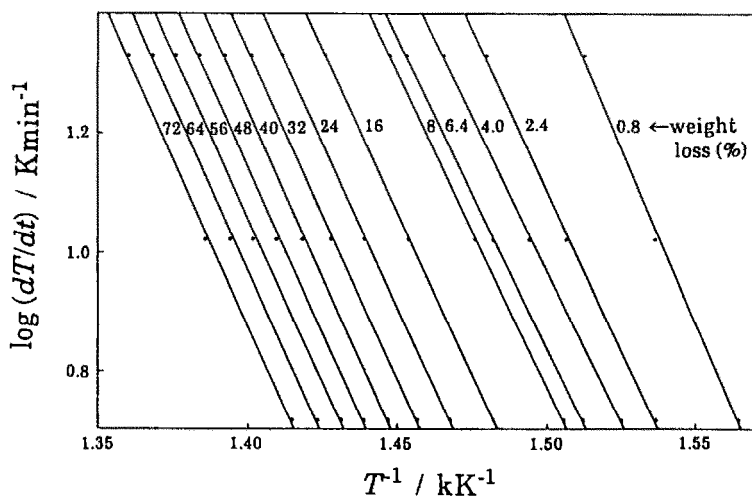


Fig. 1. Relationship between $\log(dT/dt)_i$ and reciprocal temperature at a given weight loss for PET.

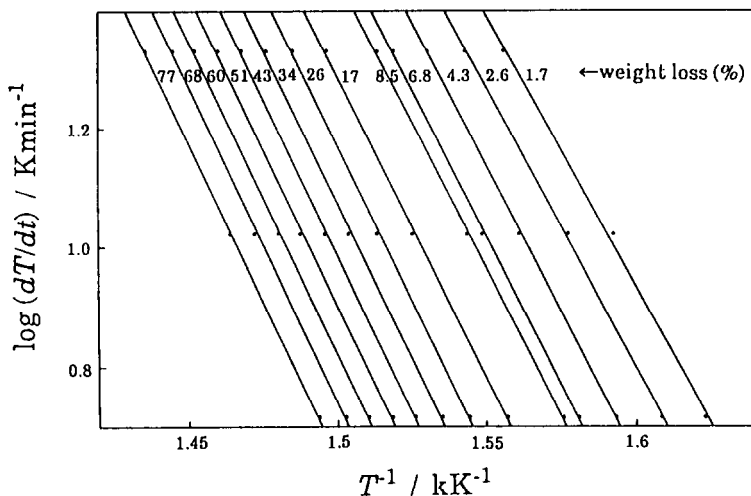


Fig. 2. Relationship between $\log(dT/dt)$, and reciprocal temperature at a given weight loss for PBT.

by consecutive reactions or by a single mechanism. The relationship between $\log(dT/dt)$, and the reciprocal temperature at a given weight loss of PBT is shown in Fig. 2. Over the weight loss range from 2% to 80%, PBT displays linear relationships with similar slopes.

The average activation energy obtained from the kinetic analysis of the TG curves was $203 \pm 6 \text{ kJ mol}^{-1}$ and was almost constant at all stages of weight loss ranging from 5% to 76% of PET. The average activation energy of PBT observed in the weight loss range between 2% and 76% was $186 \pm 10 \text{ kJ mol}^{-1}$, and the value calculated in the weight loss range from 5% to 76% was $192 \pm 6 \text{ kJ mol}^{-1}$, about 10%–6% lower than that of PET. As shown in Fig. 2, the slope of the linear relationship in the weight loss range below 5% in the initial decomposition stage of PBT is different from those observed in the later stage of decomposition: the calculated activation energy obtained in the weight loss range below 5% contained some errors.

From the spectroscopic data, carbon dioxide, benzoic acid and aromatic esters were evolved from PET throughout the decomposition temperature range. In the case of PBT, however, aromatic esters (terephthalic acid dibutyl ester, etc.) and benzoic acid were the main evolved gases and almost no carbon dioxide was observed in the initial stage of thermal decomposition, corresponding to weight losses of less than 2%. Because the SGP curves show quantitative changes in the specific gases, the kinetic parameters were evaluated from the SGP curves using an Ozawa plot.

In order to apply the kinetic analysis, the reproducibility of the spectroscopic data was examined at various heating rates. FT-IR spectra of mixed gases evolved from PBT at the peak temperature of the derivative TG curve at various heating rates are shown in Fig. 3. All spectra were

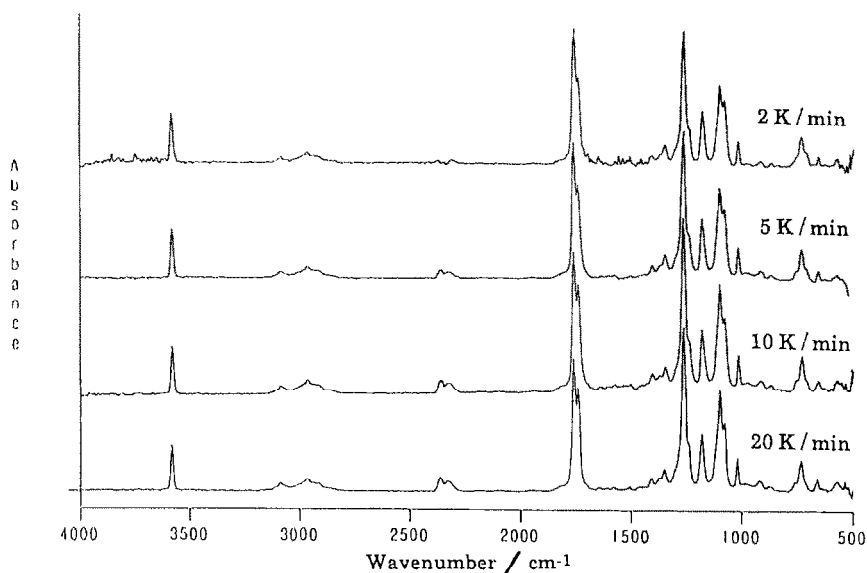


Fig. 3. FT-IR spectra of evolved gases from PBT at the derivative TG peak temperature at various heating rates.

normalized to the intensity of the absorption at 1762 cm^{-1} . As shown in Fig. 3, the spectra obtained at various heating rates are almost the same, although the spectrum obtained at 2 K min^{-1} has a high noise level. Similar results were obtained for PET. This suggests that the thermal decomposition processes of the polyesters are unaffected by the heating rate.

Figure 4 shows the absorbance intensity changes of the SGP curves with the spectrum window at $1321\text{--}1207\text{ cm}^{-1}$, which corresponds to the aromatic esters evolved from PBT at various heating rates. Because the area under the SGP curve indicates the amount of evolved gas, the evolved gas fraction was calculated by integrating the SGP curve. The

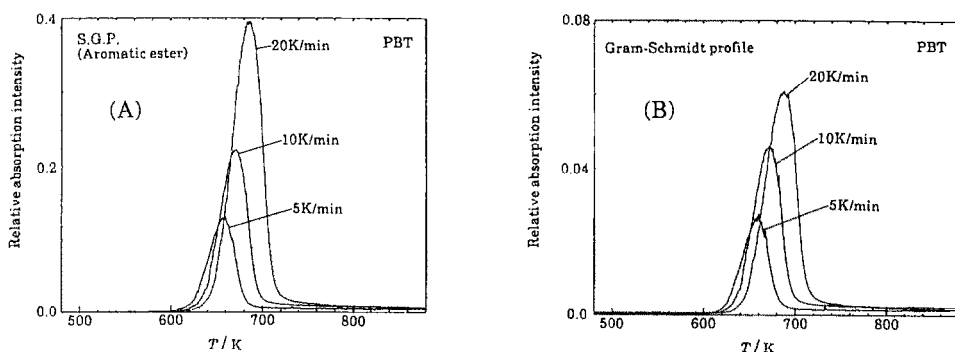


Fig. 4. (A) SGP curves at $1321\text{--}1207\text{ cm}^{-1}$, and (B) Gram-Schmidt profile, from PBT at various heating rates.

Gram–Schmidt profiles of the evolved gases from PBT, which are a measure of the integrated IR absorbance in the spectra with the window at $4000\text{--}400\text{ cm}^{-1}$ as a function of time, are also shown in Fig. 4. While the SGP curves show quantitative changes in the specific gas, the Gram–Schmidt profile indicates the approximate total change in the evolved gases. Therefore, the kinetic analyses for the SGP curves and for the Gram–Schmidt profile give the kinetic parameters for a specific gas and for all the evolved gases, respectively.

Figure 5 shows the relationship between $\log(dT/dt)_i$ and the reciprocal

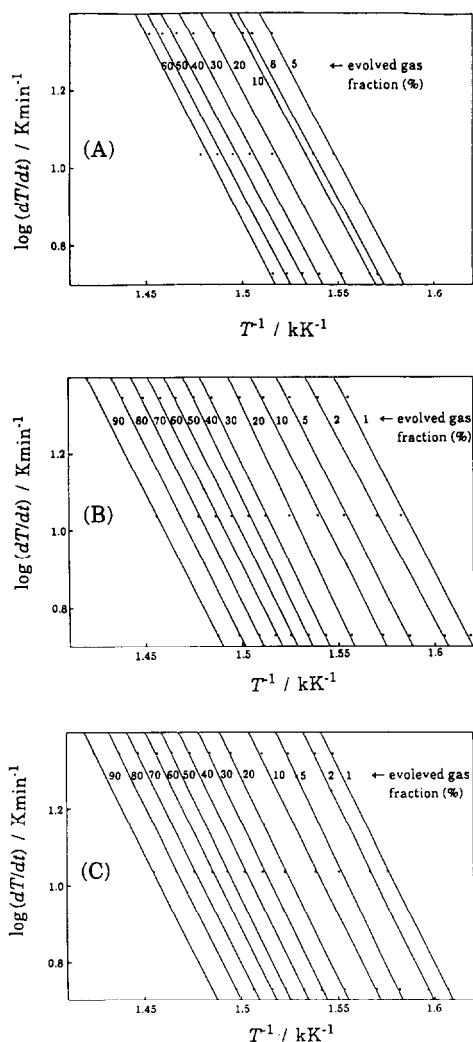


Fig. 5. Relationship between $\log(dT/dt)_i$ and reciprocal temperature for various evolved gas fractions from PBT, calculated from: (A) the SGP of carbon dioxide; (B) the SGP of aromatic esters; and (C) the Gram–Schmidt curve of evolved gases.

TABLE 1

Average activation energy in kJ mol^{-1} from the TG curves, SGP curves and the Gram–Schmidt profile in the weight loss range from 5% to 76%

Method	PET	PBT
TG	203 ± 6	192 ± 6
SGP (CO_2)	228 ± 7	169 ± 3
SGP (ester)	190 ± 7	186 ± 5
Gram–Schmidt	208 ± 5	190 ± 3

temperature for given evolved gas fractions from PET. The evolved gas fractions were calculated from two kinds of SGP curves corresponding to carbon dioxide (A) and aromatic esters (B), and from the Gram–Schmidt profile (C). A linear relationship was observed for all evolved gas fractions calculated from both the SGP curves and the Gram–Schmidt profile of PBT. The activation energy values calculated from both the TG curves and spectroscopic data are listed in Table 1. The average activation energy obtained from the SGP of carbon dioxide from PET was $225 \pm 8 \text{ kJ mol}^{-1}$ in the weight loss range from 5% to 76%. The average activation energy values were calculated from the SGP curves of carbon dioxide and aromatic ester, and from the Gram–Schmidt profiles for both PET and PBT. The activation energy obtained from the TG curves showed good agreement with the values calculated from the Gram–Schmidt profile, for both PET and PBT. In the case of PET, the activation energy obtained from the TG curves was the average of the values observed from the SGP curves of carbon dioxide and aromatic ester. However, for PBT the activation energy observed from the TG curves was close to the value obtained from the SGP of the aromatic ester. PBT evolved aromatic esters by the selective scission of the main chains. From the lower activation energy value obtained from the SGP of carbon dioxide from PBT, carbon dioxide produced in the thermal decomposition of PBT is probably the result of secondary degradation of oligomeric products.

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