# TG-DTA/FT-IR METHOD FOR ANALYZING THERMAL DECOMPOSITION MECHANISM OF POLYESTERS

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An attempt to estimate the thermal decomposition mechanism of polymers using the simultaneous TG-DTA/FT-IR system was summarized. The library search of FT-IR spectra at various temperatures and of the subtraction spectrum obtained by subtracting the spectra at different temperatures were used to determine the types of evolved gases from poly(ethylene terephthalate) and poly(butylene terephthalate) at given stages of decomposition. The quantitative analysis of evolved gases was carried out using the specific gas profiles at the specific absorption band. The kinetic parameters were estimated from both TG and spectroscopic curves measured at various heating rates.

**Keywords:** kinetics, polyesters, simultaneous TG-DTA/FT-IR system, thermal decomposition mechanism

## Introduction

Thermogravimetry (TG) is a well established method for analyzing the thermal decomposition of polymers. Recently, the combined TG/Fourier Transform Infrared absorption spectrometer (FT-IR) and TG/mass spectrometer (MS) systems have been focused to detect not only the thermal decomposition of samples but also gases evolved from samples in real-time [1–5]. MS is a highly sensitive tool, however, it is difficult to analyze mixed gases quantitatively. Usually, polymeric samples evolved organic and inorganic mixed gases during decomposition. The mixed gases containing oxides of carbon, nitrogen and sulfur are easily identified by FT-IR [1]. At present, FT-IR is a suitable tool as a detector of evolved gases from polymeric materials.

The simultaneous TG-DTA/FT-IR system was applied to analyze volatilized materials in pharmaceutical samples [3] and thermal degradation products of various polymers [5, 6] and combustion products from coals [7]. We have reported the thermal decomposition process of polyesters [8, 9] and other engineering plastics [10] using the simultaneous TG-DTA/FT-IR system. The main evolved gases from poly(ethylene terephthalate) (PET) are benzoic acid, carbon dioxide and carbon monoxide, while those from poly(butylene terephthalate) (PBT) are terephthalic acid esters and benzoic acid esters at initial stage of decomposition [8, 9].

In this study, the method to estimate thermal decomposition process of polymers using the simultaneous TG-DTA/FT-IR system was summarized and also the kinetic analysis of the thermal decomposition mechanism of polyesters with both TG and FT-IR data obtained at various heating rates was discussed.

**Experimental**

*Samples*

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

*Measurements*

Seiko SSC 5200H thermal analysis system with the Seiko thermogravimetry/differential thermal analysis module TG/DTA220 was connected with the Bio-Rad FTS40 Fourier Transform Infrared spectrometer using the Bio-Rad TGA/IR interface to create an integrated simultaneous TG-DTA/FT-IR system. A standard deuterated triglycine sulfate was used as a detector. The structure of the simultaneous TG-DTA/FT-IR system was previously reported [8].

TG-DTA/FT-IR measurements were carried out using about 5 mg samples in platinum sample containers at various heating rates from 5 $deg \cdot min^{-1}$ to 20 $deg \cdot min^{-1}$ under a dry nitrogen gas flow at 200 ml/min. The evolved gases were introduced to a gas cell in the TG-DTA/FT-IR interface from the furnace tube of TG-DTA through a heated transfer line which was controlled 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 sec. The collected spectra were identified referring the EPA vapor phase library supplied by the Bio-Rad FT-IR spectra data base.

## Results and discussion

Figure 1 shows the flow diagram of experimental and analytical procedures for the estimation of thermal decomposition mechanism of polymers using the simultaneous TG-DTA/FT-IR system. The simultaneous measurement should be carried out under the optimum condition concerning sample weight, scanning rate, flow rate and type of gas, temperatures of transfer line and gas cell to eliminate trapping and proceeding the secondary decomposition of evolved gases [8]. The stacked FT-IR spectra were collected as a function of temperature as well as TG-DTA data. During qualitative analysis, the spectrum at a given temperature and the subtraction spectrum between spectra at different temperatures were identified referring the library. The target spectra selected from the library search gave the types of evolved gases and additives. FT-IR spectra obtained through spectral windows with the limited wave number range were collected as a func-
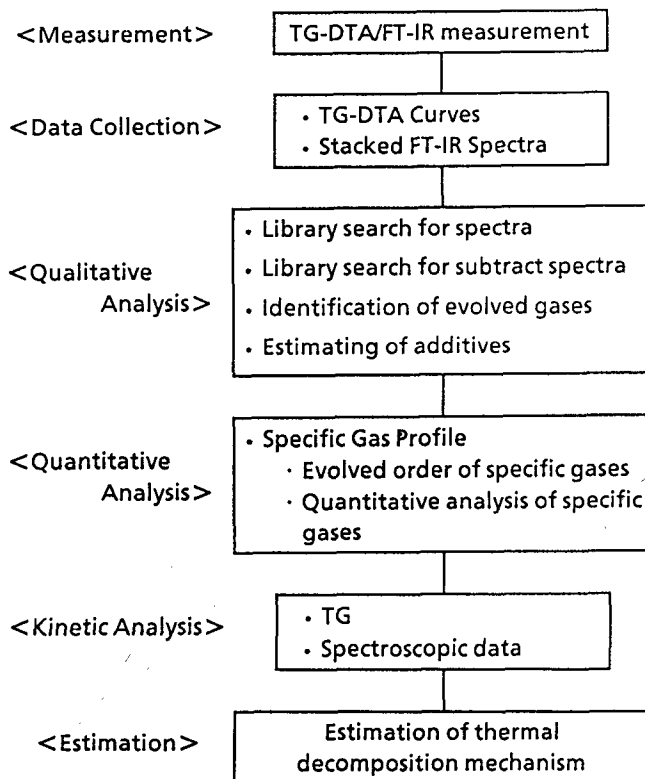
<Measurement>   | TG-DTA/FT-IR measurement

<Data Collection>
- TG-DTA Curves
- Stacked FT-IR Spectra

<Qualitative Analysis>
- Library search for spectra
- Library search for subtract spectra
- Identification of evolved gases
- Estimating of additives

<Quantitative Analysis>
- Specific Gas Profile
  - Evolved order of specific gases
  - Quantitative analysis of specific gases

<Kinetic Analysis>
- TG
- Spectroscopic data

<Estimation>   | Estimation of thermal decomposition mechanism

Fig. 1 Flow diagram of estimation of thermal decomposition mechanism using simultaneous TG-DTA/FT-IR system
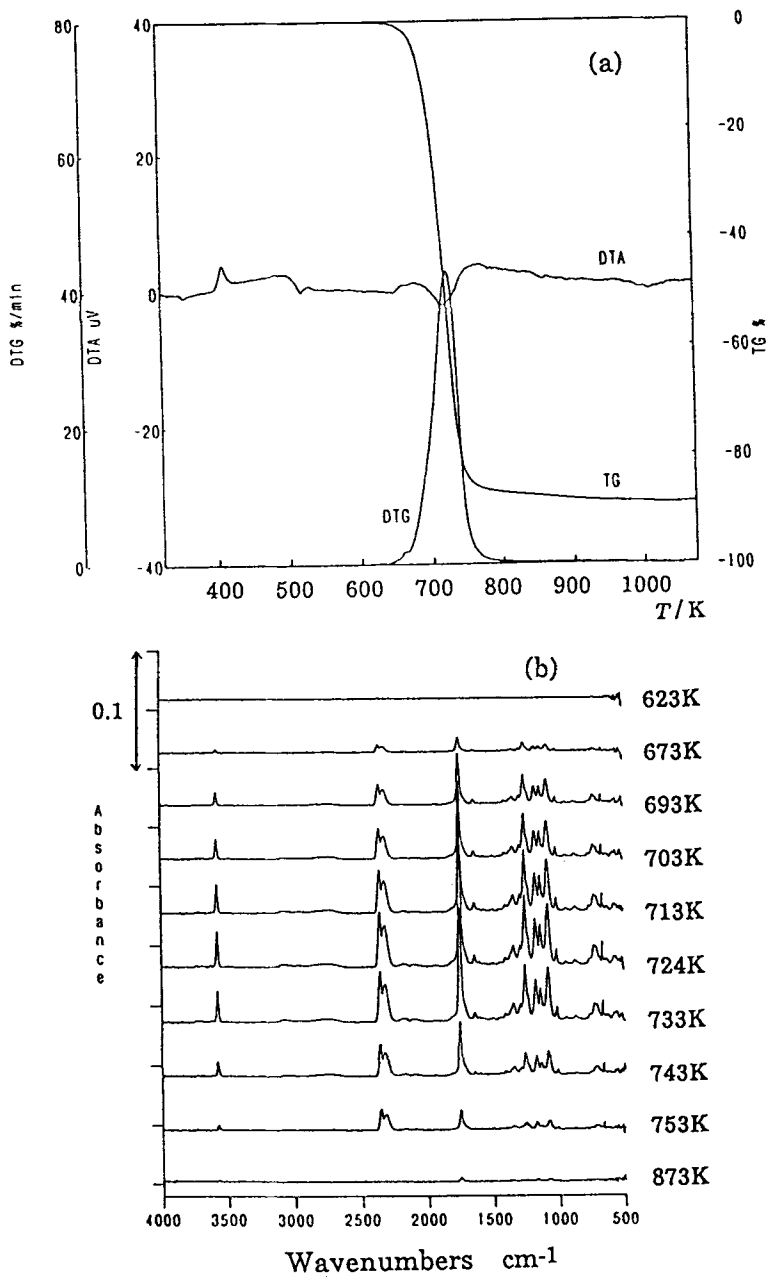
**Fig. 2** TG-DTA curve (a) of PET and FT-IR spectra of mixed gases evolved from PET at various
temperature (b)

tion of temperature. These spectra which were called the specific gas profiles (SGP) gave quantitative analysis of evolved gases. The kinetic analysis was performed for both TG curves and SGP curves obtained at various heating rates.

TG-DTA curve of PET and stacked FT-IR spectra of evolved gas from PET at various temperatures are shown in Fig. 2. A single weight loss due to thermal decomposition was observed for PET in the experimental temperature range. Similar thermal decomposition behavior was observed for PBT, however, the weight loss of PBT started at lower temperature (593 K) than that of PET (633 K). The weight loss stopped at 723 and at 823 K for PBT and PET, respectively. The residues at 973 K were about 10% and 5% of the starting materials for PET and PBT, respectively.

FT-IR spectra of evolved gases corresponding to the weight loss of PET shows the absorption bands at 2350 cm$^{-1}$ and 1760 cm$^{-1}$, the former band being due to carbon dioxide and the latter due to benzoic acid. The target spectra for the evolved gases from polyesters at a given temperature were selected from the library search according to their residual values. The value of hit quality index (HQI) was calculated by the previously reported method [11]. The evolved gases from PET at 724 K, at which temperature the derivative TG curve showed the maximum, included benzoic acid, carbon dioxide, carbon monoxide and benzoic acid derivatives.
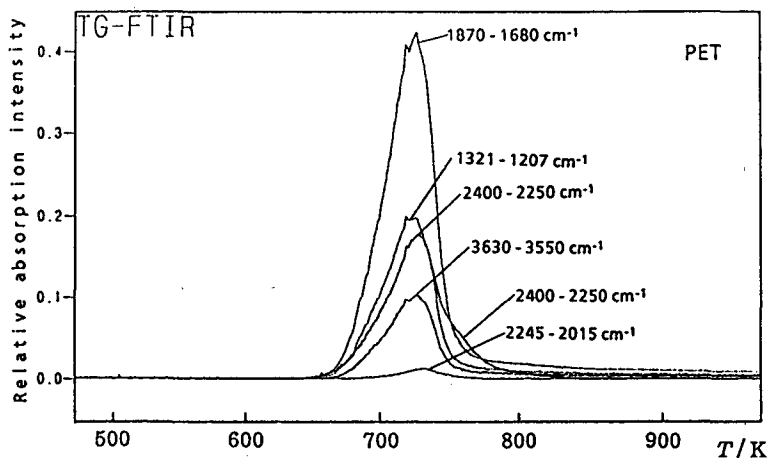


**Fig. 3** Absorption intensity changes of specific gas profiles at 3630–3550 cm$^{-1}$, 2245–2015 cm$^{-1}$, 2400–2250 cm$^{-1}$, 1870–1680 cm$^{-1}$ and 1321–1207 cm$^{-1}$ evolved from PET as a function of temperature

The library search suggested that carbon dioxide, benzoic acid and aromatic esters were evolved in the initial stage of decomposition of PET. The subtraction

spectrum obtained by subtracting the spectrum at 673 K from the spectrum at 773 K suggested that a greater ratio of benzoic acid existed in the gases evolved at 773 K than those evolved at 673 K. The subtraction spectrum obtained by subtracting the spectrum at 773 K from that at 673 K showed the existence of terephthalic acid esters and alkyl vinyl ester. Alkyl vinyl esters probably produced by thermal degradation of plasticizer in PET.

Although several kinds of gases evolved within the same temperature range, these gases may be isolated and measured through judicious selection of specific gas profiles (SGP) [12]. Figure 3 shows SGP curves obtained through spectral windows, wave number range at 3630–3550 cm$^{-1}$, 2245–2015 cm$^{-1}$, 2400–2250 cm$^{-1}$, 1870–1680 cm$^{-1}$ and 1321–1207 cm$^{-1}$ for the evolved gases from PET. The SGP curves corresponded to aromatic carboxylic acid (3630–3550 cm$^{-1}$, 1870–1680 cm$^{-1}$), carbon dioxide (2400–2250 cm$^{-1}$), aromatic esters (1321–1207 cm$^{-1}$) and carbon monoxide (2245-2015 cm$^{-1}$). Greater amounts of benzoic acid, aromatic esters and carbon dioxide were detected in the initial stage of decomposition. A smaller amount of carbon monoxide was evolved at the temperature range between 710 and 740 K.

According to Ozawa [13, 14], the kinetic parameters are obtained by following equation with TG measurements carried out at different heating rate.

$$\log(dT/dt)_1 + 0.4567(E^*/RT_1) = \log(dT/dt)_2 + 0.4567(E^*/RT_2) \qquad (1)$$

Where, $(dT/dt)_i$ is heating rate. The plots of $\log(dT/dt)_i$ vs. the reciprocal absolute temperature at a given $W$ give a straight line, and the activation energy of decomposition is obtained from the slope of this linear relationship. The average activation energy obtained from the kinetic analysis of TG curves of PBT was 192 kJ/mol. For PBT, the average values of activation energy obtained from spectroscopic data were 169 and 186 kJ/mol for carbon dioxide and aromatic esters, respectively. The activation energy observed from TG curves of PBT was close to the value obtained form the SGP of aromatic ester because PBT evolved aromatic esters by the selective scission of main chains.

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**Zusammenfassung** — Mittels eines simultanen TG-DTA/FT-IR Systemes wurde ein Versuch zur Abschätzung des Mechanismus der thermischen Zersetzung von Polymeren unternommen und beschrieben. Zur Bestimmung des Types flüchtiger Substanzen, die in bestimmten Stadien der Zersetzung aus Poly(ethylen-terephthalat) und Poly(butylen-terephthalat) entstehen, wurden die FT-IR-Spektren bei verschiedenen Temperaturen und die Differenzspektren aus Subtraktion der Spektren bei verschiedenen Temperaturen in einem Spektrenverzeichnis gesucht. Die quantitative Analyse der freigesetzten Gase wurde unter Verwendung der spezifischen Gasprofile an den spezifischen Absorptionsbanden durchgeführt. Die kinetischen Parameter wurden anhand der TG- und der spektroskopischen Kurven für verschiedene Temperaturen geschätzt.