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Application News

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Thermal Analysis

Evolved Gas Analysis of CFRP by Simultaneous TG-DTA and Py-GC/MS

Epoxy resins are typically the types of resins used in carbon fiber composite materials (carbon fiber reinforced plastic: CFRP). However, due to the limited heat resistance of this material, CFRP using high heat-resistance polyimide resin has been developed to broaden the applicable temperature range of this type of material. Here, a polyimide matrix, consisting of an intermediate composite material impregnated with carbon fibers (hereafter, referred to as prepreg), was used as the measurement sample. Use of a combination of simultaneous thermogravimetric and differential thermal analysis (TG-DTA, see Fig. 1) and pyrolysis–gas chromatography–mass spectrometry (Py-GC/MS, see Fig. 2) makes it possible to conduct qualitative analysis of the gas that is evolved, and quantitative analysis of the change in mass when the sample is heated to permit a more detailed analysis of the decomposition reaction.

Polyimide/Carbon Fiber Composites

Epoxy resin-based CFRP has a heat resistance of about 120 °C, and is therefore unsuitable for high-temperature applications. Studies using polyimide resin-based CFRP, which displays excellent heat resistance, are currently underway. The investigation conducted here focuses on the thermosetting polyimide prepreg (Fig. 3).
(Samples provided by the Advanced Composite Research Center, Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA))

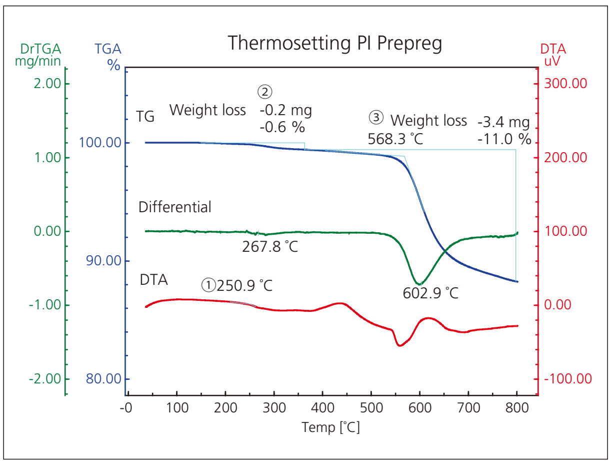

Fig. 4 TG-DTA Curves of Thermosetting Polyimide Prepreg

Fig. 1 Overview of DTG-60

The simultaneous thermogravimetric and differential thermal analyzer (DTG-60) heats the sample, and the mass changes that accompany the reactions due to vaporization, volatilization, desorption, decomposition, etc., are measured quantitatively by the TG, while simultaneously, differential thermal changes are measured by the DTA.

Fig. 2 Overview of Py-GC/MS

The Py-GC/MS heats the sample and measures the mass spectrum of the volatilized substances that are generated through volatilization, desorption, or decomposition. Conducting a library search of the mass spectra permits identification of compounds and quantitation of trace substances. Further, use of the EGA (evolved gas analysis) mode makes it possible to measure the temperature correlation between the generated gas and the heating temperature (thermogram).

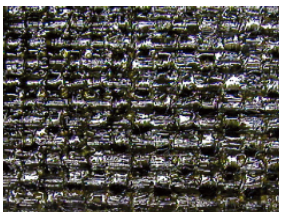

Fig. 3 Thermosetting Polyimide Prepreg

Table 1 Instruments and Analytical Conditions

DTG	Instrument	: DTG-60
	Heating Rate	: 20 °C/min
	Hold Temp.	: 800 °C
	Atmosphere	: N_2
Py-GC/MS	Instrument	: QP2010Ultra+EGA/PY-3030D
	Atmosphere	: He
	Column	: UA-DTM 2.5 m × 0.15 mm I.D.
	PY Temp.	: 100 °C (5 min) – 20 °C/min – 800 °C

Results

Fig. 4 shows TG and DTA curves of the thermosetting polyimide prepreg. The glass transition (1) of the polyimide can be seen in the vicinity of 250 °C in the DTA curve. A small amount of weight loss (2), about 0.6 %, can be seen in the vicinity of 270 °C in the TG curve. In addition, a large weight loss (3) associated with decomposition can be seen beginning from about 550 °C. Detailed analysis of these weight loss events associated with generated gases was conducted by Py-GC/MS. Peaks associated with generated gas can be seen in the vicinities of 270 °C and 610 °C in the thermogram of Fig. 5. Fig. 6 shows the EGA thermogram per occurrence of gas generated with respect to heating temperature, in addition to the substances identified from the obtained mass spectrum. The weight loss seen in the vicinity of 270 °C of the TG curve of Fig. 4 was determined to be due to *N*-methyl-2-pyrrolidone (NMP). NMP is a solvent used for dissolving thermosetting polyimide. Since residual NMP is not only associated with the occurrence of voids, but the lowering of the glass transition temperature as well, it is noteworthy that Py-GC/MS can be used to effectively verify the presence of residual NMP.

A detailed analysis of the gas components generated at around 600 °C revealed the presence of aniline, phenol, CO, and CO_2. These were presumed to be degradation products of aromatic polyimide. Thus, the use of Py-GC/MS provides a more detailed mechanism for generating gases. In addition, as the peaks in the differential TG curve of Fig. 4 are nearly identical to the peaks seen in the thermogram of Fig. 5, a clear correlation can be seen between the quantitative analysis results associated with Fig. 4 and the qualitative analysis of the evolved gases based on Fig. 6.

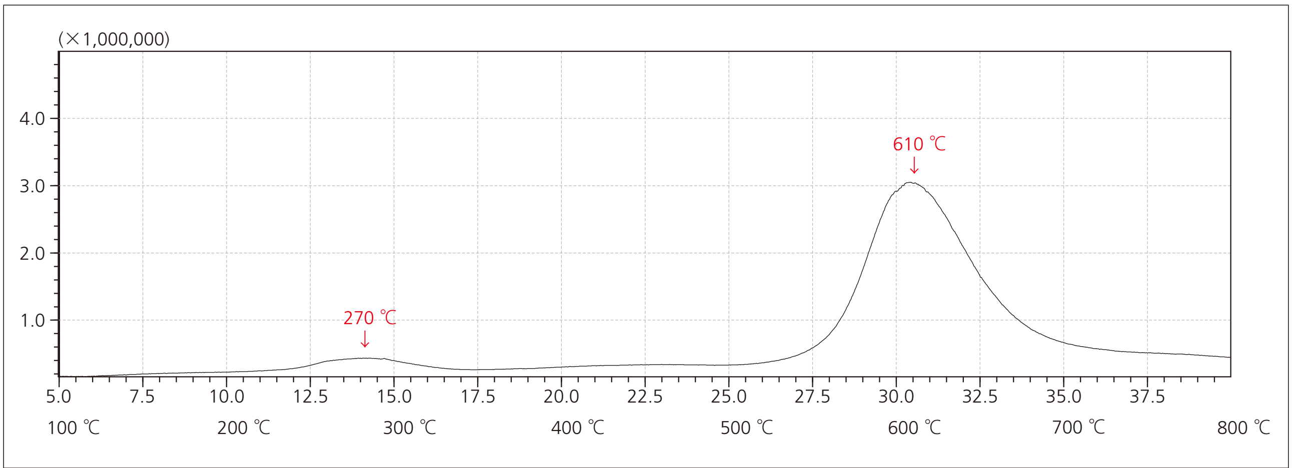

Fig. 5 Thermogram of Thermosetting Polyimide Prepreg

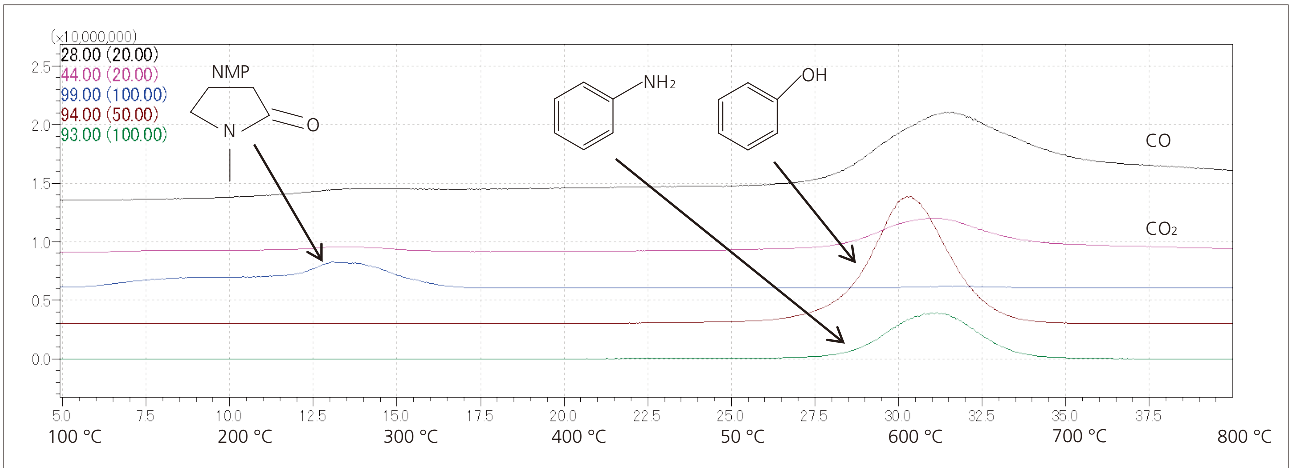

Fig. 6 Thermogram of Thermosetting Polyimide Prepreg

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