Thermal Analysis Application

Thermal Analysis Application No. UC 175
Application published in METTLER TOLEDO Thermal Analysis UserCom 17

Analysis of complex decomposition reactions by TGA-GC-MS

Introduction

Thermogravimetric experiments provide important quantitative information for the characterization of the thermal behavior of materials.

Simple reactions, such as a dehydration process, can usually be completely accounted for by a TGA measurement. To elucidate more complex reactions, the TGA is often coupled to a mass spectrometer (MS) or an infrared spectrometer (IR) to identify the gaseous products evolved during the decomposition of the sample. When complex materials such as the starting materials for syntheses, polymers or bitumens decompose, mixtures of gases are produced whose individual constituents cannot be identified with absolute certainty by MS or FTIR analysis. In such cases, the online coupling of a TGA with a GC-MS system offers important advantages. Gases simultaneously evolved are first separated by gas chromatography (GC) and then identified by MS.

In this article, we describe the online combination of a TGA/SDTA851^e and a Hewlett Packard (HP) GC-MS (HP6890 and HP5973) system.

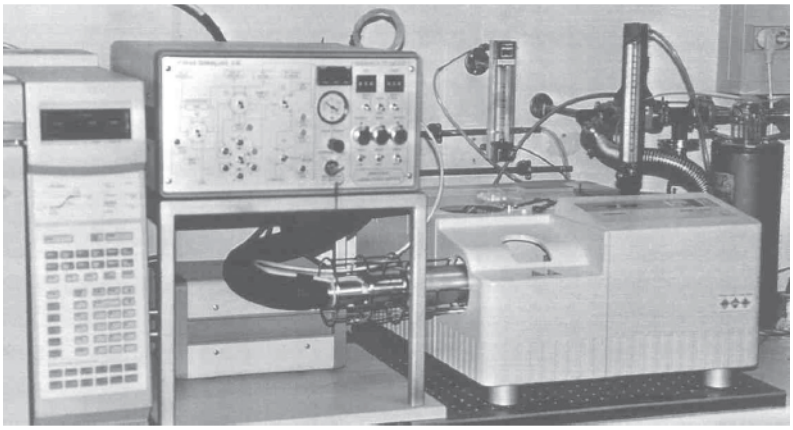

Fig. 1. The gas inlet system for the GC-MS (HP6890/HP5973) coupled to the TGA/SDTA851e.

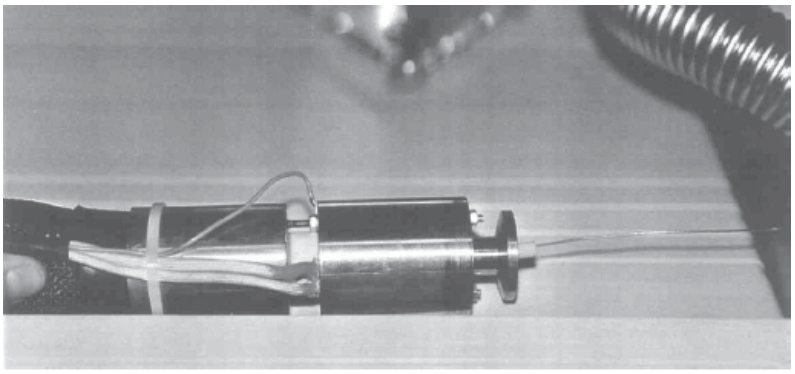

Fig. 2. The coupling of the TGA/SDTA851e to the GC-MS. The capillary tube for the transfer of decomposition gases to the GC-MS is embedded in a heated tube. The inlet of the capillary tube is located close to the sam-ple in the furnace chamber of the TGA/SDTA851e.

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Experimental

A special gas inlet system was designed for the TGA/SDTA851^e-GC-MS combination. This allowed the GC-MS system to be operated independently of the TGA/SDTA851^e when desired, and also provided additional sample preparation possibilities (Tenax adsorption, flash desorption). Six different sample collection vessels were available for the TGA/SDTA851^e. These could be used to the collect gaseous decomposition products evolved at different times during a thermogravimetric experiment. The switching of valves to fill or empty the collection vessels was triggered by the GC-MS system so that automatic operation was also possible. To prevent condensation, the collection vessels, transfer lines, valves, etc., could be heated to 290 °C. Figures 1 and 2 show the gas inlet system for the GC-MS coupled to the TGA/SDTA851^e.

TGA-GC-MS analysis of a foam containing silicone and phenol resins

The sample (83.251 mg) was heated at 10 K/min in a 900-µl alumina crucible with a pierced lid using argon (50 ml/min) as purge gas. The TGA curve (Fig. 3) shows a broad weight loss step between 300 and 500 °C.

The shoulder on the DTG curve at about 480 °C suggests that two processes overlap in this region. Based on this TGA/DTG information, the temperature range 300 to 500 °C was chosen for GC-MS analysis.

The decomposition gases were analyzed by GC-MS from 350 °C onward at intervals of 3 minutes. Different linear and cyclic methyl siloxanes were identified as decomposition products. These are specific for the silicone resin part of the sample. A chromatogram of the decomposition products evolved at 440 °C is shown in Figure 4 to illustrate this. Table 1 summarizes the compounds identified by GC-MS in the individual GC peaks numbered in Figure 4. The confidence coefficient, Q, indicates the level of certainty of identification by MS; a Q value of 100 corresponds to 100% certainty.

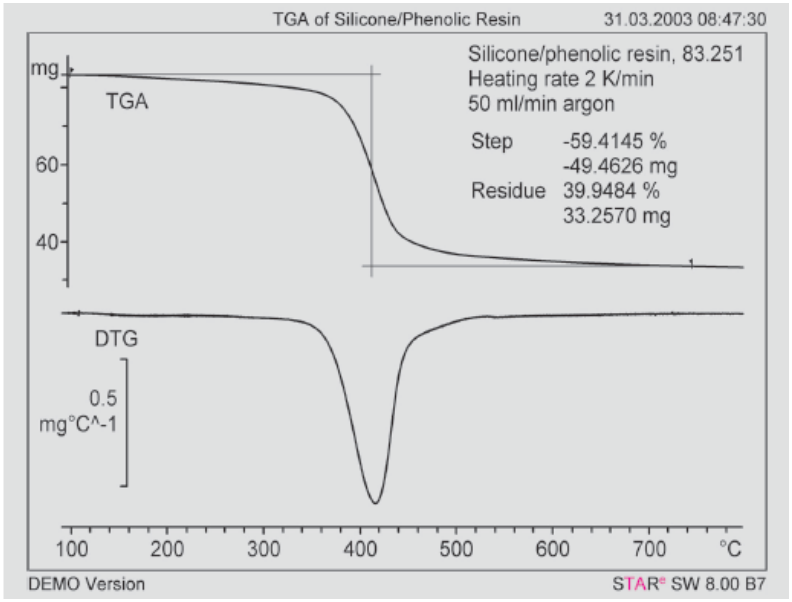

Fig. 3. Pyrolysis of a sample of expanded foam containing silicone and phenolic resins.

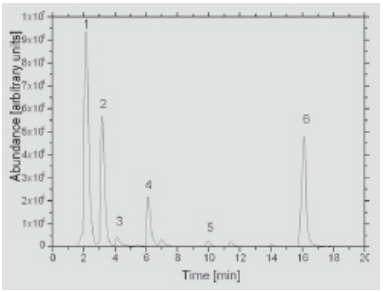

Fig. 4. Gas chromatogram of the products obtained from the decomposition of a sample of expanded foam containing silicone and phenolic resins at 440 °C in the TGA. The compounds responsible for the different peaks in the chromatogram were identified by MS.

The chromatograms showed that decomposition products from the silicone part of the foam were evolved continuously throughout the pyrolysis. The times at which the products are formed can be followed by analyzing the retention times and areas of the peaks in the chromatograms. Figure 5 displays curves showing the formation of particular decomposition products.

With the chromatography column used here, it was only possible to analyze decomposition products of the silicone resin part of the foam. A different column

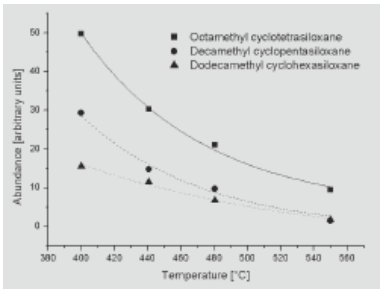

Fig. 5. Relative amounts of particular decomposition products formed during the decomposition of a sample of foam containing silicone and phenolic resins.

would have to be used to characterize decomposition products of the phenolic resin part (e.g. CO_2, CH_4).

Conclusions

The METTLER TOLEDO TGA/SDTA851^e can be relatively easily coupled to a GC-MS system. The advantage of the technique is that the various decomposition products can be identified and in principle quantified, even in complex decomposition reactions. A TGA-GC-MS system is therefore a powerful and versatile tool for the analysis of complex decomposition processes.

Peak in the chromatogram	Compound	Confidence coefficient, Q
1	Hexamethyl cyclotrisiloxane	90
2	Octamethyl cyclotetrasiloxane	78
3	Decamethyl tetrasiloxane	90
4	Decamethyl cyclopentasiloxane	91
5	Dodecamethyl cyclotetrasiloxane	91
6	Dodecamethyl cyclohexasiloxane	91

Table 1. Decomposition products of the silicone part of the foam identified by GC-MS.

Publishing Note:
This application has been published in the METTLER TOLEDO Thermal Analysis UserCom No. 17.
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