

## THERMAL ANALYSIS OF EPOXY-RESINS: IDENTIFICATION OF DECOMPOSITION PRODUCTS

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### ABSTRACT

Thermal decomposition products from organic polymers were efficiently collected in an adsorption filter appropriately connected to a commercial thermogravimetric analyzer. Separation and analysis of the thus obtained mixture was performed using combined gas chromatography and mass spectrometry. The scope of this easy to install combination between a thermoanalytical and spectroscopical method aiming at the quantification and identification of the thermal decomposition products is demonstrated for an epoxy resin sample.

### INTRODUCTION

Thermogravimetry (TG) and Differential Thermal Analysis (DTA) are powerful techniques for the thermal characterization of a variety of materials. In particular, organic polymers tend to degrade when exposed to higher temperatures with formation of decomposition products. However, neither their composition nor their structures can be elucidated by TG or DTA. The identification and quantification of such decomposition products would be very useful especially aiming at the development of better engineering plastics, e.g. for high temperature applications.

Some attempts have been made to couple other analytical techniques to the TG/DTA experiment, most notably infrared spectroscopy (IR) and mass spectrometry (MS) (ref. 1 and references cited therein). Mass spectrometry is the method of choice due to its inherent advantages of being highly sensitive, very fast and delivering good quality structural information.

The direct coupling of a mass spectrometer to the TG thermolysis chamber provides readily interpretable spectra, if the thermolysis products are of low molecular weight and/or few and simple molecules, such as H<sub>2</sub>O, CO, CO<sub>2</sub>, and SO<sub>2</sub> from e.g. mineral samples (ref. 2). On the contrary, the decomposition products from organic polymers usually consist of a multicomponent mixture. The mass spectra directly obtained from such a mixture are rather complex and usually cannot be interpreted in terms of structure and relative amounts of the constituents.

To overcome these difficulties, a fractionating procedure must be intercalated between TG and MS analysis. Gas Chromatography (GC) is especially advantageous in this context, since the combination of GC and MS is well established and commercial systems are readily available. The successful use of a combined TG-GC-MS-system was reported only very recently (ref. 3), with using a condensation trap connected via a multiport valve between TG and MS.

In this communication, we wish to report on the use of an adsorption filter as an inexpensive sample collection unit, which can easily be fitted to the TG and, as an off-line coupling unit, offers some advantages.

## EXPERIMENTAL

A schematic diagram of the combined TG-GC-MS-system is depicted in Figure 1. A METTLER TA 2000 C TGA/DSC Thermal Analyzer was used to thermolyze polymer samples of 10 to 100 mg weight in Pt crucibles at a heating rate of 1 to 5 K/min. The decomposition products were flushed by nitrogen or air (50 to 100 ml/min) into the adsorption filter (Charcoal adsorption filter type 002607, 5 mg, Brechbühler AG, CH-8952 Schlieren), which was, O-ring sealed, fixed in the oven housing, with one end of the filter tube being rather close to the sample crucible in the pyrolysis oven (see Figure 2). Since the oven housing serves mainly as heat reflector, the temperature of the adsorption filter does not rise significantly above RT during a pyrolysis experiment up to 600°C. Only very volatile compounds (H<sub>2</sub>O, CO<sub>2</sub> ...) escape through the filter as has been checked by collecting them in a liquid nitrogen cooled trap in series with the filter tube.

Different fractions of decomposition products were collected during one TG experiment by changing the adsorption filter at appropriate times/temperatures. The decomposition product mixture was then eluted from the filter with a few ml of methylene chloride or carbon disulfide. After evaporation of most of the solvent, the solution was injected into a capillary GC coupled to a FINNIGAN quadrupole mass spectrometer system. Mass spectra were recorded under different ionization conditions (electron impact 70 eV, chemical ionization using methane or deuterio-methanol as reagent gas).

## RESULTS AND DISCUSSION

To illustrate the performance of the TG-GS-MS-system described, we wish to present in brief the results of a seemingly simple experiment, which is the thermal decomposition of a catalytically cured (2.6 phr 2-ethyl-imidazole, cure 6h/80°C, 4h/180°C) pure standard epoxy resin (diglycidyl-ether of bisphenol-A, Araldite GY 250). Thermal decomposition under nitrogen occurs essentially in a single step between 380 and 450°C, accompanied by a 75 % weight loss. Decomposition in air starts similarly with subsequent oxidation

Fig. 1. Schematic diagram of the off-line coupling between a thermal analyzer and a GC-MS-system.

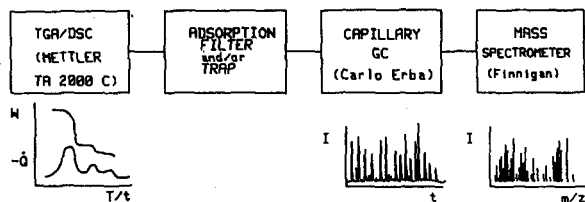


Fig. 2. Details of the decomposition product sampling system as described in the text.

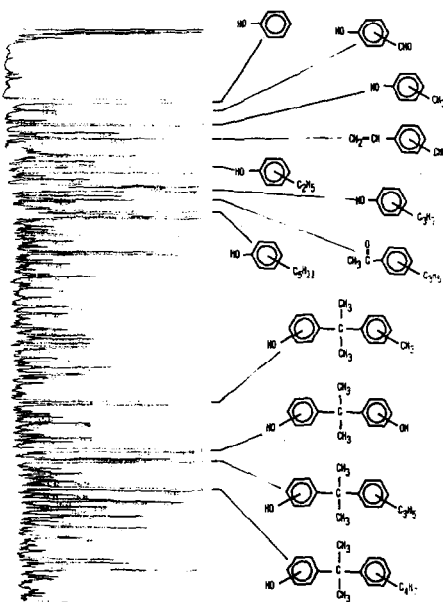
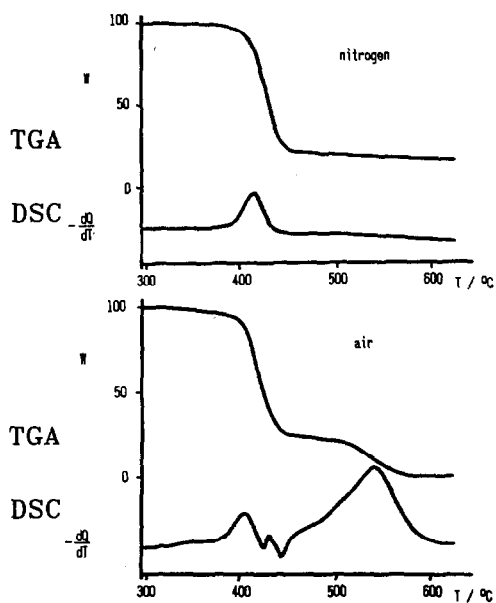
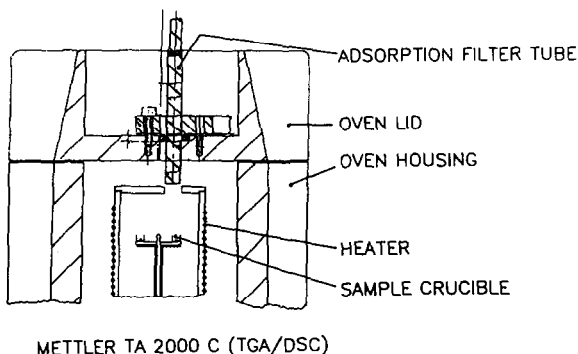


Fig. 3. TGA and DSC diagrams of catalytically cured epoxy resin (cf. text).

Fig. 4. Gas chromatogram of epoxy resin decomposition products collected in the temperature range 380 - 425°C, thermolysis under nitrogen.

of the carbonized sample between 510 and 580°C (cf. Figure 3).

The gas chromatograms of products formed in the first decomposition step reveal the formation of almost a hundred decomposition products, most of which have been identified according to their mass spectra as variously substituted alkylated (C<sub>0</sub> to C<sub>5</sub>) phenol and aromatic ether derivatives.

In Figure 4, a representative gas chromatogram is reproduced together with the principal formulas of the main decomposition products. The strongest peaks of the diphenylpropane-derivatives correspond in most cases to the p,p'-isomer, with the o,p'-, m,p'- and o,m'-isomers occurring with lower abundance. Compared to previous findings (ref. 4), our experimental arrangement allows a more efficient collection and identification of higher molecular weight products.

The composition of fractions sampled during the main decomposition step (380 to 450°C, 5 fractions) does not change very much qualitatively, although an increase of the relative amounts of higher molecular weight compounds was observed. Products and product distributions from pyrolysis under air and nitrogen are very similar in the corresponding temperature ranges.

The main advantages of the off-line coupling between TG and GC-MS as described in this paper are the independent nonexclusive use of both instruments and, even more important, the possibility of running several GC-MS experiments with a decomposition product mixture of one TG analysis. This is of particular interest if one takes full advantage of different ionization techniques resulting in mass spectra complementing each other. Electron impact ionization yields normal mass spectra with usually moderate, or often absent, molecular ion signals. Chemical ionization using methane as reagent gas produces protonated molecular ions and the use of e.g. deuterio-methanol shifts the mass number of the pseudo-molecular ion by a number of units, which is directly correlated to the number of chemically exchangeable protons in the molecule, in our cases mostly aromatic OH protons. The combined information of these differently recorded mass spectra significantly simplifies the structure elucidation of the constituents of the decomposition products.

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