

AN AUTOMATED HI-RES TG/MS SYSTEM FOR THE CHARACTERISATION OF FUEL TRANSPORT ADDITIVES

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Volatilization and decomposition data are given for two polymer derivatives used as fuel oil additives.

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Introduction

An understanding of the thermal and oxidative stability of fuel and oil additives is essential when formulating blends that may experience temperatures in the region of 200°C in an oxidative environment. These additives are designed to optimise several different properties of the base blend stock, including flow properties at high and low temperatures as well as oxidative stability. Clearly, it is important to ensure that these additives retain their desired properties throughout the temperature range of use.

The aim of this study has been to investigate structure/property relationships by assessing the effect on thermal stability of a range of additives with different structural groups.

Experimental

A TA Instruments high-resolution (Hi-ResTM) thermogravimetric analyser TGA 2950, with autosampler accessory and TA 2100 thermal analysis controller, was used to measure the weight loss profiles of the fuel additives. The TGA 2950 was used in its standard (constant heating rate) and high-resolution modes. Posi-

tive resolution indices were used to produce dynamic rate experiments, with heating rate being dependent on the rate of sample weight loss. The instrumentation has been described in detail elsewhere [1].

The evolved degradation products were passed into a VG quadrupole mass spectrometer, model 300. Commercial and 'in-house' software were used to analyse the thermogravimetric and mass spectrometric data.

Samples of 5–10 mg were heated in platinum pans at constant or dynamic rate from ambient to 700°C in a flowing air or nitrogen atmosphere at 50 ml/min. For combined TG/mass spectrometric analyses a purge gas mixture of 20% oxygen in argon was used to minimise background signals.

Results and discussion

Oxidation vs. volatilisation

The use of the system in characterising oxidation/volatilisation behaviour was evaluated with a commercially available polyether: $C_{12}H_{15}O[CH_2CH(CH_3)O]_6H$. Figure 1 shows the derivative weight loss profiles of Oxilube 500 heated at 50 deg·min⁻¹, resolution index +4, in an oxidising and inert environment. A single, sharp weight loss is observed due to the complete oxidation of the material, with a maximum rate of weight loss of just under 20%/°C at 190°C. The temperature of the peak in the derivative profile may be indicative of a particular chemical structure fragment within the molecule.

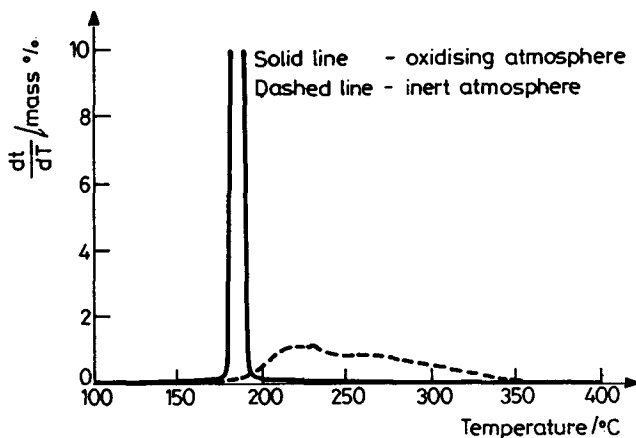


Fig. 1 DTG curves Oxilube 500 under oxidising and inert atmospheres

Under nitrogen the volatilisation of the polyether occurs at higher temperatures and over a wider temperature range. Consequently the maximum rate of weight loss is $1.1\%/^{\circ}\text{C}$ at 220°C ; this is some 30°C higher and nearly 20 times slower than under an oxidising atmosphere.

These characteristic profiles and temperatures make it possible to characterise an additive with respect to its propensity to volatilise/oxidise under end-use conditions.

Characterisation by TG/mass spectrometry

Phenyl-chloroformate (mol. wt. 156.6) has high vapour pressure at room temperature and starts to lose weight almost immediately when heated at $15\text{ deg}\cdot\text{min}^{-1}$. By 100°C it has completely volatilised leaving no residue.

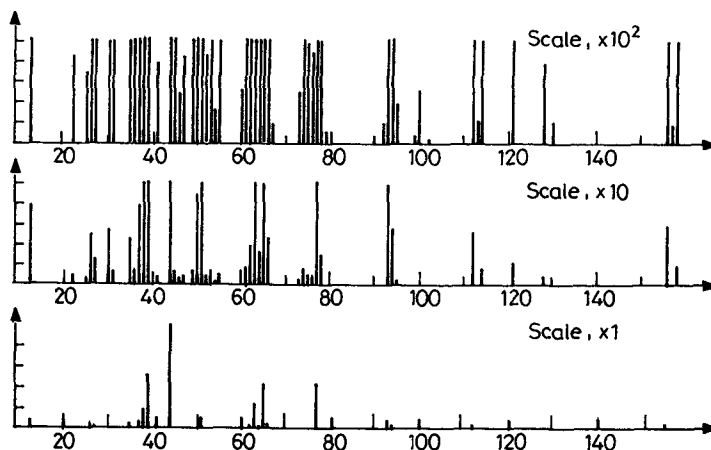


Fig. 2 Mass spectra for phenyl chloroformate after 6.42 minutes

The main m/e plots against time obtained from the mass spectrometer obtained during the TG experiment give a single peak with maximum intensity at 6.42 min. This corresponds to the maximum rate of weight loss observed during TG (allowing for the TG to mass spectrometer transfer time). The mass spectrum at this time is given in Fig. 2 and corresponds to that of phenyl chloroformate. The observed mass fragments are characterised as follows:

$156 = M^+$ ($158 = M^{+2} \text{Cl}^{37}$ isotope)

$112 = \text{PhCl}_2$, with a loss of 44 CO_2 ($114 = \text{PhCl}^{37}$ isotope)

$94 = \text{PhO}^+$

78 = PhH⁺

77 = Ph⁺

65 = ClCO⁺

The TG/mass spectrometer combination can thus help in assessing volatilisation/oxidation behaviour. If a material does decompose on heating, the breakdown products can potentially be identified and a mechanism for the degradation constructed. In this example there is no degradation and the material passes from the condensed into the vapour phase intact.

Structure/property relationships

Materials studied as potential additives generally consist of two or three parts: (i) a polymer backbone to impart solubility and thermal stability, (ii) an optional coupling agent, (iii) a 'property enhancing' group. In assessing the structure/property relationship, a variety of materials have been synthesis, these consisting of a range of polymers, coupling agents and property-enhancing groups. The overall aim is to achieve structures that are stable over a wide temperature range but that eventually break down without leaving a residue. Any carbonaceous residue would have a detrimental effect on an engine's performance.

Polymer derivative A

Initial work using conventional TG on a number of additives revealed very gradual weight loss profiles. Figure 3 shows the derivative weight loss profile for polymer derivative A obtained during conventional and Hi-Res TG after the loss of a low-boiling solvent, the material gradually and continuously decomposes between 150° and 350°C. The mass spectrometer data show that the first weight loss is due to toluene, the solvent used during preparation of the material, followed by

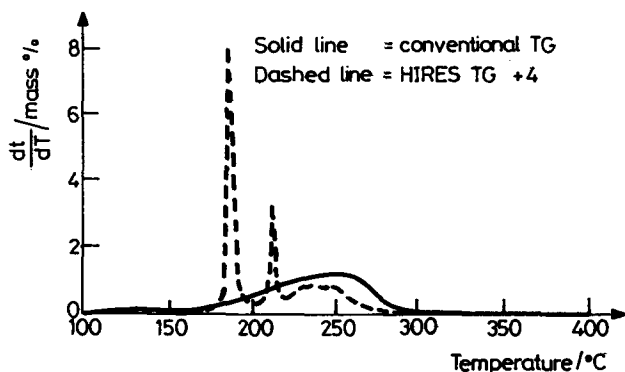


Fig. 3 Comparison of Hi-Res and conventional TG first derivatives for polymer derivative A

fragments derived from the polymer. Conventional TG gives little stoichiometric information about the breakdown mechanism due to the very gradual weight loss. There are no inflection points within the derivative that may be used to perform weight loss calculations. Due to the overlapping weight losses it is not possible to establish which part of the molecule is the most thermally labile.

Table 1 Summary of Hi-Res TG data for polymer derivative A

Mass loss step	Temperature of maximum rate of weight loss / °C	Weight loss /% calculated on the dried mass at 160°C
1	184	44.75
2	212	15.45
3	237	38.34

By contrast, the same material analysed using Hi-Res TG with a resolution index of +4, gives far superior weight loss and derivative weight loss resolution. After the loss of toluene, there follow clear weight loss steps. Table 1 summarizes the degradation steps; the weight at 160°C, after the loss of solvent, has been ratioed to 100% to allow all calculations to be made on a 'dried' basis.

Polymer derivative B

The conventional and Hi-Res TG derivative weight loss profiles for polymer derivative B at 15 deg·min⁻¹ are compared in Fig. 4. At least two weight loss steps are apparent with a small DTG minimum at 200°C that could be used for weight loss calculation. Far superior weight loss resolution was found for this material at

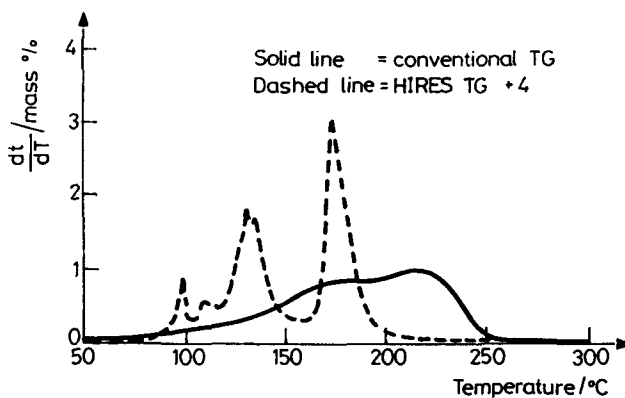


Fig. 4 Comparison of Hi-Res and conventional TG first derivatives for Polymer Derivative B

Hi-Res index +4 and a heating rate of 50 deg·min⁻¹. Not only is baseline resolution obtained for the two main weight loss steps, but also two smaller weight loss steps are apparent at lower temperatures.

Table 2 Summary of Hi-Res TG data for polymer derivative B

Weight loss step	Temperature of maximum rate of weight loss / °C	Weight loss /% calculated on the dried weight at 75°C
1	99	6.29
2	111	5.48
3	132	39.1
4	174	49.1

Conclusions

The Hi-Res TG/mass spectrometer combination is a powerful tool for characterising modern fuel and oil additives. Additional information, both quantitative and qualitative, is obtained, compared to conventional TG. The enhanced resolution aids in characterising volatilisation/decomposition processes as well as aiding in the stoichiometric assessment of degradation mechanisms. This information can be used to understand the 'weak links' in the molecule and aid the synthetic chemist in building thermally stable compounds with tailored end-use properties.

References

- 1 P. S. Gill, S. R. Saurbrunn and B. S. Crowe, *J. Thermal Anal.*, 38 (1992) 255.

Zusammenfassung — Es werden Angaben über die Verflüchtigung und Zersetzung von zwei als Heizöladditive verwendeten Polymerderivaten beschrieben.