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THE DETERMINATION OF THE GASES RELEASED DURING HEATING OF A FLAME RETARDANT FOR POLYMERS

Coupling of TG with FTIR, MS and GC–MS

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Abstract

The oxidative degradation of HET-acid (1,4,5,6,7,7-hexachlorobicyclo [2.2.1] hept-5-en-2,3-dicarboxylic acid) is studied by the combination of TG, FTIR, MS and GC–MS. The gases evolved during the decomposition of this flame retardant are investigated on-line by FTIR and by MS. Simultaneously the evolved gases are collected by an adsorbent and, after the thermal experiment, desorbed to release the volatile products for identification using GC–MS. The combination of these techniques offers the unambiguous identification of the evolved products as a function of temperature. The main identified products are CO_2, H_2O, Cl_2, HCl, C_2Cl_4, maleic acid anhydride, HET-acid anhydride, chlorinated cyclic hydrocarbons and chlorinated unsaturated linear hydrocarbons.

Keywords: EGA, flame retardant, HET-acid, polymer

Introduction

Due to the variety of additives present in many polymers the combination of thermogravimetry (TG) with evolved gas analysis (EGA) has become an indispensable tool for the characterization of materials. According to the ICTA nomenclature EGA is a technique which determines the nature and amount of volatile product or products formed during thermal analysis [1].

This contribution shows the on-line coupling between TG and Fourier transform infra-red (FTIR), the on-line coupling between TG and mass spectrometry (MS) and the off-line coupling, using thermal desorption (TD), between TG and gas chromatography–mass spectrometry (GC–MS) performed on the combustion of a flame retardant.

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Experimental

On-line coupling TG–FTIR and TG–MS

TG experiments are performed with a TA Instruments 2000–TGA951. The heating rate of the TG is 20°C min^{-1} in a dynamic air purge of 50 $\text{cm}^3\,\text{min}^{-1}$, being the maximum rate recommended for the study of thermally unstable materials (ASTM E698-79).

The FTIR is a Bruker FTIR IFS 48 coupled on-line with the TG unit [2]. The outlet of the TG is connected to the FTIR by an interface that consists of a gas cell (22 ml) that is heated up (200°C) to prevent condensation on the windows. A heatable transfer line connects the interface with the TG. The detector is a liquid nitrogen cooled Hg–Cd–Te (4800–600 cm^{-1}) detector. The FTIR spectrometer is used at a speed to acquire 4 complete IR spectra within 1 second at a spectral resolution of 8 cm^{-1}.

The MS is a Fisons VG Thermolab quadrupole mass spectrometer coupled online with the TG unit using a flexible, heated, silica-lined steel capillary. As TG proceeds at atmospheric pressure whereas MS must operate below 10^{-5} mbar, further pressure reduction was obtained by using a molecular leak (silicon carbide frit).

Off-line coupling TG–GC–MS via thermal desorption of a tenax tube

The released gases are collected on a tenax adsorbent in a collecting tube as illustrated elsewhere for the oxidative degradation of polystyrene [3]. After the TG experiment the tubes are thermally desorbed by a Dani thermal desorption apparatus 3350. The released products are transferred into a Varian 3400 gas chromatograph coupled with a Finnigan TSQ 70 quadrupole mass spectrometer. The individual components are identified by their mass spectra through interactive library search.

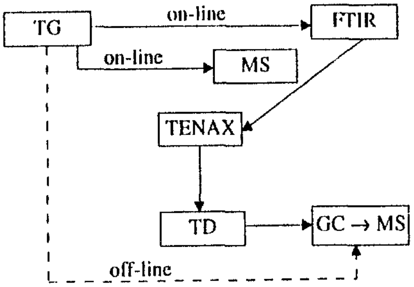

Fig. 1 Flow chart of the combination of different techniques

A flow chart of the combination of the different techniques is given in Fig. 1.

Results and discussion

On-line coupling between TG and FTIR

Figure 2 shows the mass (%), the temperature and the derivative (% min^{-1}) of a sample as a function of the time during heating at 20°C min^{-1} in dry air.

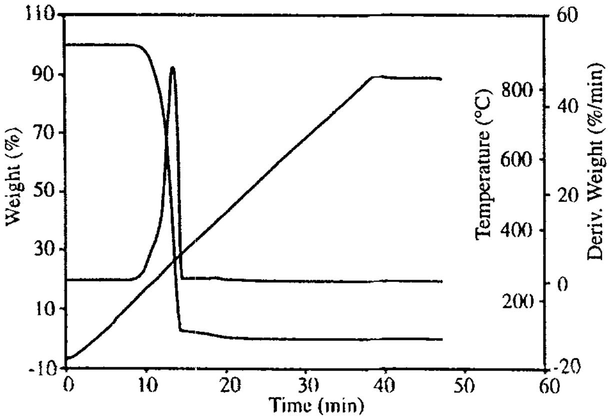

Fig. 2 Thermal degradation of HET-acid in 50 cm^3 min^{-1} air at a heating rate of 20°C min^{-1}

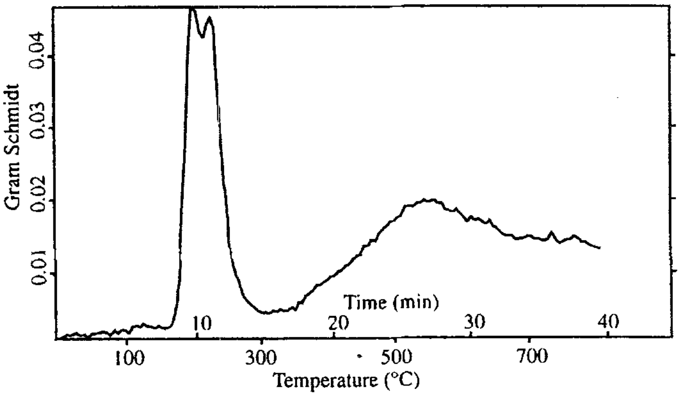

Fig. 3 Total (4000–600 cm^{-1}) FTIR signal of the gases released by heating HET-acid in air as a function of time or temperature

The total IR signal is given as a function of time or temperature in Fig. 3.

In the temperature region 220–280°C where the main weight loss takes place, the FTIR spectra consist of characteristic bands of H_2O (1500–1600 and 3600–3800 cm^{-1}), CO (2100–2300 cm^{-1}), CO_2 (600–700 and 2300–2400 cm^{-1}) and the HET-acid anhydride (800–1300 and 1750–1900 cm^{-1} [4]). The FTIR plot taken at 780°C shows that at high temperature also HCl (2700–2900 cm^{-1} [5]) is detected. The FTIR spectra with the bands of the gases released at 225°C are given in Fig. 4. The high sensitivity of FTIR (and MS) is clearly shown by the spectra obtained at 565 and 780°C (Figs 5 and 6) as in this temperature region the mass loss is only 0.05%.

On-line coupling TG–MS

Some characteristic results obtained by the on-line coupling between TG and MS are shown in Fig. 7 and confirm the formation of HCl (*m/e* 36 for $H^{35}Cl$, 38 for $H^{37}Cl$, 35 and 37 for the fragments ^{35}Cl and ^{37}Cl).

An additional result from the TG–MS experiments is the detection of the IR inactive Cl_2 at a temperature higher than 350°C (*m/e* 70 and 72).

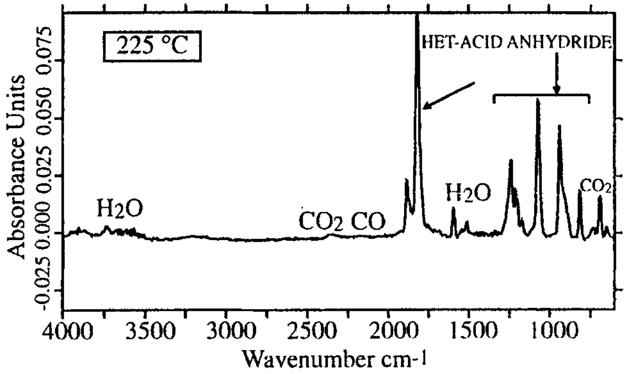

Fig. 4 FTIR spectra of the gases released by heating HET-acid in air at 225°C

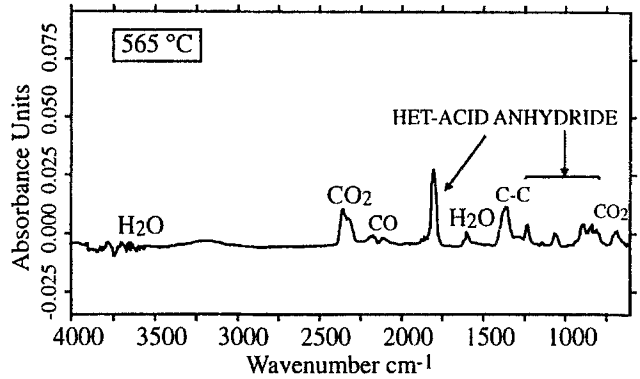

Fig. 5 FTIR spectra of the gases released by heating HET-acid in air at 565°C

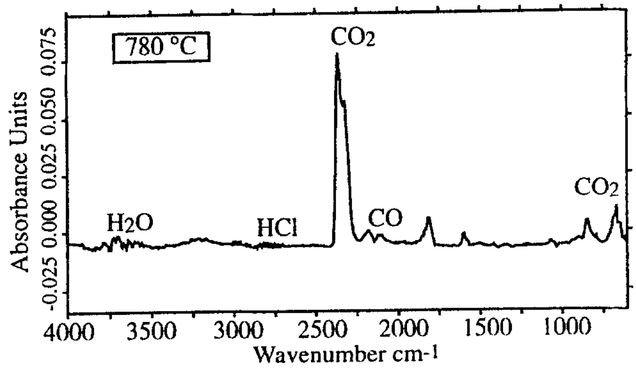

Fig. 6 FTIR spectra of the gases released by heating HET-acid in air at 780°C

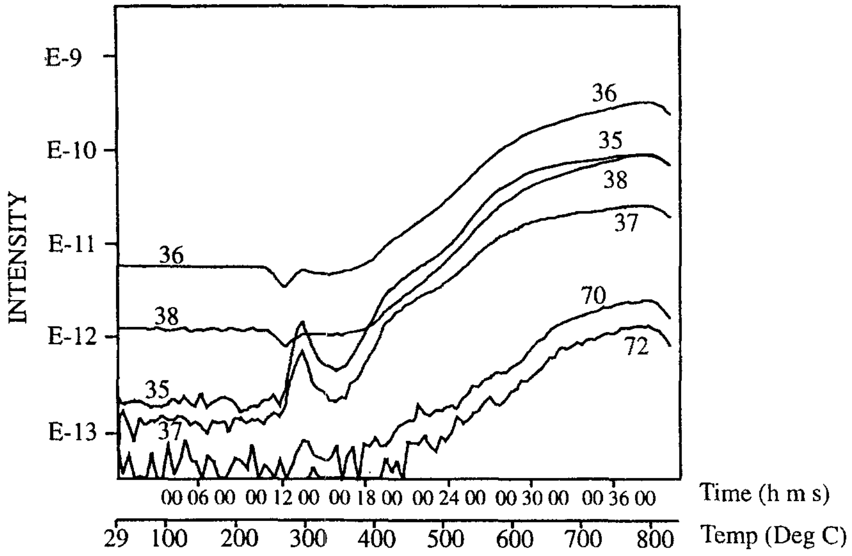

Fig. 7 MS results of the gases released by heating HET-acid in air as a function of time or temperature

Off-line coupling between TG and GC–MS: TG–Tenax–TD–GC–MS

Important additional information on the organic volatile compounds released during a TG experiment and collected on the tenax adsorbent for an off-line analysis by GC–MS, can be obtained from the combination TG–GC–MS. The ion chromatogram is shown in Fig. 8 and the compounds identified by library search are given in Table 1.

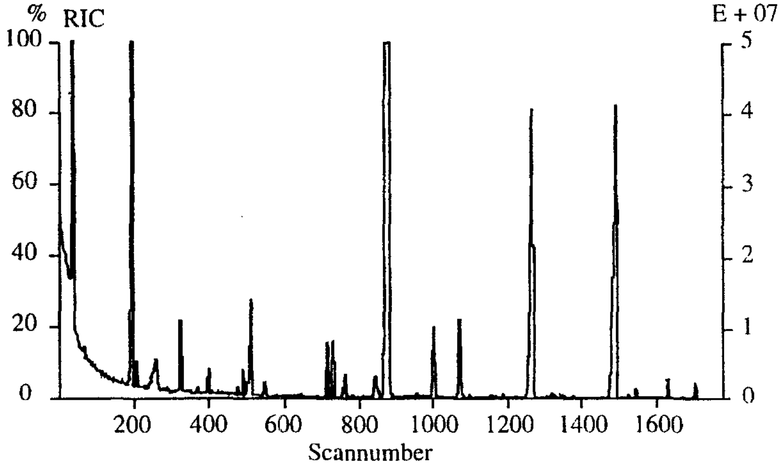

Fig. 8 TG–Tenax–TD–GC–MS of HET-acid: GC–MS ionchromatogram of the volatile compounds adsorbed on a tenax tube during the TG experiment in air and released by TD

Table 1 Volatile compounds adsorbed on tenax during the TG–Tenax–TD–GC–MS experiment of HET-acid (Fig. 8) and identification by GC–MS

Scan number	Identified compound (library search)
194	tetrachloroethene
257	maleic acid anhydride
323	tetrachlorosubstituted hydrocarbon
396	trichloropropenoylchloride
475	tetrachlorocyclopentadiene
490	chlorinated hydrocarbon
500	chlorinated hydrocarbon
509	tetrachlorocyclopentene
547	hexachloroethane
715	hexachloropropene
729	hexahlorobutadiene
760	tetrachlorosubstituted hydrocarbon
843	tetrachlorosubstituted hydrocarbon
882	hexachlorocyclopentadiene
1000	chlorinated hydrocarbon
1072	pentachlorobenzene
1266	1,2,3,4-tetrachloro-1,3-cyclopentadiene
1491	HET-acid anhydride

Conclusion

The main weight loss takes place in the temperature region 220–280°C with the formation of the anhydride by the split off of water. In this region degradation takes also place by the formation of carbon monoxide, carbon dioxyde and the split off of chlorine. From 280°C the degradation continues by the elimination of chlorine and hydrochloric acid, reversed Diels-Alder reactions and the oxidation of the formed double bounds. Chlorinated cyclic hydrocarbons and chlorinated unsaturated linear hydrocarbons are formed.

The combination of TG–FTIR, TG–MS and TG–GC–MS as applied to the oxidative degradation of HET-acid is a good example of the possibilities of the combination of complementary analytical techniques for the unambiguous identification of the gaseous decomposition products as a function of the temperature. As an alternative to the use of a solid adsorbent such as tenax, one can also use appropriate solvents for the collection of the evolved gases as has been illustrated elsewhere for the degradation of a latex [6].

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