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EVALUATION OF OUTGASSING PROCESSES OF PLASTICS AND RUBBERS USING ON-LINE THERMAL DESORPTION - GC - FTIR - MS

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ABSTRACT

For the evaluation of outgassing processes of plastics and rubbers a combined simulation and characterisation technique has been developed, capable of on-line temperature-controlled outgassing, gaschromatographic separation of the evolved species and subsequent simultaneous detection and identification by Fourier transform infrared spectroscopy and electron-impact or chemical ionisation mass spectrometry. The thermal desorption unit is capable of accommodating Tenax trapping tubes, thereby enabling off-line sampling with preconcentration of, for instance, workplace and oven atmospheres and thermogravimetric equipment with subsequent separation and identification of the trapped volatile components. The experimental set-up is presented together with a number of representative results.

INTRODUCTION

Knowledge of outgassing processes is a prerequisite for the successful application of plastic and rubber parts in the electronics industry. Outgassing and degradation phenomena of plastics and rubbers both during processing and in product applications are of technological importance with respect to product lifetime, toxicological aspects, mould and environmental contamination, surface appearance, suitability for finishing processes, reprocessability, permitted temperature use range etc.

A well-known technique for studying these thermal degradation phenomena is thermogravimetry (TG), providing weight loss information as a function of temperature and time. Although useful information can be obtained about the overall rate and extent of thermal degradation, no information is provided about the nature of the evolved species. In addition, the often complex degradation processes of plastics and rubbers hinder the proper interpretation of the weight loss curves. These inherent limitations of the TG technique can be bypassed by coupling a thermal desorption technique with chemical analytical methods.

We developed such a combined simulation and characterisation technique, capable of on-line temperature-controlled outgassing i.e. thermal desorption (TD), gaschromatographic separation (GC) of the volatiles and subsequent detection and identification by means of Fourier transform infrared spectroscopy (FTIR). The on-line TD-GC-FTIR technique has been successfully employed for several years now in our laboratory [1]. This technique has recently been extended to include mass spectrometry (MS) in order to enhance and facilitate the identification of evolved species and to lower the detection limits from ppm to (sub)ppb level. In addition, by using off-line sampling techniques with preconcentration via Tenax absorption cartridges the species evolved during TG experiments or present in workplace atmospheres can be sampled with subsequent analysis of the trapped components via TD-GC-FTIR-MS.

The instrumentation and experimental set-up together with some representative results are presented and discussed in this paper.

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EXPERIMENTAL

The TD-GC-FTIR-MS equipment configuration is shown in Figure 1. The TD-GC-FTIR part is described elsewhere [1] and will only be discussed briefly here. The thermal desorption cold-trap injector (TCT, Chrompack) is used for the temperature-controlled outgassing of the samples with a maximum temperature of 350 °C. The volatile components are transferred to the cold trap by the carrier gas and preconcentrated. After completion of the outgassing process the cold trap is heated very quickly, causing on-column injection of the trapped components onto the gas chromatograph (PU 4500/11, Philips Scientific) for separation. The chromatograph has been equipped with a Chrompack wall-coated open tubular fused-silica capillary column (25 m, 0.32 mm i.d., 1.2 μm CpSil5CB).

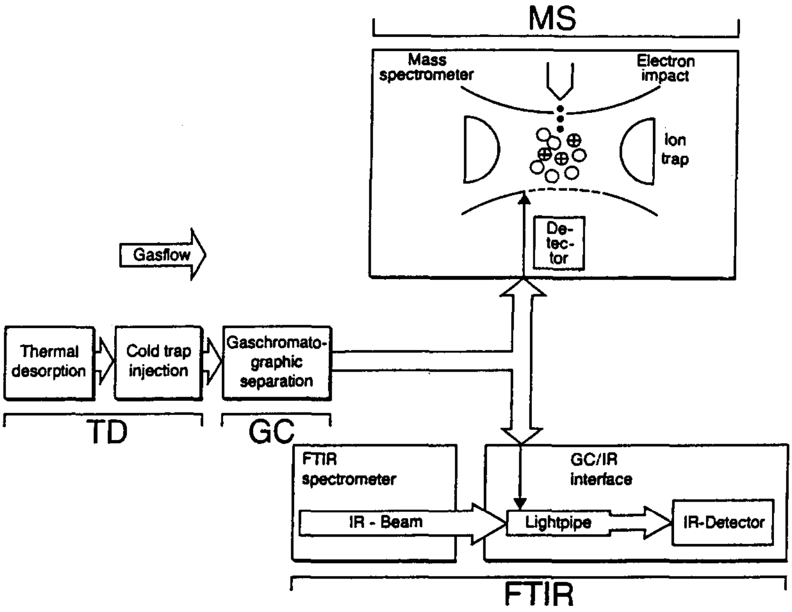

Figure 1 Flow chart of the TD-GC-FTIR-MS system

Detection of the separated components is provided by a FTIR spectrometer (20 SXB, Nicolet) with GC interface and an ion-trap mass spectrometer (ITD 800, Finnigan Mat) with a heated transfer line [2]. The ITD provides positive ion detection while scanning a mass range of 20 - 650 amu throughout the GC run. The components are ionized inside the ITD by conventional electron-impact ionization (EI) with a filament [3]. Automatic Gain Control software enhances high-quality EI spectra in a large concentration range. For molecular weight confirmation, chemical ionization (CI) is used, providing a soft ionization capability via charge transfer of a reagent gas e.g. methane [4]. An IBM PC-AT controls the ITD equipment and the data acquisition including library search routines.

Figure 1 shows the parallel FTIR-MS configuration [5] as opposed to tandem FTIR-MS operation [6,7]. By using a dead volume splitter, make-up gas and suitable capillary tubes, approximately 99 % of the column effluent is fed into the FTIR and the remainder into the MS. Parallel FTIR-MS operation is preferred to tandem FTIR-MS for several reasons. First of all, the rather large volume of the FTIR light pipe causes peak broadening and thus loss of resolution for the MS detection. Secondly, water is a frequently observed component in outgassing studies of plastics and rubbers causing deterioration of the KBr windows of the FTIR light pipe. For this reason an open-ended light pipe is used. Thirdly, the unmatched sensitivities of FTIR and MS bring about overloading of the MS ion source.

Off-line sampling of the outlet of the thermogravimetric equipment (951/990 Dupont) is performed via Tenax adsorption cartridges (Chrompack), which are then desorbed in the TCT. The Tenax cartridges are connected via a Swagelok fitting to the oven of the TG equipment.

RESULTS AND DISCUSSION

The examples presented below are part of larger study programmes in our laboratory. A number of other investigations have been evaluated covering a wide range of plastic and rubber materials.

Decomposition of polyesterurethanes

The thermal decomposition of polyesterurethanes follows a first- order reaction as proposed by Grassie et al. [8]. We have monitored the decomposition by a TG experiment at a heating rate of 5 °C/min up to 600 °C in air, figure 2a. Tenax adsorption cartridges were coupled at the outlet of the TG equipment and subsequent TD-GC-FTIR-MS analysis revealed the presence of CO_2, water, tetrahydrofurane, cyclopentanone, dicarbonic acid and aliphatic diols and esters. Figure 2b shows the chromatogram reconstructed from infrared data [1] of the first 25 % weight loss which is in accordance with the MS data.

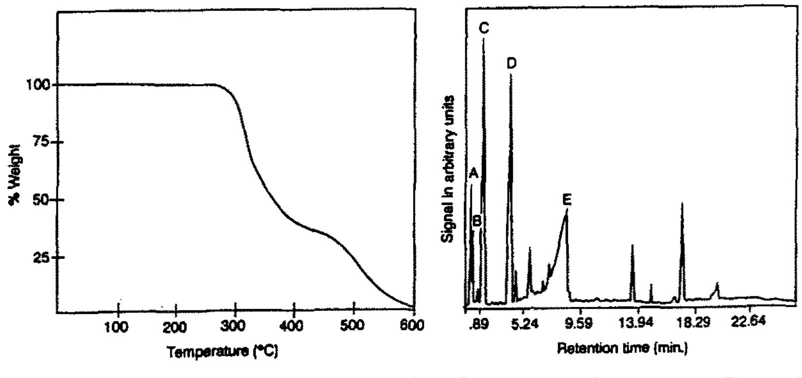

Figure 2 (a) Thermal decomposition of polyesterurethane in a TG analyzer at a heating rate of 5 °C/min up to 600 °C in air.
(b) Reconstructed chromatogram of the first 25 % weight loss trapped via a Tenax adsorption cartridge and desorbed in the TCT. (A) CO_2, (B) H_2O, (C) tetrahydrofurane, (D) cyclopentanone, (E) dicarbonic acid. The other peaks are aliphatic diols and esters.

Analysis of polycarbonate

A sample of 40 mg of a commercial polycarbonate was desorbed in the TCT for 5 minutes at 300 °C. After gaschromatographic separation of the volatile components, detection and identification was performed via FTIR and both EI and CI MS. Besides water, chlorobenzene and phenol, a p-alkylphenol was also identified. Figure 3a shows the infrared spectrum of the alkyl compound. In this example, FTIR, while providing functional group information, does not reveal the exact structure of the p-alkyl group. The CI mass spectrum, figure 3b, shows a highest mass of 207, which corresponds with a molecular weight of 206. This information in combination with the FTIR and EI mass spectrum, shown in figure 3c, enabled a positive identification of the p-alkylphenol as p-(1,1,3,3,tetra-methylbutyl)phenol, a chain regulator in the polycarbonate polymerisation process [9].

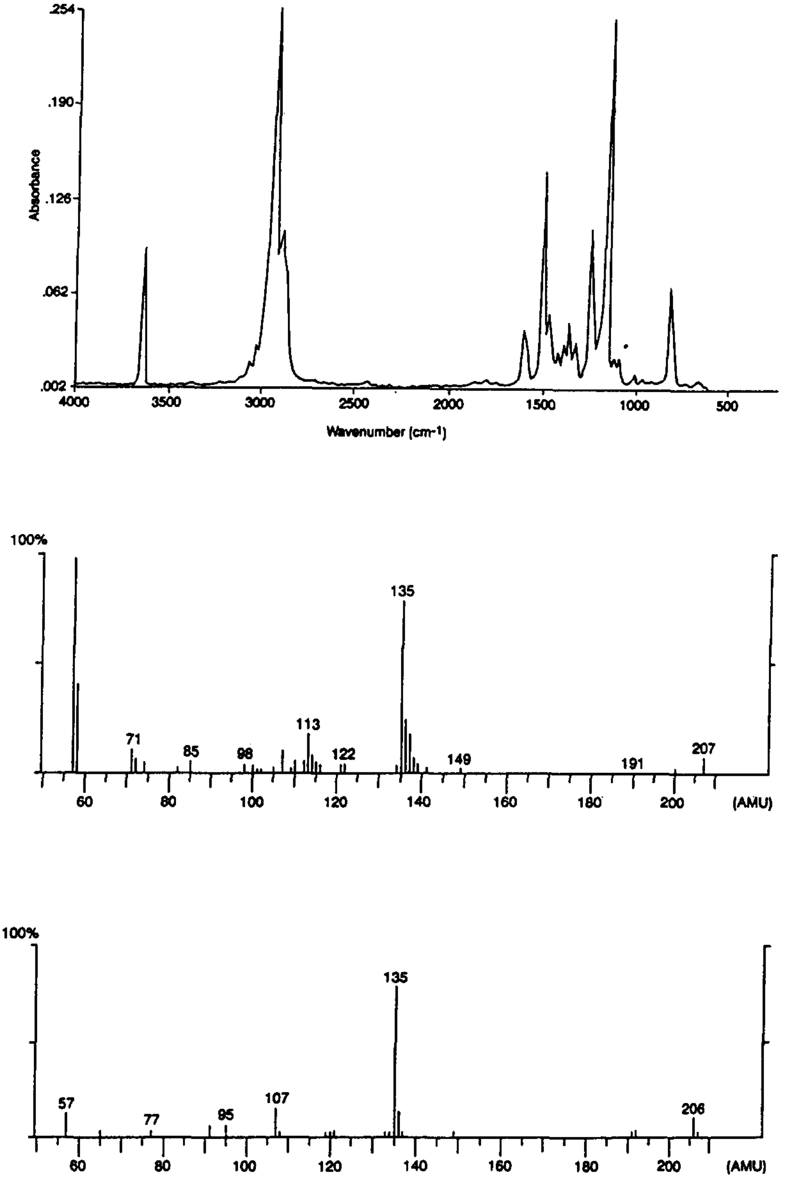

Figure 3 Spectra of p-(1,1,3,3,tetra-methylbutyl)phenol from 40 mg polycarbonate after 5 min at 300 °C.
(a) IR spectrum, (b) CI-MS spectrum, (c) EI-MS spectrum

Detection of PCB s in peroxide cured silicone rubbers

Polychlorinated biphenyls (PCB s) are formed in the curing and post-curing reactions of silicone rubbers with 2,4-dichlorobenzoylperoxide [10]. Figure 4a shows a part of a typical ion current chromatogram [2] of the outgassing products of a silicone rubber part obtained after desorption for 10 minutes at 200 °C in the TCT. In this example the chromatographic column is coupled directly with the MS without splitter, in order to obtain the required sensitivity at ppb level. By selecting a mass range of 290 - 294 amu, corresponding with the molecular weights of tetrachlorobiphenyls, the MS can be used as a selective detector for these substances. This mass range selection executed in figure 4a results in a chromatogram as shown in 4b. Figure 4c shows the mass spectrum of a tetrachlorobiphenyl, which corresponds with the strongest peak in figure 4b.

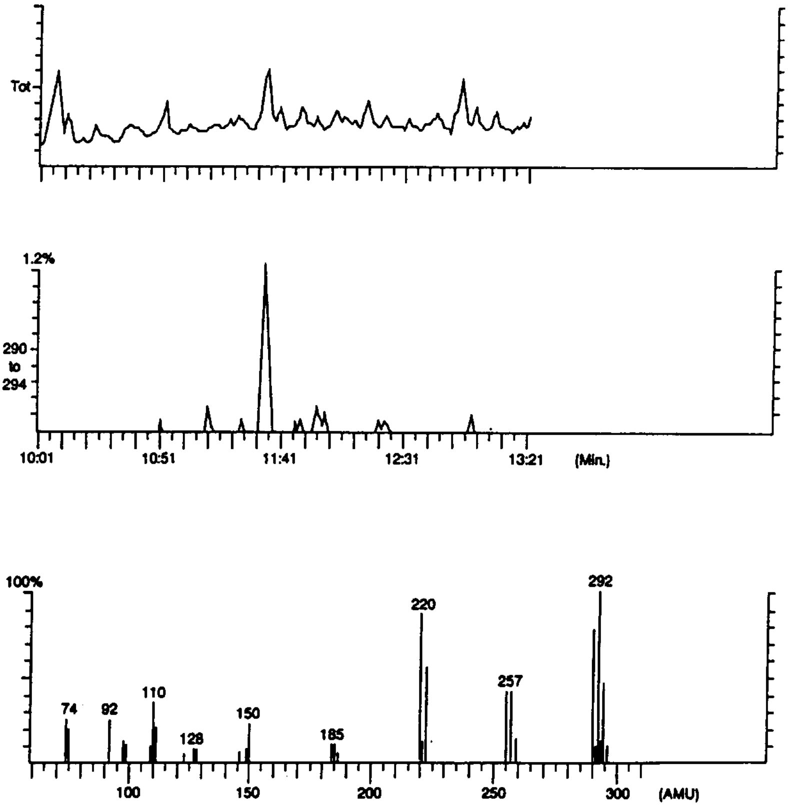

Figure 4 Reconstructed chromatograms of volatiles originating from a silicone rubber product after 10 min at 200 °C.
(a) Total ion current chromatogram
(b) Chromatogram of a selected mass range from 290 - 294 amu
(c) EI-MS spectrum of a tetrachlorobiphenyl.

CONCLUSIONS

The coupling of thermal desorption and chemical analytical techniques constitutes a powerful means for the detailed characterisation of outgassing processes with many applications in the field of plastics and rubbers. Compared to FTIR alone, the parallel configuration of FTIR and MS enhances and facilitates the elucidation of the evolved species and furthermore lowers the detection limits from ppm to (sub)ppb level.

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