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Application of on-line thermal desorption–gas chromatography–Fourier-transform infrared spectroscopy–mass spectrometry for the characterisation of polymers

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Abstract

On-line thermal desorption gas chromatography with combined Fourier-transform infrared (FT-IR) and mass spectrometry (MS) detection is a very powerful tool in identifying unknown organic components. It has been used in order to identify the building blocks of polymer blends in two plastic optical fibres of different compositions. When no reference spectra are available, both detectors provide useful information which can be used to improve the identification process in combination with other analysis techniques. The system was also used to study the effect of ageing of the optical fibres, resulting in the detection of additional degradation products in the aged fibre. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymeric materials are widely used in products manufactured by Philips. These materials are obtained as raw material of which polymer parts are made in our own production facilities. In addition a great deal of polymer parts are purchased as finished products, supplied by other manufacturers. It is of great technological importance to know the composition of these polymer blends in relation to e.g. toxicological aspects [1,2], product lifetime, mould and environmental contamination, suitability for finishing processes and allowable exposure temperature.

To characterise specific polymer blends we use a thermal desorption unit, coupled to a commercially available gas chromatograph with combined Fourier-

transform infrared and mass spectrometric detection (TD–GC–FT-IR–MS). By themselves GC–MS and GC–FT-IR are already very powerful analytical tools, a combined GC–FT-IR–MS system provides the possibility of reliable qualitative analysis. Library search results from the GC–MS data can be confirmed by the FT-IR data and in case library results are not available, the spectral information of both detectors can be of great help in identifying unknown components.

Previously, we reported the benefits of the use of a combined thermal desorption GC–MS–FT-IR system in outgassing processes of plastics and rubbers [3,4]. A commercially available GC–FT-IR had been extended with an ion-trap mass spectrometer in order to enhance and facilitate the identification of components released from the plastics and rubbers after the thermal desorption process and to lower the detection limits in order to trace minor components. The instrumentation we currently use has several

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advantages over the system used in the past. Because of its special design, the sensitivity of FT-IR is about 5 times better compared to other commercial GC-FT-IR instruments. A gold-coated light-pipe with a small internal volume of about 100 μl , is provided with a helium sweep-flow resulting in neglectable loss of peak resolution. The use of a quadrupole type mass spectrometer is preferred because of the absence of the so-called 'self-chemical ionisation' effect which makes an ion-trap type mass spectrometer less suitable for identification with standard library searches.

This paper presents the use of the thermal desorption GC-FT-IR-MS system for the characterisation of plastic optical fibres. Plastic optical fibres are often made of polyacrylates and polymethacrylates which tend to undergo depolymerisation under conditions at elevated temperatures [5]. For instance, poly(methyl methacrylate) (PMMA) yields primarily methyl methacrylate monomer when heated. In case depolymerisation does not occur, it is often possible to release residual monomer from the polymer by applying relatively low temperatures in the thermal treatment of the samples. In some cases, the monomers are easily identified using MS or FT-IR because of the availability of reference spectra. For most other monomers, such reference spectra are not available and spectral as well as elemental information needs to be obtained in order to identify the unknown monomer.

In case the polymer is pyrolysed as a result of the thermal desorption process, identification of the degradation products can help to identify the original polymer structure, especially if combined with information obtained using other techniques such as NMR and elemental analysis [6].

Two different types of plastic fibres were analysed. Both fibres are a mixture of several polymers making it difficult to identify the building blocks using FT-IR or NMR. For one particularly fibre, the effect of ageing on the chemical composition is determined using the analysis technique described in this paper. Two similar optical fibres, made of PMMA, were analysed. One fibre has been used in a system for optical communication for a period of two years.

The thermal desorption unit is capable of accommodating Tenax trapping tubes, which allows off-

line sampling with preconcentration, subsequent separation and identification of the trapped volatile components. In this configuration, the TD-GC-FT-IR-MS system is used for a wide range of analytical requests such as process control and environmental analysis.

2. Experimental

2.1. GC-FT-IR-MS apparatus and conditions

All experiments were performed on a HP 5890 Series II gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) hyphenated with a 5865 FT-IR spectrometer (Bio-Rad, Cambridge, MA, USA) and a HP 5872A quadrupole MSD (Hewlett-Packard) in series. The GC system is equipped with a CP4020 thermal desorption unit (Chrompack, Middelburg, Netherlands). An empty glass thermal desorption tube was used as a reagent tube. The cold trap used was a CP-Sil5-CB fused-silica wide-bore GC-column (Chrompack) of 28 cm \times 0.53 mm I.D. and 5 μm film thickness and was cooled with liquid nitrogen. All the samples inside the reagent tube were heated under the same conditions. After cooling the cold trap for 5 min at a temperature of -125°C , the sample was heated for 10 min at a temperature of 280°C . Components released from the heated sample were trapped at the cold trap which was held at a temperature of -125°C during the thermal treatment of the sample. To prevent column overloading and cross-contamination, the thermal desorption unit was used in the split mode. Injection of the trapped components on the GC column was performed by heating the cold trap as quickly as possible to a temperature of 280°C and remain at this temperature for 1 min.

The released components were separated on a CP-Sil5-CB low-bleed MS capillary fused-silica column (Chrompack) of 30 m \times 0.32 mm I.D. and 1.0 μm film thickness. The GC was programmed from 60°C (hold 2 min) to 100°C at a rate of 5°C min^{-1} followed by a ramp of $15^\circ\text{C min}^{-1}$ up to 250°C (hold 9 min). Helium at a pressure of 65 kPa (constant pressure mode) was used as carrier gas.

The FT-IR spectrometer was equipped with a Narrow-band MCT detector ($750\text{--}4000\text{ cm}^{-1}$) and was used at a resolution of 8 cm^{-1} . In the full-scan mode 1 spectrum s^{-1} was collected. The transfer lines and the flow cell were all at a temperature of 280°C . The sweep-flow regulator was set at 100 kPa. The mass spectrometer was set at 70 eV in the electron-ionisation mode and full-scan mass spectra were collected at 2 scans s^{-1} in a mass range of 29–700 u. The transfer line was set at a temperature of 280°C resulting in a source temperature of 154°C . In the chemical-ionisation mode, ammonia was used as a reagent gas at a pressure of 100 kPa.

2.2. Reagents

The helium carrier gas was of 99.9995% purity (Air Products, Vilvoorde, Belgium) and the ammonia used for the chemical-ionisation experiments was of 99.95% purity (Scott Speciality Gases, Plumsteadville, USA). To confirm the results of the analysis of fibre 1, diallyl diglycolcarbonate of 99% purity was analysed (Polyscience, Warrington, PA, USA). The quartz wool inside the reagent tube was obtained from Brand with a standard grade purity (Wertheim, Germany).

2.3. Analytical procedure

An empty glass thermal desorption (TD) tube was filled with a small amount of quartz wool at the bottom to prevent the sample falling through. This reagent tube was placed in the thermal desorption unit and was pre-cleaned by performing at least 10 short runs (3 min). During this pre-clean phase, the desorption temperature and the injection temperature were set at 300°C . After cooling the desorption oven, the top-cover of the TD tube was removed and a small amount of fibre (0.3 mg) was brought into the tube. All this time, the thermal desorption unit was held in the 'stand-by back-flush' mode, preventing oxygen to enter the TD tube. Before starting the analytical run, the thermal desorption unit, with its top-cover back in position, was kept in the 'stand-by back-flush' mode for 5 more min in order to flush the TD tube with helium.

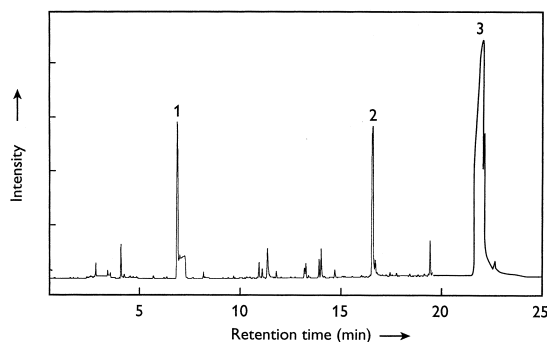


Fig. 1. MS total-ion current chromatogram of TD-GC-FT-IR-MS analysis of fibre 1. Components identified: 1=methyl methacrylate; 2=unknown; 3=unknown. The identification of both the unknown components is discussed in paragraph Section 3.1.

3. Results and discussion

3.1. Unknown fibre 1

The MS total-ion current chromatogram of fibre 1, obtained under the conditions described in the paragraph above, is shown in Fig. 1. The analysis of this fibre reveals three main components.

Peak 1 can be easily identified as methyl-methacrylate. Library searches of both the FT-IR spectrum and the mass spectrum result in the identification of this component. For the other components, peak 2 and peak 3, no reference MS or FT-IR spectra are available. The mass spectrum of component 3 is shown in Fig. 2 and the FT-IR spectrum is shown in Fig. 3. The mass spectrum as well as the FT-IR spectrum of component 2 resemble those of component 3. Therefore it is very likely that this com-

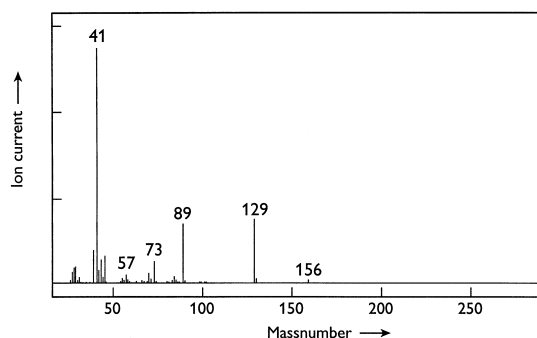


Fig. 2. Mass spectrum of component 3 of fibre 1.

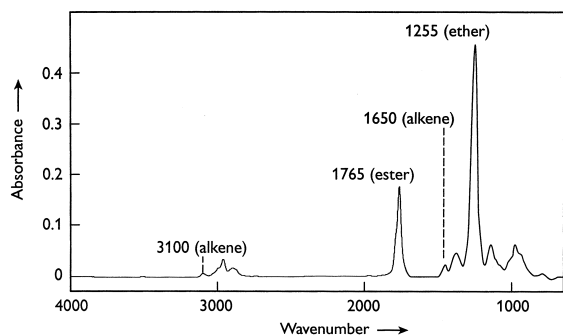


Fig. 3. FT-IR spectrum of component 3 of fibre 1.

ponent is an isomer or a degradation product of component 3.

Ammonia chemical-ionisation MS reveals a molecular mass for component 3 of 274 u. A large peak in the mass spectrum at m/z 41 indicates the presence of a $\text{CH}_2=\text{CH}-\text{CH}_2-$ in the molecule, which is confirmed by the presence of absorption bands at 1650 cm^{-1} (C=C, alkene) and 3100 cm^{-1} (C-H, alkene) in the FT-IR spectrum. The presence of a 1255 cm^{-1} band and a 1765 cm^{-1} band indicate an ester group in the molecule. Looking at the mass spectrum of the component and knowing that the molecular mass is 274 u, it is very likely that the molecule is symmetric. Supported by the results of NMR analysis of the fibre, the unknown component could be identified as diallyl diglycolcarbonate of which the structural formula is shown in Fig. 4. This component is widely used in the production of plastic optical fibres and analysis of the pure component confirmed the correct identification of this component.

3.2. Unknown fibre 2

The thermal desorption GC-FT-IR-MS analysis of fibre 2 shows that this fibre contains ethyl

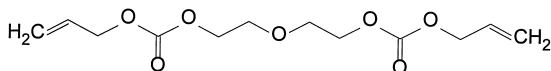


Fig. 4. Structural formula of diallyl diglycolcarbonate.

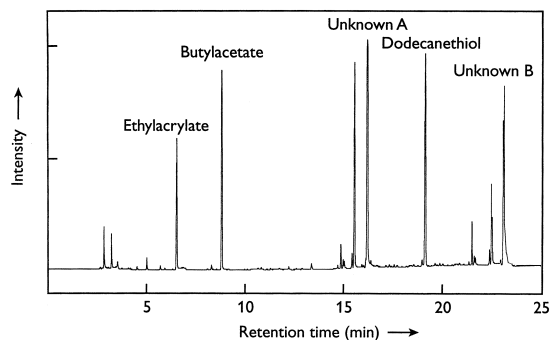


Fig. 5. MS total-ion current chromatogram of TD-GC-FT-IR-MS analysis of fibre 2.

acrylate, large amounts of butyl acetate and dodecanethiol. These components could be easily identified through library searches. Butyl acetate is probably used as a solvent and mercaptanes are often used in linear polymerisation to control molecular mass distribution through chain transfer. The MS total-ion current chromatogram is shown in Fig. 5.

Two major components, peaks A and B in Fig. 5, could not be identified using MS or FT-IR library search. These are probably degradation products formed as a result of the thermal treatment of the original material. The FT-IR spectra of component A and B are similar in appearance and indicate the presence of ester and ether groups in the pyrolysis products. The FT-IR spectrum of component B is shown in Fig. 6.

Ammonia chemical-ionisation MS reveals molecu-

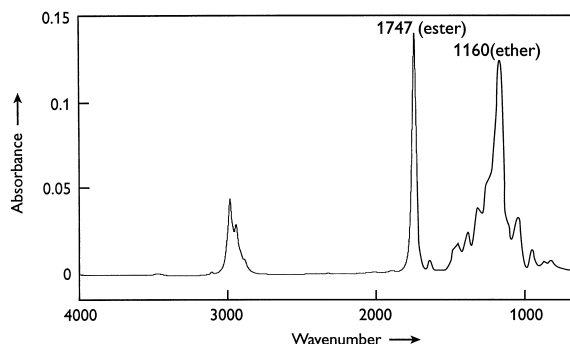


Fig. 6. FT-IR spectrum of component B of fibre 2.

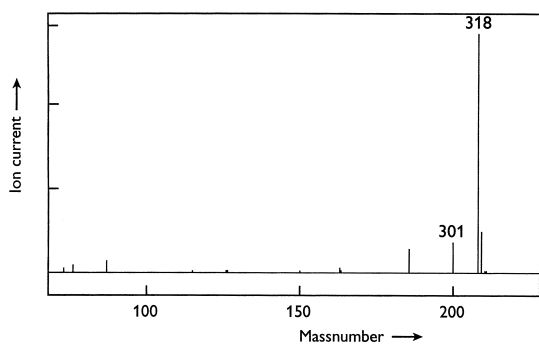


Fig. 7. Ammonia chemical-ionisation mass spectrum of component B of fibre 2.

lar masses of 200 u for component A and 300 u for component B. The chemical-ionisation mass spectrum of component B is shown in Fig. 7.

In this case, the ^{13}C NMR indicated that the fibre is a polyester formed by the polymerisation of ethylene glycol and 2,3-dimethylsuccinic acid [7]. According to the literature [5,8–11], thermal treatment of aliphatic polyesters results in cyclic monomer and oligomers as dominant degradation products. Combined with a molecular mass of 200 u, component A is identified as a cyclic monomer with a structural formula as shown in Fig. 8. Component B (molecular mass=300 u) is identified as a cyclic oligomer with a structural formula also shown in Fig. 8. The identification of these pyrolysis products show that the NMR results are very likely.

The results of the analysis of this sample show that it is not always possible to solve an identification problem using TD–GC–FT–IR–MS on its own. Sometimes the results of other analysis techniques are used to identify the building blocks of polymer

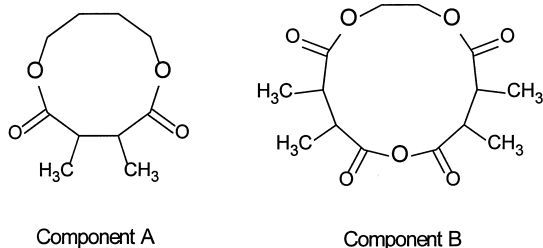


Fig. 8. Structural formula of component A and component B of fibre 2.

blends. In these cases, the results of the TD–GC–FT–IR–MS analysis are complementary and can be used to support or to exclude the results of other analysis techniques.

3.3. Ageing of plastic optical fibres

The effect of ageing of plastic optical fibres is also determined using the analysis technique described in this paper. Two similar optical fibres, made of PMMA, were analysed. One fibre has been used in a system for optical communication for a period of more than two years. The MS total-ion current chromatogram of the unused fibre is shown in Fig. 9A and the MS total-ion current chromatogram of

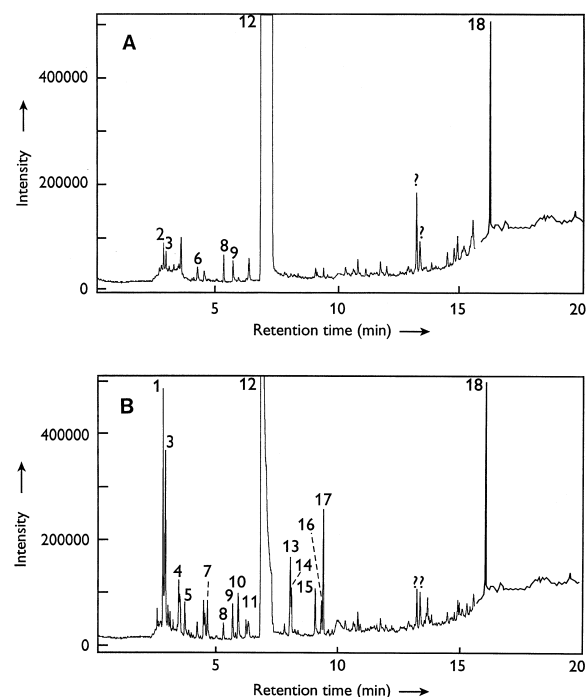


Fig. 9. (A) MS total-ion current chromatogram of TD–GC–FT–IR–MS analysis of an unused fibre. (B) MS total-ion current chromatogram of TD–GC–FT–IR–MS analysis of an used fibre. Components identified in the TD–GC–FT–IR–MS analysis of an used and an unused fibre: 1=methanol; 2= acetaldehyde; 3= 2-methyl-1-propene; 4=acetone; 5=formic acid; 6= hydroxyacetaldehyde; 7=butenal; 8=methylpropionate; 9=1-hydroxy-2-propanone; 10=butanol; 11=propanoic acid; 12=methyl metacrylate; 13=butanoic acid; 14=crotonic acid; 15= methylthiobutane; 16=sulfuric acid, dimethyl ester; 17=methyl 2-methoxypropenoate; 18=dimer methyl methacrylate.

the used fibre is shown in Fig. 9B. The used fibre shows a range of additional degradation products which are not present, or in a lesser amount in the unused fibre.

In this analysis, the absolute amount released of each single component, except methyl methacrylate, is below the detection limit of the FT-IR spectrometer but within the detection range of the mass spectrometer. This results in a positive identification through library searches of the main part of the components detected. The difference in sensitivity of the FT-IR spectrometer and the mass spectrometer makes the FT-IR less suitable for identification purposes in the analysis of additives and low concentration degradation products in polymeric material. Although the sensitivity of our dedicated FT-IR spectrometer is better than the standard FT-IR spectrometers, used as a detector in gas chromatography, the sensitivity of the mass spectrometer is still about two orders of magnitude higher.

The significance of the analysis results described in this paragraph, is still a matter of further investigation.

4. Conclusion

On-line TD–GC–FT-IR–MS is a very powerful tool for the identification of unknown components in optical fibres and polymer blends in general. The use of a system with combined FT-IR and MS detection results in more reliable library search identifications. When no reference spectra are available, both detectors provide useful information that can be used to improve the identification process in combination with the results of other analysis techniques such as NMR and elemental analysis.

The FT-IR detector is less suitable for identification purposes in the analysis of low concentration components in polymers because it is less sensitive than the mass spectrometer detector.

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