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DETERMINATION OF HALOGENATED HYDROCARBONS IN INSULATING POLYMERIC FOAMS

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Abstract

A simultaneous thermal analysis/mass spectroscopy system was used for the determination of halogenated hydrocarbons in polymeric foam insulation materials. The investigation of ten different polymeric foams show that this equipment is a sensitive and reliable tool for the identification and determination of the bubbling agent. The results are compared with the Purge and Trap method.

Keywords: bubbling agents, halocarbons, rigid foam polymers, simultaneous TG/MS

Introduction

Nowadays it is accepted that the release of volatile halocarbons, especially chlorofluorocarbons (CFC) and chlorofluorohydrocarbons (HCFC), into the atmosphere contributes to the distruction of the earth's ozone layer and to the increase of the greenhouse effect. These compounds are also used as bubbling agents for plastic foams, especially for rigid foam plastics. Therefore, the majority of nations agreed in 1987 in the Montreal Protocol to phase out the production and use of harmful CFCs.

In Germany since 1995 the production and the trade of polymeric foams which are blown with CFCs is no longer permitted [1]. The use of partially halogenated chlorofluorocarbons has to be gradually reduced world wide up till 2030. For the proper monitoring of halocarbons in polymeric foams and for the implementation of EU-rules as well as national regulations, reliable analytical methods are urgently needed for the screening and differentiation of halocarbons as well as their quantification.

The half value time for the diffusion of the CFC/HCFC for 2 to 3 cm thick samples of rigid foam plastics is between 30 and 50 years. Therefore, the bubbling agents are enclosed in these materials and they are only released by heating

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over the glass transition and/or the melting point of the foam. A problem is the small sample weight because of the low density of the foams. However, the application of a thermogravimetric equipment coupled with a mass-spectrometer should solve this problem [2].

In this paper, we describe the investigation of ten polystyrene and polyurethane foams to analyze and estimate the content of the various bubbling agents.

Experimental

TG/MS equipment and measuring conditions

The TG/MS-analysis system consists of a TG/DTA 220 (Seiko) and a QMG 421C quadrupole mass spectrometer (Balzers). The thermobalance (TG) is based on a horizontal differential system. A specially arranged quartz-capillary system is used to reduce the pressure from ambient pressure to high vacuum in order to permit the simultaneous recording of the mass spectra.

Figure 1 shows the TG/MS-interface for the coupling of the capillary system to the thermobalance. The temperature of the second oven can be held up to 200°C

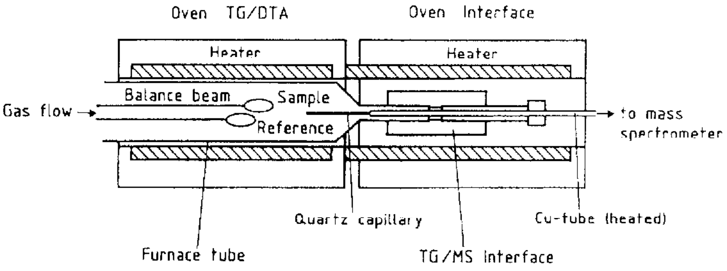

Fig. 1 Pattern of the TG-MS-Interface for the coupling of the heated quartz capillary

During the whole measurement the MS pressure was adjusted to 10^{-5} mbar and kept at this value by a self-regulating valve. The ionization was achieved by means of a rhenium cross beam ion source with 70 eV and the registration by means of a 90° off axis SEM or alternatively a Faraday cup.

All experiments were carried out in helium or nitrogen at a flow rate of 200 ml min^{-1}. The applied heating rate was 10°C min^{-1} from ambient temperature up to 200°C before the degradation of the foams begins. The quartz capillary line was maintained at a temperature of 100°C to avoid condensation of the evolved gases at the surface.

The results were processed in the so-called bargraph-mode with the mass-range from 5 Da to 160 Da together with the total ion current (TIC) trace as a function of time and/or in the multiple ion detection mode (MID), which allows the simultaneous and continuous registration of up to 64 selected fragments, and represents the evolved gas profiles as a function of temperature or time.

The sample weights were in the order of 3 mg in platinum pans with an empty Pt-pan as reference.

Samples

Ten different foamed polymeric materials based on polystyrene and polyurethane were investigated. Two samples were about 10 years old.

Results and discussion

Figure 2 shows the measurement results for a rigid foam polystyrene in the bargraph mode. The mass spectra were provided during the heating process at 35°C (underground) and at 125°C (above the glass transition temperature of the sample). The identified mass fragments of the evolved gases hint to ClF_2C-CH_3 as bubbling agent.

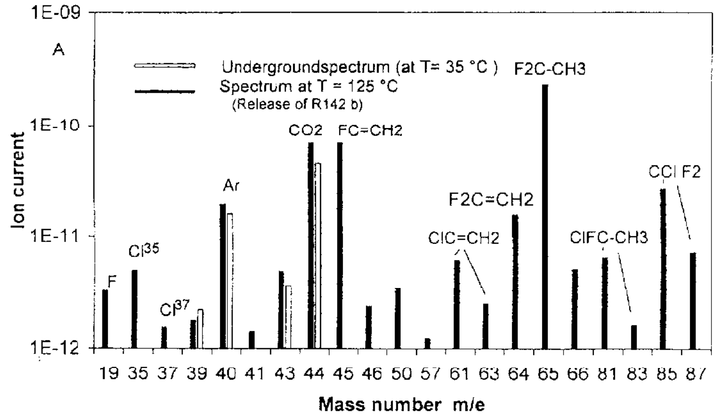

Fig. 2 Bargraph mode measurement of the foam polystyrene 3000 S at two temperatures (Remark: the mass difference of 2 DA for the ions containing Cl corresponds to the two isotopes of chlorine)

Figures 3–5 show examples for measurements in the multiple ion detection mode of two foamed polystyrenes and a foamed polyurethane as a function of the temperature. In all samples, the enclosed bubbling agents are released in the melting region. Based on the different mass fragments, they can be identified as CCl_3F (R11) , CCl_2F_2 (R12) and ClF_2C-CH_3 (R142b). The most intensive mass value of all samples is the mass fragment with the composition: $M-Cl^{35}$ with M as the molecular mass of the bubbling agent.

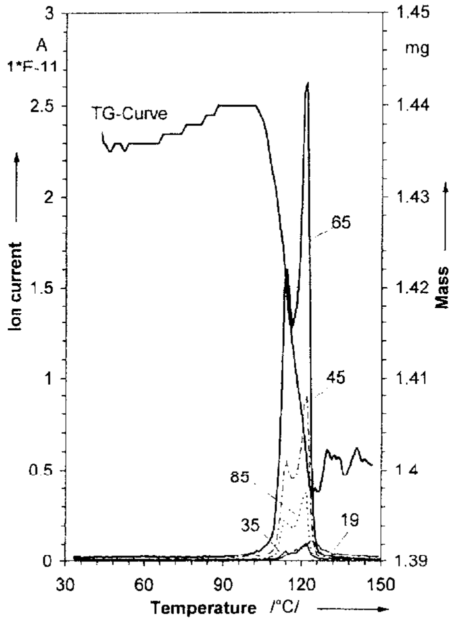

Fig. 3a TG/MS-curves of a foam polystyrene with R 142b as bubbling agent

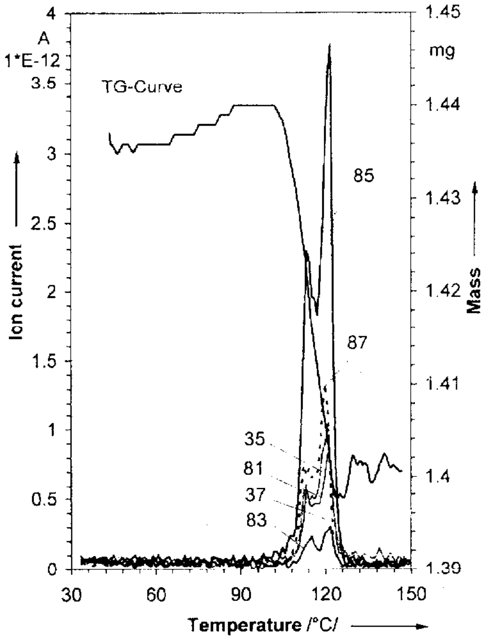

Fig. 3b Detailed TG/MS-curves of a foam polystyrene with R 142b for the chlorine-containing fragments

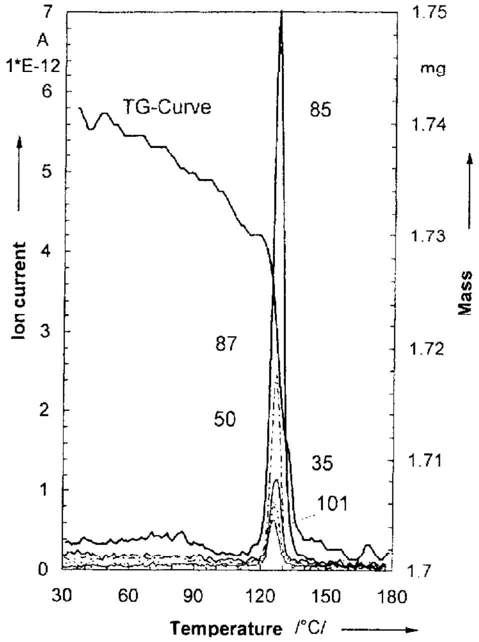

Fig. 4 TG/MS-curves of a foam polystyrene with R 12 as bubbling agent

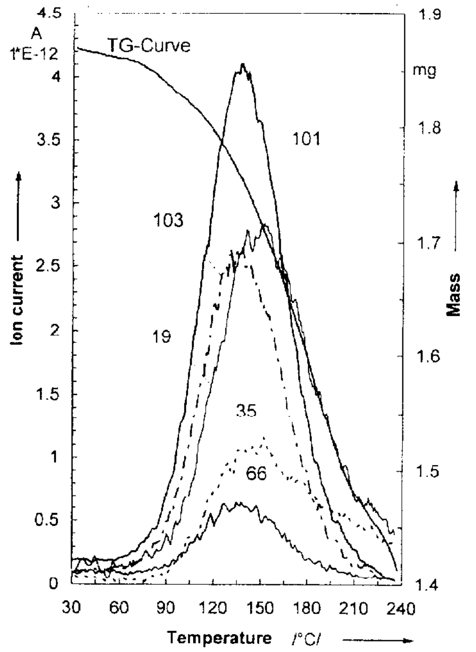

Fig. 5 TG/MS-curves of a foam polyurethane with R 11 as bubbling agent

Figure 6 shows the TG/MS curves of a new product which was foamed with CO_2. Here the bubbling agent could only be identified over the fragments of $m/z=28$ and 14. The missing $m/z=44$ (CO_2) hints to the fact that this foamed polystyrene possesses mainly an open porous structure and no closed cells. Therefore, a gas exchange took place.

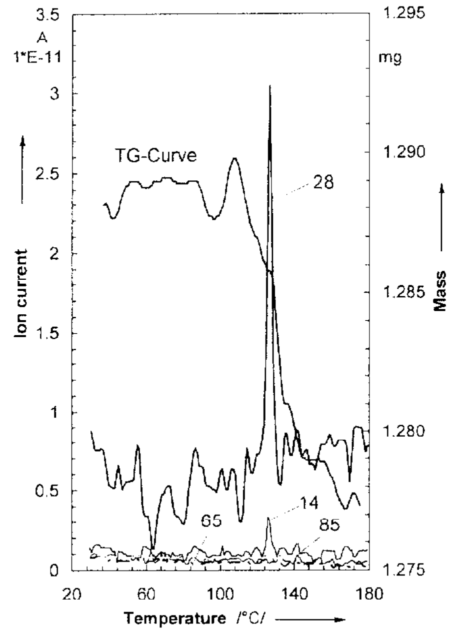

Fig. 6 TG/MS-curves of a foam polystyrene with CO_2 as bubbling agent (mass loss only ~10 μg)

Table 1 Detected bubbling agent fragments in various foams

Sample	Key ions				Bubbling agent
PU-Foam	$CCl^{35}Cl^{35}F$ $m/e=101$	$CCl^{35}Cl^{37}F$ $m/e=103$	Cl^{35}, F $m/e=35,19$	$CCl^{35}F$ $m/e=66$	CCl_3F R 11
PS-Foam	$CCl^{35}F_2$ $m/e=85$	$CCl^{37}F_2$ $m/e=87$	Cl^{35} $m/e=35$	CF_2 $m/e=50$	CCl_2F_2 R 12
PS-Foam	$F_2C{-}CH_3$ $m/e=65$	$FC{=}CH_2$ $m/e=45$	$CCl^{35}F_2$ $m/e=85$	Cl^{35}, F $m/e=35, 19$	$ClF_2C{-}CH_3$ R 142b
PS-Foam	CO_2 $m/e=44$	CO(?), N_2 $m/e=28$	N, CO^{2+} (?) $m/e=14$		CO_2

The content of the bubbling agent of the investigated materials was between 2 and 8 Ma%. Table 1 gives an overview of the investigated materials and of the identified foaming gases.

The representativeness of the sampling is essential to obtain comparable results. The foaming gas content depended on the position of sample in the test material. The difference between the fringe (marginal zone) and inside of the test material amounted up to 2 Ma%.

A comparison with other analytical methods (Table 2) showed that the TG/MS method is more effective than for example the Purge and Trap – GC/MS method [3]. The Purge and Trap method measures only the volatile compounds which are contained in the open elements and not in the closed pores of the polymeric foam.

Table 2 Comparison of the TG/MS- and the Purge and Trap-methods

Method	Concentration of HCFC in Styrodur 3000S/mg g^{-1}	σ/%
TG/MS	61±8	13
Purge and Trap gas ¹⁾	16±4	25
Purge and Trap liquid ²⁾	22±4	18

1) sample cut
2) sample dissolved in benzyl alcohol

Conclusions

The investigation of foamed polymeric materials shows that the on-line coupling of a thermobalance with evolved gas analysis mass spectrometry is a powerful method for the determination and characterization of the bubbling agents in rigid foam plastics. Furthermore, it is possible to estimate the quantities of the agents in the foamed polymeric materials. A sample mass of about 2 mg is sufficient for the measurement. This method can be easily adapted to other volatile organic compounds (VOCs).

References

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