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Gas chromatographic-mass spectrometric analysis of some potential toxicants amongst volatile compounds emitted during large-scale thermal degradation of poly(acrylonitrilebutadiene-styrene) plastic

M. M. SHAPI*

Analytical Chemistry Division, Department of Chemistry, University of Helsinki, Vuorikatu 20, SF-O0100 Helsinki 10 (Finland)

and

A. HESSO

Institute of Occupational Health, Haartmaninkatu 1, SF-00290 Helsinki 29 (Finland)

ABSTRACT

A **number of compounds emitted during the thermal degradation of plastics are potentially toxic. This study was aimed at identifying the volatile compounds emitted during large-scale thermal degradation of poly(acrylonitrile butadiene-styrene). About** 5 g **of the sample were degraded at between 25 and 470°C in air and nitrogen in a device that can simulate temperature-programmed thermogravimetry. The volatiles were collected in dichloromethane using the solvent trap technique. Some of the 92 compounds identified by gas chromatography-mass spectrometry were found to have no hitherto documented toxicological profiles, even though they are potentially dangerous.**

INTRODUCTION

Styrene- and acrylonitrile-containing thermoplastics such as poly(acrylonitrile-butadiene-styrene) (ABS) are widely used in a variety of industrial applications [1]. A representative chemical structure of ABS plastics is given in Fig. 1. The order of the acrylonitrile, butadiene and styrene monomers that constitute the ABS terpolymer and the values of X , Y and Z depend on the manufacturing **conditions and vary from type to type. ABS plastics are usually subjected to relatively high temperatures during their processing, which often lead to decomposition to gaseous and volatile compounds as well as non-volatile residues. The types and amounts of the observed thermal decomposition compounds depend on the degradation conditions, the plastic composition and the method of analysis.**

Although the polymer itself is considered to be biologically inert, the thermaloxidative fumes of ABS have been shown to have biochemical effects on rats [2].

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Fig. 1. Representative structure of ABS.

Deciding which of the numerous components of the complex mixture are responsible for the observed biochemical effects is best achieved by carrying out an elaborate bioassay. This task is greatly facilitated by a knowledge of the chemical components present in the mixture. Identified compounds include alcohols, aldehydes, ketones, aromatic hydrocarbons, nitriles and nitrogen heterocyclics [3-9]. However, most previous studies have been aimed at fundamental research, which usually involves very small (microgram) amounts of sample and is not representative of large-scale commercial processes or fires where secondary pyrolysis of the initial compounds is also believed to occur. In addition, they have also tended to ignore minor components even though it is wrong, from a health-risk assessment point of view, to exclude them from the list of potentially toxic compounds. Aliphatic nitriles, which form a fairly significant proportion of ABS thermal degradation volatiles, can be toxic even in small amounts [10-13].

This study was aimed at identifying the volatile compounds, including the minor components, emitted by ABS during fire or large-scale thermal degradation in order to establish the chemicals with which a person exposed to the fumes is liable to come into contact.

EXPERIMENTAL

Chemicals

The plastic sample, ABS 550-27, manufactured by Dow Chemicals GB, was obtained from Algol (Helsinki, Finland). Its specifications were not available^a. The standard (C_7-C_{36}) *n*-alkanes were purchased from a variety of sources. The analytical grade 20 ppm 2-methylbutene stabilized dichloromethane was obtained from Merck (Darmstadt, F.R.G.). Helium, nitrogen, and air were obtained from AGA (Helsinki, Finland).

 \degree As long as a polymer contains the microstructures X, Y and Z shown in Fig. 1 it is called ABS and is designated the *Chemical Abstracts* number [9003-56-9] regardless of the proportions in which the microstructures occur or its molecular weight. If any other compounds or ingredients, such as antioxidants, are incorporated in the structure it should correctly be called a compound. Polymers differing in the microstructures are called types.

Thermal degradation

Degradation was conducted in a tubing device similar to that used by Peltonen [14]. It consisted of a glass tube (1500 \times 17 mm I.D.), fitted with a moving oven $(100 \times 18 \text{ mm})$. One end of the tube was connected to the purge gas and the other to a solvent trap collector. The collector consisted of two 50-ml series-connected containers half filled with dichloromethane through which the purge gases carrying the volatiles were allowed to bubble via molecular sieves. Very volatile molecules such as hydrogen cyanide and non-volatile or high-molecular-weight compounds which condensed before reaching the solvent trap or could not pass through the molecular sieves were not expected to be found amongst the collected volatiles. The characteristic temperature distribution inside and around the oven moving at various speeds and a temperature of 350°C have been outlined [15]. Similar distributions were assumed for the temperature used in these experiments.

About 5 g of the ABS sample were evenly distributed over a length of about 70 cm of the tube. The purge gas and solvent trap collector were connected and the oven was allowed to travel over the sample at 7.26 mm/min. The oven temperature controller was set at 470°C and purge gas, synthetic air or nitrogen flowrates of 1000 ml/min were used. Decomposition in air and nitrogen occurs by different mechanisms because, unlike inert nitrogen, the oxygen of air is capable of reacting with the polymer molecules and is known to penetrate polymer films [16]. An air atmosphere represents the beginning of a fire, whereas a nitrogen atmosphere represents the stage of a fire when all the oxygen has been consumed. Selection of the degradation temperature was based on preliminary thermogravimetric (TG) experiments, which showed that the sample used in this study was completely decomposed at about 470°C. Although the oven temperature was set at 470°C, decomposition of the sample cannot be said to have taken place at this temperature because of mass transport effects. The temperature approaches the oven temperature as one moves from the cold to the hot end of the tube. The sampling technique can therefore be said to resemble a TG experiment in which the sample is heated from room temperature (25°C) to 470°C at an unknown rate related to the oven speed. On completion of the degradation, the solvent-trapped compounds were collected in one container and diluted to 50 ml, ready for gas chromatographic-mass spectrometric (GC-MS) analysis.

Gas chromatography-mass spectrometry

The GC-MS instrument used was a Finnigan-MAT 8200 B double-focusing mass spectrometer equipped with an INCOS data system and a Varian 3700 gas chromatograph. The injector temperature was kept at 250°C and helium at a flow-rate of 2 ml/min was used as the carrier gas. The GC column was kept at 50°C for 1 min, then heated to 240°C at 5°C/min and kept at 240°C for 20 min. A 27 m \times 0.2 mm I.D. SP-2330 column with a 0.2- μ m stationary phase thickness was used. The solution containing the ABS volatiles was introduced into the gas chromatograph by splitless injections involving $1.0-2.0 \mu$ of a dichloromethane solution. The split valve was kept closed for 25 s. A direct GC-MS interface kept at 250°C was used. Sample ionization was by electron impact (EI) at 70 eV with an emission current of 0.5 mA. Resolution was set at 1000 and the scan range was *m/z* 45-450 at a rate of 1 scan per second. Temperature-programmed retention indices were determined using samples injected together with *n*-alkane (C_7-C_{36}) standards.

The library facilities of the GC-MS data system and the literature [17,18] were utilized as much as possible in the identification of the collected volatiles. The Finnigan-MAT soft software includes a copy of the NBS-NIH-EPA library. It consists of *ca.* 38 700 common chemical compounds which form the mass spectral database of the system. The entry for each compound includes a 70-eV mass spectrum with up to 50 peaks and the compound's name, molecular weight, formula and *Chemical Abstracts* Service (CAS) registry number. The algorithm used in this study performs a forward search in which an unknown is compared with a number of library entries for compounds that resemble a current data spectrum. It reports the best matches together with parameters that describe the quality of the match. First it performs a data reduction of the unknown spectrum to eliminate most of the low-intensity peaks by creating mass-weighted ions which identify the compound more unambiguously. To save time, a presearch compares the sixteen most intense peaks of the unknown with the eight most intense weighted peaks of each library spectrum to find up to 50 library spectra that most resemble the unknown for use in the main search where PURITY and FIT matches are performed. PURITY measures the match between mass limits and locally normalized ion intensities. FIT measures the degree to which the library spectrum is included in the spectrum of the unknown. Apart from displaying the spectrum of the unknown together with the spectra of up to three entries that best match the unknown, the program also lists up to nine library compounds that best match the unknown.

Some of the structures in this study had to be deduced manually using fragmentation patterns owing to a lack of reference spectra in the available library facilities. The elemental compositions of less obvious compounds were obtained from high-resolution ($R = 3000$) GC-MS experiments. Not all the detected compounds could be identified because some were produced in minor amounts that were insufficient to give elemental compositions. In addition, some of the peaks were ignored on account of being much smaller than the analysed peaks.

Some of the compounds in this study were not fully identified because their spectra could not be differentiated from similar spectra belonging to other compounds or isomeric forms. Confirmation of isomeric forms is usually achieved by a combination of matching spectra and GC retention indices [19]. Owing to a lack of reference compounds, the temperature-programmed retention indices were not of much help in identification. They proved useful, however, in matching compounds common to decomposition in air and nitrogen.

Toxicological documentation

A search for the number of research papers pertaining to biochemical, environmental or toxicological studies for the period 1967-1989 that have been published on each identified compound was carried out using the STN International [20] computer library search system.

RESULTS AND DISCUSSION

Figs. 2 and 3 show expanded and detailed GC-MS total ion current traces for volatile compounds emitted during degradation of the ABS sample in air and nitrogen, respectively. The compounds corresponding to the peak numbes shown on the diagrams are given in Table I, where the temperature programmed retention indices are also reported. A total of 53 compounds for decomposition of the sample in air and 87 for decomposition in nitrogen were analysed. Of these compounds, 48 were common to decomposition in both atmospheres. Decomposition of the sample in air and nitrogen gave a total of at least 92 different compounds. The term "at least" is used here because, as pointed out above, some peaks were ignored on account of being much smaller than the analysed peaks. Substances common to decomposition in air and nitrogen accounted for about 95.3% of the total yield of volatiles for decomposition in air and about 90.1% of volatiles for decomposition in nitrogen. Apart from a few heterocyclics, nitrogen-containing compounds occurred mainly as aliphatic nitriles or dinitriles. There were 29 nitrogen-containing compounds for decomposition in air. These accounted for about 31.3 % of the total yield. The 45 nitrogen-containing compounds for decomposition in nitrogen accounted for about 38.1% of the total yield. Formation of oxygen-containing compounds during decomposition in air was about 1.0% and insignificant for decomposition in nitrogen. The remainder of the compounds were hydrocarbons.

Thermal degradation of ABS is centred on the formation of macroradicals following initial cleavage at weak points associated with trace impurities and subsequent autocatalysed free radical unzipping (depolymerization) type chain reactions which terminate in the formation of volatiles and conjugated or crosslinked structures [3,21-25]. Termination is brought about by combination of active radical intermediates. Macroradicals formed through reaction with oxygen in the air atmosphere are responsible for the different compounds for degradation in air and nitrogen.

It was found that some of the 92 tentatively identified volatile compounds of the complex fumes emitted during thermal degradation of ABS, which may find their way into the environment, are undocumented or have no documented toxicological profiles. Results of the literature search are summarized in Table I, where the number of articles pertaining to toxicological studies and CAS registry numbers of the documented compounds are also given.

From a risk assessment point of view, the unclarified isomers in this work can

VOLATILE COMPOUNDS EMITTED DURING DEGRADATION OF ABS 550-27 IN AIR AND NITROGEN AT 25-470°C WITH NUMBER OF TOXIC-VOLATILE COMPOUNDS EMITTED DURING DEGRADATION OF ABS 550-27 IN AIR AND NITROGEN AT 25-470°C WITH NUMBER OF TOXIC-ITY REFERENCES FOR THE PERIOD 1967-89. ITY REFERENCES FOR THE PERIOD 1967-89.

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RI - Programmed mode retention index. ^{*a*} RI – Programmed mode retention index.
 $b = \text{No information.}$

 $-$ No information.

Nil = Not present.

 $n =$ Less than 0.1% or negingible. ^c Nil = Not present.
 $a_n = 1$ css than 0.1% or negligible.

 $\overline{1}$

be taken care of by considering all possible isomers of a given peak^{α}. Their registry numbers and number of references pertaining to toxicity studies are not included in Table I, however, because toxicological literature on most of them is available. On the other hand, if it is not enough to suspect a compound of being emitted during thermal degradation of ABS, isomeric clarification can be carried out by use of retention indices of reference compounds, which can either be synthesized or bought. It is important that there is good agreement on at least two stationary phases of different polarity. Another possible way of distinguishing isomeric forms which give similar 70-eV mass spectra is to change the electron energy to a value, usually lower than 70 eV, at which the isomeric forms yield different spectra. However, this also entails the use of reference compounds and has the added disadvantage of the low sensitivity characteristic of low-energy El ionization [26]. In the absence of reference compounds, some of the tentatively assigned structures of this work can be confirmed by a combination of tandem and chemical ionization mass spectrometry.

CONCLUSION

As some of the potentially toxic chemicals found among volatile compounds emitted during fire or large-scale thermal degradation of ABS plastics have no documented toxicological profiles, there is need for a more systematic assessment of the full health and environmental risks posed by these plastics.

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 \degree For an institution that wishes to reduce costs, it may not be essential to clarify the exact isomer belonging to a given peak if the compound is well known and is suspected of being emitted during thermal degradation of ABS. Because of the large number of compounds and cost, isomeric clarification of compounds in this study was restricted to a selected few that are of interest to our institutes.

REFERENCES

- 1 G. Lindenschmidt and R. Theysohn. *Kunststoffe*, 77 (1987) 982.
- 2 A. Zitting and H. Savolainen, *Arch. Toxicol.,* 46 (1980) 295.
- 3 A. Hoff, S. Jacobsson, P. Pfaeffli, A. Zitting and H. Frostling, *Scand. J. Work Environ. Health,* 8 (1982) Suppl. 2.
- 4 M. P. Luda di Cortemiglia, G. Camino, L. Costa and M. Guaita, *Thermochim. Acta,* 93 (1985) 187.
- 5 J. V. Rutkowski and B. C. Levin, *Fire Mater.,* 10 (1986) 93.
- 6 N. Lichtenstein and K. Quellmalz, *Staub-Reinhalt. Lull,* 44 (1984) 472.
- 7 Y. Feng and J. Wu, *Lanzhou Daxue Xuebao, Ziran Kexueban,* 18 (1982) 69.
- 8 G. Le Mona, *Bull. Acad. Natl. Med.,* 166 (1982) 43.
- 9 G. Hempel and U. Ruedt, *Dtsch. Lebensm.-Rundsch.,* 84 (1988) 239.
- 10 F. R. Johannsen and G. J. Levinskas, *Fundam. Appl. Toxicol.,* 7 (1986) 690.
- 11 H. Tanii and K. Hashimoto, *Arch. Toxicol.,* 55 (1984) 47.
- 12 C. C. Willhite and R. P. Smith, *Toxicol. Appl. Pharmacol.,* 59 (1981) 589.
- 13 A. E. Ahmed and M. Y. H. Farooqui, *Toxicol. Lett. (Amsterdam),* 12 (1982) 157.
- 14 K. Peltonen, *Analyst (London),* 111 (1986) 819.
- 15 K. Peltonen, *J. Anal. Appl. Pyrol.,* I0 (1986) 51.
- 16 A. Torikai, T. Takeuchi and K. Fueki, *Polym. Photochem.,* 3 (1983) 307.
- 17 S. R. Heller and G. W. A. Milne, *EPA/NIH Mass Spectral Data Base,* Vols. 1~4, U.S. Government Printing Office, Washington, DC, 1978.
- 18 *Eight Peak Index of Mass Spectra*, Vols. 1-3, Mass Spectrometry Data Centre, AWRE, Aldermaston, 1974.
- 19 C. E. Rostad and W. E. Pereira, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 9 (1986) 328.
- 20 R. E. Maizell, *How to Find Chemical Information,* Wiley, New York, 1987, p. 193.
- 21 M. C. Gupta and J. Nambiar, *J. Colloid Polym. Sci.,* 261 (1983) 709.
- 22 J. B. Adeniyi and E. G. Kolawole, *Eur. Polym. J.*, 20 (1984) 43.
- 23 L. Zlatkevich, *Polym. Eng. Sei.,* 24 (1984) [421.
- 24 D. M. Chang, *Polym. Eng. Sci.,* 22 (1982) 376.
- 25 J. B. Adeniyi, *Eur. Polym. J.,* 20 (1984) 291.
- 26 B. J. Millard, *Quantitative Mass Spectrometry,* Heyden, London, 1978, p. 45.