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THERMAL DEGRADATION OF WELDABLE POLY(VINYL CHLORIDE) SAMPLES AT LOW TEMPERATURES

BARBRO ANDERSSON

National Institute of Occupational Health, Analytical Chemistry Division, P.O. Box 6104, S-900 06 Umeå (Sweden)

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SUMMARY

A study was performed to determine possible emission products during plastic welding that may be responsible for health problems. Thermal degradation of poly(vinyl chloride) samples was carried out at 170°C in a thermal desorption gas chromatography (GC) injector and in a modified impinger in a GC oven, in combination with various analytical techniques, thermogravimetric analysis, capillary GC, GC–mass spectromety, high-performance liquid chromatography and isotachophoresis. Some of the degradation products found are known to be eye irritants.

INTRODUCTION

Electromagnetic welding is used for joining polymeric materials[1]. Polymers based on poly(vinyl chloride) PVC have suitable chemical and physical properties for this technique and the high content of plasticizers (10–40%) in PVC materials improves their welding properties. Various products, ranging from plastic folders for the office to large military tents, are manufactured by means of this technology.

Pure PVC polymers are unstable at high temperatures, degradation commencing at about 100°C with the emission of hydrogen chloride[2]. This instability is a limitation on the use of PVC, and various additives have been used to stabilize such polymers. In addition to plasticizers and stabilizers, PVC products contain other additives, such as dyes, flame retardants and fillers[3,4]. In heat treatment of PVC materials the emitted compounds originate from the additives as well as from the polymer itself.

Several investigations on the thermal degradation and pyrolysis of PVC have been published and have been reviewed[3–6]. Thermogravimetric analysis is the method most frequently used for the determination of weight losses, and gas chromatography–mass spectrometry (GC–MS) for identification of the compounds emitted. The degradation products formed are highly dependent on the temperature[7–9] and on the purity of the polymer. A large number of compounds has been reported above 200°C: hydrogen chloride, benzene and other aromatic hydrocarbons, aliphatic hydrocarbons, halogenated aromatics and esters of phthalic acid and adipic

acid[2,4-6,10]. Some compounds, such as carbon monoxide[2,5,6], vinyl chloride[11] and phosgene[12], are highly hazardous. A few reports concern degradation temperatures below 200°C[2,13-15]. These are studies of the dehydrochlorination reaction and were carried out by following the emission of hydrogen chloride, with no attempts to determine other products. The emission of benzene has been reported at temperatures just above 200°C[2,16].

In test animals, thermal decomposition products are mainly responsible for causing lesions in the respiratory system[17-21], and hydrogen chloride is considered to be the principal contributor[17,20]. Occupational illnesses have been reported in workers exposed to degradation compounds. Workers engaged in meat-wrapping are reported to have developed pulmonary illness[16,22] although the air concentrations of hydrogen chloride and other organic compounds are far below the occupational threshold limit values. Neurological lesions have been reported in the PVC-processing industry, phthalate esters (plasticizers) being considered to be responsible[23,24].

An investigation of leakage fields around industrial plastic-welding machines revealed that the occupational ceiling values for the electric and magnetic fields are frequently exceeded and that occupational health problems, including eye troubles, occur[25,26]. The aim of the current laboratory investigation was to identify possible volatile products emitted by PVC samples at low welding temperatures that may be responsible for the eye problems.

EXPERIMENTAL

Plastic material

Seventeen different PVC samples (approx. 0.5-m² sheets) from three factories were investigated, representing products ranging from writing pads and raincoats to large dust covers.

Thermogravimetric analysis

The analysis was performed by means of a Stanton Redcroft Simultaneous Thermal Analyzer equipped with a Commodore CBM Model 4032 data system. Samples (15 mg) were heated from 20 to 500°C (30°/min) in an airflow of 40 ml/min.

Thermal degradation

The degradation was performed in two different types of equipment. For the analysis of volatile organic compounds, 15-mg samples were heated in empty glass tubes belonging to a GC injector for thermal desorption, Fig. 1 (Thermodesorption Cold Trap Injector, Chrompack). The glass tube contained silylated glass wool at one end. The compounds emitted were collected in the cold trap and injected in one portion into the capillary gas chromatograph. The cold trapping was performed by means of liquid nitrogen in a 10-l Dewar vessel. Nitrogen gas was passed into the vessel through a 24 cm × 5 cm I.D. copper helix (copper line, 3.9 m × 2 mm I.D.) connected to the cold trap. The trap cooling (− 120°C) was started 3 min before the sample was applied. The desorption oven was heated to 170°C for 4 min and and the trap to 230°C (2 min) during the injection. The trap was then immediately cooled to − 120°C again and maintained at this temperature during the experiment. The desorption gas was nitrogen or air with a flow-rate of 5 ml/min during the desorption.
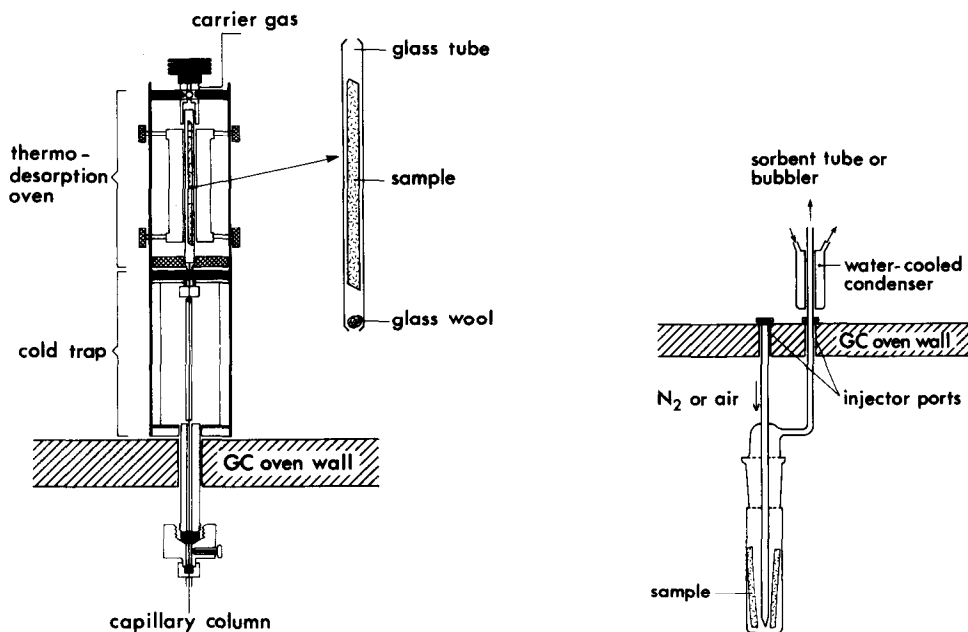
Fig. 1. Chrompack GC injector for thermal desorption. Enlarged view of the glass tube with a PVC sample.

Fig. 2. Equipment for thermal degradation of polymer samples and simultaneous sampling of emitted compounds. A modified glass impinger in a gas chromatograph was supplied with a condenser before sampling.

Otherwise, the flow-rate was 1 ml/min. When air was used, the injector port was plugged during the desorption period and the column was then reinstalled before admitting the carrier gas (nitrogen or helium).

For analysis of aldehydes, hydrogen chloride and less volatile compounds, degradation was performed in an impinger that was modified to fit inside a GC injector for packed columns with two injector ports (Fig. 2). The flask inlet was fitted tightly in one injector port and the outlet passed through the other. The outlet was supplied with a water-cooled metal condenser before it was connected to an adsorbent tube or bubbler. The airflow was 200 ml/min and the oven temperature 170°C.

Sampling on adsorbent and in a bubbler

For the aldehyde analysis, 2-g plastic samples were heated for 25 min. The aldehydes were sampled as their 2,4-dinitrophenylhydrazones; formaldehyde and acetaldehyde on reagent-coated Amberlite XAD-2[27], the other aldehydes in 10 ml reagent solution (250 mg 2,4-dinitrophenylhydrazine in 100 ml 2 M hydrogen chloride) in a bubbler[28]. The compounds were desorbed with 1 ml acetonitrile and analyzed by liquid chromatography (LC). The reagent solution was extracted with 2 × 20 ml diethyl ether, evaporated to dryness and dissolved in 3 ml acetonitrile prior to LC analysis.

For the hydrogen chloride analysis, a 2-g sample was heated for 15 min, collection being performed in silica tubes[29] and analysis by isotachophoresis.

The less volatile compounds, emitted by 500-mg samples heated for 10 min, were collected in Amberlite XAD-2 tubes. Desorption was carried out with 1 ml diethyl ether before GC analysis.

Gas chromatographic equipment

GC analysis was carried out on an Hewlett-Packard Model 5880A gas chromatograph with flame ionization detection (FID) and an injector for thermal desorption. The chromatograph was equiped with a 25 m × 0.20 mm I.D. fused-silica capillary column (Ultra A2 cross-linked 5% phenyl methyl silicone with 0.32-mm film thickness, Hewlett-Packard). Nitrogen was used as the carrier gas with a column flow of 1 ml/min and a detector temperature of 250°C.

In the thermal desorption experiments, the oven temperature was held at 60°C for 3 min and then raised at a rate of 15°/min to 250°C, which was held for 20 min.

In analyzing the less volatile compounds, injection was made in the split mode (2 µl, splitting ratio 1/30). The temperature of the injector was 250°C and that of the detector was 300°C. The column temperature was held at 250°C for 1 min and then raised at a rate of 15°C/min to 300°C, which was held for 10 min.

GC–MS system

The gas chromatograph above was combined with a Finnigan Model 4021 mass spectrometer system. The capillary column was connected to the ion source via a heated copper line (150°C). Helium was used as the carrier gas and the column and other GC parameters were as above. The temperature of the mass spectrometer separator oven and ion source was held at 250°C. Spectra were recorded in the electron impact (EI) mode at 70 eV, with an electron multiplier voltage of 1800 V and a preamplifier setting of 10^{-8}.

Liquid chromatographic equipment

A Waters high-performance liquid chromatographic (HPLC) system with an M-510 pump, a 20-µl loop injector (Rheodyne) and a Radial-Pak A column (100 mm × 5 mm I.D., octadecyl silane, 10-µm particles) was supplied with a Pye Unicam LC3 UV detector (365 nm). The mobile phase was a gradient of acetonitrile–water (from 80:20 to 100% acetonitrile in 12 min) with a flow-rate of 1 ml/min.

Isotachophoretic equipment

The analyses were performed by means of a Shimadzu IP-2A isotachophoretic analyzer.

Reagents

Amberlite XAD-2 sorbent tubes (glass tubes with two sections of 80 and 40 mg; SKC, Lot 289), 2,4-dinitrophenylhydrazine-coated XAD-2 tubes and silica gel tubes (Acid Mist tubes, 400 mg, Supelco, Orbo-53, Lot 492-32) were employed. The following solvents and standards were used: acetonitrile (HPLC grade, Rathburn), diethyl ether (May and Baker), 2,4-dinitrophenylhydrazine (puriss, Fluka), acetaldehyde (puriss, Fluka), cyclohexanone (99%, Aldrich), 2-(2-butoxyethoxy)ethanol (99%, EGA-Chemie), di-*n*-butyl phthalate (99%, Aldrich), diethyl phthalate (99%, Aldrich), di-2-ethylhexyl phthalate (Pfaltz & Bauer), formaldehyde (36.6% in water, Fisher), *n*-hexanal (99%, Aldrich) and *n*-nonanal (97–98%, EGA-Chemie).
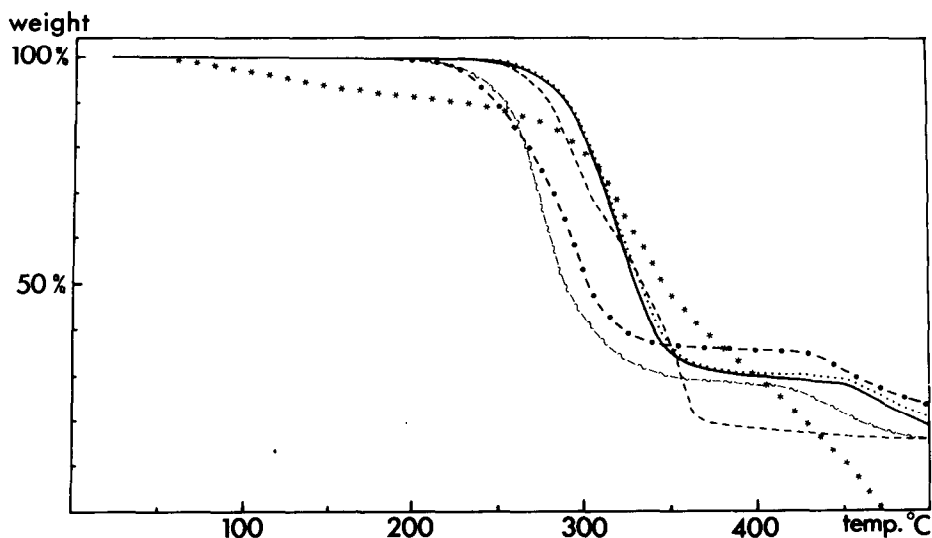
weight

Fig. 3. Thermogravimetric analysis of six PVC samples from the same factory.

RESULTS AND DISCUSSION

PVC samples from three factories, with an high incidence of eye problems among the employees, were used in this study. In the thermogravimetric analysis, the degradation curves from the polymer samples show similar shapes, with drastic degradation above 250°C (Fig. 3). The welding temperature was 120–170°C and weight loss started during this interval. A computer-aided calculation showed weight losses of 0.3–1.5% for 15 of the 17 samples tested in the temperature interval 20–200°C. For the other two samples, the losses were 4 and 8%, respectively.

The results of the thermal degradation of the polymer samples monitored with various analytical techniques are presented in Table I. No attempt has been made to determine the quantity of the compounds emitted. As in earlier reports, the emission of hydrogen chloride has been confirmed. The other products found have not been reported earlier as emission products from PVC at this low temperature (170°C). They are not typical degradation products of pure PVC polymers but probably originate from the various additives. Benzene has not been detected at this low degradation temperature.

The thermal degradation experiments, in combination with GC and GC–MS, were performed at 170°C in an atmosphere of air, nitrogen or helium (Fig. 4). At this temperature the atmosphere used in the degradation experiments did not a effect the main compounds emitted. For GC analysis of high- and middle-volatile compounds, degradation in the GC injector for thermal desorption (Fig. 1) proved to be very suitable. However, low-volatile compounds such as phthalic esters gave bulky chromatogram peaks when this equipment was used. In this case, degradation was carried out in the modified impinger (Fig. 2) in combination with adsorbent sampling. After liquid desorption, the samples were analyzed by GC–MS. This degradation equip-

TABLE I

DEGRADATION PRODUCTS FROM PVC SAMPLES AT 170°C

a, b, c are retention times respectively from thermal desorption GC, GC on Amberlite XAD-2 and HPLC of hydrazones.

Group	Compound	t_R (min)		
		a	b	c
Aliphatic	C_4	2.0		
hydrocarbon	C_8	9.6		
	C_{11}	19.0		
	C_{12}	19.7		
	C_{13}	27.0		
Halogenated hydrocarbon	1,1-Dichloroethylene	1.5		
Aromatic hydrocarbon	Trimethylbenzene	9.5		
Alcohol	1-Nonanol	13.6		
	1-Decanol	16.3		
Alkoxyalcohol	2-(2-Butoxyethoxy)ethanol*	14.2		
Phenol	Phenol	8.4		
Aldehyde	Formaldehyde*			1.7
	Acetaldehyde*			2.0
	Hexanal*	3.9		3.8
	Nonanal*	11.8		6.4
Ketone	Cyclohexanone*	6.1		3.3
Acid	2-Ethylhexanoic acid	13.5		
Ester	Diethyl phthalate*		3.0	
	Di-n-butylphthalate*		4.1	
	Di-2-ethylhexyl phthalate*		7.2	
Hydrogen chloride*				

* A reference compound was used.

ment, supplied with a bubbler, was also used for sampling hydrogen chloride. Isotachophoresis also revealed the emission of hydrogen chloride.

The MS analysis of the various samples was performed by comparing the mass spectra of the most frequently occurring peaks with the 36 000-entry NBS reference library. A spectrum matching index ("fit") threshold higher than 900 of a possible 1000 was the limit for a positive analysis[30]. With this limitation, it was not possible to determine some of the low-volatile compounds. In some cases, reference samples were used to confirm the identity of the compounds. A further confirmation of aldehyde identity was made by degradation of the samples in the modified impinger and, during sampling, conversion of the aldehydes into 2,4-dinitrophenylhydrazones. These derivatives were analyzed by HPLC and by comparing retention times with
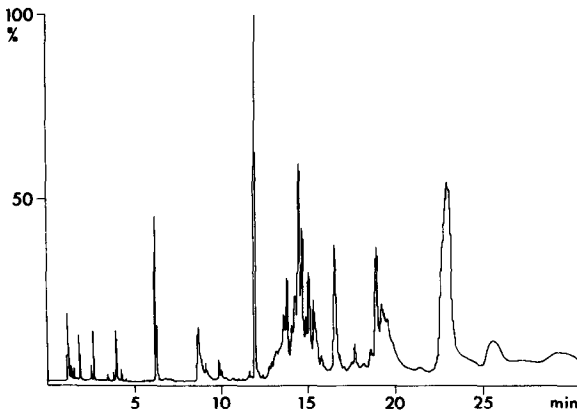
Fig. 4. Reconstructed ion chromatogram from the analysis of a PVC sample with a thermal desorption injector (GC–MS). Degradation was performed at 170°C for 4 s in an helium atmosphere.

the respective reference compounds. Moreover, in this analysis formaldehyde and acetaldehyde were also detected

Sample degradation at temperatures lower than 170°C was also performed. This showed that the emission of the main compounds started at as low as 50°C (Fig. 5). Thus, the emission compounds are the result of degradation of the PVC polymer and its additives as well as evaporation of additives and solvents used in the preparation of the PVC materials.

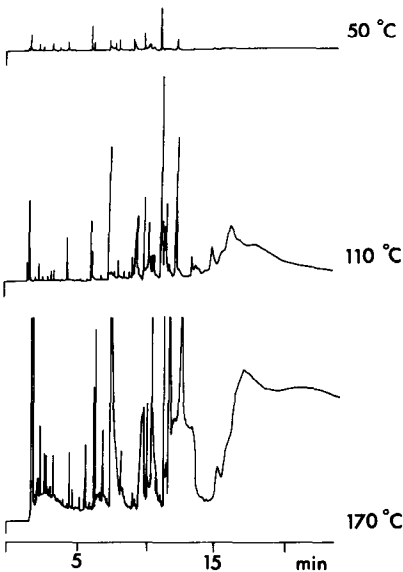The current laboratory investigation has revealed the occurrence of volatile

Fig. 5. Chromatograms from thermal degradation (in a GC injector) of a PVC sample and capillary GC at three different degradation temperatures in a nitrogen atmosphere.

emission compounds, alcohols, aldehydes, a ketone and a phenol and hydrogen chloride, that are known irritants, especially to the eyes[31]. These compounds, as well as the esters of phthalic acid, which affect the nervous system, may contribute to the health problems found in the medical study. Thus, these compounds should be tested for in occupational exposure measurements in electromagnetic welding of PVC. Based on the air levels found, an assessment should be made of whether the the chemical environment is responsible for some of the symptoms reported.

ACKNOWLEDGEMENTS

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