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Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride

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Abstract

Emissions evolved from the pyrolysis and combustion of polyvinyl chloride (PVC) were studied at four different temperatures (500, 700, 850 and 1000 °C) in a horizontal laboratory tubular quartz reactor in order to analyse the influence of both temperature and reaction atmosphere on the final products from thermal and oxidative reactions. It was observed that the CO_2/CO ratio increased with temperature. Methane was the only light hydrocarbon whose yield increased with temperature up to 1000 °C. Benzene was rather stable at high temperatures, but in general, combustion at temperatures above 500 °C was enough to destroy light hydrocarbons. Semivolatile hydrocarbons were collected in XAD-2 resin and more than 160 compounds were detected. Trends on polyaromatic hydrocarbon (PAH) yields showed that most had a maximum at 850 °C in pyrolysis, but naphthalene at 700 °C. Formation of chlorinated aromatics was detected. A detailed analysis of all isomers of chlorobenzenes and chlorophenols was performed. Both of them reached higher total yields in combustion runs, the first ones having a maximum at 700 °C and the latter at 500 °C. Pyrolysis and combustion runs at 850 °C were conducted to study the formation of polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs). There was more than 20-fold increase in total yields from pyrolysis to combustion, and PCDF yields represented in each case about 10 times PCDD yields.

Keywords: PVC; PAHs; Dioxins; Chlorobenzenes; Chlorophenols; Hydrocarbons

1. Introduction

Thermal treatments, both pyrolysis and combustion, are important alternatives to the disposal of plastic waste in landfills. Polyvinyl chloride (PVC) is currently the third most consumed plastic in Western Europe, accounting for 5792 million tonnes in 2002, only surpassed by polyethylene (PE) and polypropylene (PP) [1]. Some of the numerous applications of PVC are pipes, window frames, cables, flooring, packaging and car under-floor protection.

According to a report produced for the European Commission Environment Directorate to assess the influence of PVC on the quantity and hazardousness of flue gas residues from incineration [2], about 15% of total PVC waste is incinerated, and most is landfilled; end of life PVC, when disposed by incineration, mainly involves municipal solid waste (MSW) incinerators; the influence of PVC on MSW composition is mainly related to the chlorine content of the waste sent to incineration; PVC is responsible for 38–66% of the chlorine content in MSW (total Cl in MSW containing PVC is 5.3–7 kg Cl/tonne MSW); PVC also influences the heavy metal content in the MSW (10% of cadmium in MSW is attributable to PVC); the presence of PVC in MSW has a direct effect on the quantity of chlorine in the raw gas and therefore on the corresponding effluents generated by the different gas treatment systems.

Many studies have justified concern about compounds evolved when PVC is burnt. According to some authors [3–5], PVC thermal degradation consists of two main steps: hydrogen chloride is firstly released and then, aromatic hydrocarbons are subsequently formed from cyclization reactions of the remaining polyene chain and also a residual char is generated. The presence of oxygen in the atmosphere instead of an inert gas allows the char to volatilize completely.

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Due to the high temperatures, the presence of oxygen and the chlorine content of the polymer, combustion of PVC produces different kinds of compounds, some of them with a high level of toxicity. Benzene, which is a carcinogenic compound, is one of the main products resulting from the thermal degradation of PVC [3–5]. Other substituted monoaromatic and polyaromatic hydrocarbons (PAHs) are reported to appear in pyrolysis and combustion of PVC at different temperature ranges [5–13]. Some PAHs are classified in EPA's National Toxic Inventory as hazardous air pollutants (HAP), and even, seven of them are thought to be probable human carcinogenic compounds [14].

Apart from hydrogen chloride, chlorinated aromatic compounds are evolved during pyrolysis or combustion of PVC, such as light chlorinated aliphatic hydrocarbons [5], chlorinated PAHs [15], chlorobenzenes (ClBzs) [6,16,13], chlorophenols (ClPhs) [13], chlorobiphenyls (PCBs) [13,17], polychlorodibenzo-*p*-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) [11,13,17–22].

Formation of chlorobenzenes may occur by different ways, according to Ballschmiter et al. [23]: (i) direct scission of non-totally dehydrochlorinated PVC chain, (ii) chlorination of benzene or lower chlorinated benzenes by Cl_2, (iii) cyclization of chloro-C_1/C_2 units and (iv) pyrolytic isomerization of the chlorobenzenes formed. Lattimer and Kroenke [3] reported that direct scission of PVC chains to form chlorinated-containing compounds is a very minor decomposition pathway because an inappreciable amount of chlorine remains in the polyene after dehydrochlorination. However, McNeill et al. [19] suggested the possibility of a small-scale readdition of HCl or Cl_2 to polyenes after dehydrochlorination in the vicinity of head-to-head defects already containing chlorine atoms to create zones of high Cl concentration that can eventually lead to chlorinated aromatics such as PCDD/PCDFs.

Chlorobenzenes can form PCBs in pyrolytic conditions. Biphenyls can then generate PCDFs by oxidation with the loss of one or two chlorine atoms or two H atoms from the *ortho* position [24]. Chlorophenols can be formed from chlorobenzenes in the presence of oxygen via reaction of a chlorophenyl radical with an ·OH radical. [23]. ClPhs can subsequently react to form both PCDDs and PCDFs [25,26].

PCDD/Fs are one of the most toxic chemicals known. They have been demonstrated to occur ubiquitously in the environment and they appear as by-products of chemical processes such as the manufacture of herbicides, the smelting of copper and scrap metal and incineration processes. Heterogeneous formation of PCDD/Fs on the surface of fly ash particles is generally accepted to be much more important than homogeneous formation in gas-phase. Two formation pathways relevant to incinerator conditions have been identified to generate PCDD/Fs on heterogeneous formation: (i) reactions between chlorinated aromatic precursors previously formed in gas-phase and (ii) de novo synthesis, in which the carbon present in the solid phase material of fly ashes reacts in the presence of chlorine, oxygen and hydrogen to give chlorinated aromatic compounds, both PCDD/Fs or precursors [27–29]. Reactions are catalysed by metals, such as Cu, and principally occur in the post-combustion zone of incinerators where temperatures ranging 250–450 °C favour formation [30].

There are many papers in which PCDD/F formation from combustion of PVC alone or the influence of PVC as a chlorine source in MSW incinerators have been studied, as in [31–33]. Results obtained are sometimes difficult to compare because of the variety of operating conditions and systems used. But there is not much research on concurrent emission analysis of PAHs, ClBzs, ClPhs and PCDD/Fs from the pyrolysis and combustion of PVC at different temperatures [13]. The aim of this work is to provide a comprehensive laboratory study of the pyrolysis and combustion products of pure PVC at different temperatures, mainly focusing on a detailed analysis of the great amount of PAHs generated by pyrosynthesis reactions and the chlorine aromatic compounds evolved. Some hypotheses are discussed concerning the relationship between PCDD/Fs and ClBzs and ClPhs precursors. Since the PVC used in this work, hardly, has no inorganic content and forms no ashes on combustion, the catalysed formation of PCDD/Fs by metals has been assumed not to occur.

2. Experimental

2.1. Material

Experiments were carried out with white powdery PVC resin Etinox-450 free of additives obtained by emulsion polymerization, which is commonly used in low viscosity plastisols. It has a medium molecular weight (104,000 and 40,000 for M_w and M_n, respectively) and a very small particle size, ranging between 1.4 and 24.4 μm. Table 1 shows the chemical composition of PVC analyzed by two complementary techniques: elemental analysis with a Perkin-Elmer 2400 CHN (for C, H, N and S) and X-ray fluorescence with an automatic sequential spectrometer model PW1480 (semiquantitative analysis for elements with an atomic weight higher than that of Mg).

Table 1
Chemical composition of PVC resin

Element	In wt.%
Cl	55.2
C	38.4
H	4.80
S	1.40
Na	0.12
O	0.076
Zn	0.034
K	0.018
Ca	0.017
Si	0.0095
Al	0.0057