Decomposition of two types of electric wires considering the effect of the metal in the production of pollutants

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HIGHLIGHTS

► Haloge-free and PVC wires are studied at different decomposition conditions.
► Runs are performed in the presence and in the absence of the metal conductor.
► Analysis of the pollutants emitted is done.
► Important differences were found at the different experimental conditions.
► Metal enhances chlorinated compounds emission while decreases aromatics.

ARTICLE INFO

ABSTRACT

Combustion runs at 700 °C in a horizontal laboratory furnace were carried out on two different electric wires (PVC and halogen-free wire). Tests were performed in the presence and in the absence of the metal conductor of the wires. The analyses of the polycyclic aromatic hydrocarbons (PAHs), chlorobenzenes (CBzs), chlorophenols (CPhs), mono- to octa-chlorodibenzo-p-dioxin and dibenzofurans (PCDD/Fs), and dioxin-like PCBs are shown. Regarding semivolatile compounds, PAHs production decreases in the presence of metal, while a higher amount of chlorinated compounds are emitted. Respect to the PCDD/Fs, the PVC wire in the presence of metal presents the highest emission, with a much more emission of furans than dioxins. The maximum emission is with 2 or 3 chlorine atom PCDD/Fs. PCBs emission correlates with PCDD/F production and represents 3–4% of total toxicity, determined by using WHO2005 factors.

1. Introduction

The wire and cable industry manufactures a wide range of products that support a multitude of applications. Some of the major markets are communication cables, power and cable wire, automotive wiring, control and signal cables, and building wiring. Generally wires differ in conducting and isolation materials. The classic conductor material has been copper but aluminum is also used frequently today.

Many wire insulation and covering compositions contain materials, such as lead, halogenated compounds, and other compounds, that impart electrical insulation and fire performance properties. Specifically, fire retardants are used to avoid the propagation of fire. One of the most frequently used types of fire retardant, Halogenated Flame Retardants (HFRs), have been proven to be a hazard

to human life and environment, which has led to regulations on their use with the ultimate goal of removing from the market.

Recently, The European Parliament has considerate to review the Restriction of Hazardous Substances (RoHS) Directive to include compounds not previously covered by the legislation such as PVC and some HFRs in electronic equipment. The former directive is closely related to the directive on Waste Electrical and Electronic Equipment also known as WEEE directive (2003). WEEE directive promotes the reuse, recycling, and recovery of these wastes as well as the collection of electrical and electronic wastes as a separate waste stream, which enhances the prospects for economic recycling. In this sense, End-Of-Life (EOL) communications and low-voltage cables are valuable because these consist of approximately 50% copper by weight. The high price of copper ensures that an estimated 95% of EOL cable and wire is recycled.

In traditional metal recycling, physical techniques are used to separate metals and plastics. The result of this operation is a waste formed by a single mixed fraction of different polymers (PVC, PE, LLDPE, HDPE, PP, etc.). Until now plastic fractions of EOL cables

have been landfilled because it was considered as a waste product with low value; however, today it is known that this waste has a great value and it is suitable for recycling, by material, chemical or energy recovery. In all cases previous polymer separation is advisable. Material recovery is an attractive option for PVC; whereas either material or energy recovery are equally attractive for polyolefin waste (Hagstrom et al., 2006).

Thermal treatment of PVC wastes it is a problematic way of recovery. Besides hydrogen chloride, chlorinated aromatic compounds are evolved during pyrolysis or combustion of PVC, such as chlorobenzenes (CBzs), chlorophenols (CPhs), chlorobiphenyls (PCBs) and, polychlorodibenzo-p-dioxins and polychlorodibenzofurans (PCDD/Fs) (Aracil et al., 2005). This could be especially alarming when the process is uncontrolled. Illegal recycling, open burning at landfills or accidental fires involves a serious damage to health and to environment. Moreover, when copper is present during combustion process, a catalytic formation of chlorinated compounds and dioxins, both in gas and solid phases, from phenols have been observed (Stanmore, 2004; Ryu et al., 2005; Ryu, 2008; Altarawneh et al., 2009).

Behavior of cables and wires considering their heat release has been previously studied (Hirschler, 1994), showing that cables with excellent fire performance can be made by using a variety of materials, so that it would seem to follow that it is important to specify fire performance and leave material choice to manufacturers.

There is not extensive information of the emissions from thermal degradation processes of electric wires in oxidative atmosphere, and less in the presence of conductive metal (Chaala et al., 1997; Thibert and Gautier, 1999; Gullett et al., 2007; Kantarelis et al., 2009). The present work aims to extend the information in this issue providing the basis for the analysis of environment impact and development of new products, taking special interest on the effect of the metal on the decomposition and the previsible differences between PVC and halogen-free wires.

2. Material and methods

2.1. Electrical wires

Supplied by General Cable, Co., two kinds of commercial cables have been employed in this work. The first one is a common wire (designed as P), with PVC cover and reticulated polyethylene as insulation. The second one is a special fire-resistant and halogen-free wire (designed as H). Fig. 1 shows the scheme of electrical wire, the composition of the two materials used and the weight percentage of each part. As we can see in Fig. 1, the material used in the cover (or jacket) of the halogen free wire is a mixture of polyethylene, a thermoplastic elastomer, and aluminum trihydroxide (PE-TPE-ATH). Elemental analysis of the wires and some more details can be found in a previous work (Conesa et al., 2010). To ensure the homogeneity, the samples were crushed (1–3 mm) using a laboratory blender by DINKO, 8010 model (DINKO, Barcelona, Spain).

In order to study the effect of the presence of copper during the decomposition, for each kind of wire two different samples were prepared: one consisting of the plastic parts, named P1 + P2 and

H1 + H2, and the other one representing the entire wire named P1 + P2 + P3 and H1 + H2 + H3, where P3 and H3 refers to the metal (see Fig. 1).

2.2. Experimental system

Experiments were performed in a moving tubular reactor which consists in a quartz tube (10 mm wide), were the material is introduced uniformly along. This tube is introduced in a horizontal furnace, maintained at the desired temperature, at constant velocity using a horizontal actuator. Fig. SM-1 (Supplementary information) shows a scheme of the experimental system. More details of the equipment can be found elsewhere (Barneto et al., 2009; Conesa et al., 2011). In all runs the temperature of the oven was 700 °C. Synthetic air was introduced parallel to the sample, with gas flowing at 300 mL min^{-1} (measured at 1 atm and 20 °C). All runs were performed under fuel-rich atmosphere, with a oxygen ratio of 0.5 (ratio between actual and stoichiometric oxygen (Conesa et al., 2007, 2009)).
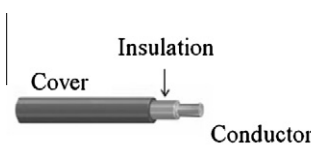
The outlet gas stream was sampled to analyze semivolatile compounds such as PAHs, CPhs and CBzs, PCDD/Fs, and dioxin-like PCBs. Emitted gases were collected using a poliaromatic Amberlite® XAD-2 resin as sorbent (Supelco, Bellefonte, USA) placed at the outlet of the furnace during the whole experiment. Before the decomposition runs, a control containing no sample was carried out using the same experimental conditions (blank).

Amberlite® XAD-2 resin was extracted in toluene by Accelerated Solvent Extraction (ASE-100, Dionex-Thermo Fisher Scientific Inc., California, USA) and the extracted solution was divided as follows: approximately 30 wt.% was employed to analyze PAHs (US-EPA 8270D method), CPhs and CBzs; the rest (over 70 wt.%) was used for the analysis of PCDD/Fs and "dioxin-like" PCBs (EPA 1613 and 1668A methods).

PAHs, CPhs and CBzs were analyzed by GC–MS in SIM mode (Agilent GC 6890N/Agilent MS 5973N, Agilent Technologies, USA) using the isotope dilution method. CPhs and CBzs were also specifically analyzed in SIM mode with mixture standards containing all isomers, following an analogous procedure to that of the 16 PAHs. Additionally, the identification of each isomer was confirmed by checking the ratio between the areas of the primary and the secondary ions, since they are known due to presence of ^{35}Cl and ^{37}Cl.

For the analysis of PCDD/Fs and "dioxin-like" PCBs, cleanup was performed using the Power Prep system (FMS, Inc., Boston, MA) with three different columns: silica, alumina, and activated carbon (FMS, Inc., Boston, MA). The analysis was completed by HRGC/HRMS. For HRGC, an Agilent HP5890 gas chromatograph equipped with programmable temperature vaporization (PTV) inlet with a septumless head was used. For HRMS, a Micromass Autospec UlitmaNT mass spectrometer (Micromass, Waters, UK) with a positive electron impact (EI+) source was employed. All congeners of dioxins and furans were determined, from mono- to octachlorinated species.

The standards used for the analysis of 16 PAH were supplied by Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) and the standards of CPhs, CBzs, PCDD/Fs and "dioxin-like" PCBs were obtained from Wellington Laboratories (Ontario, Canada). All the solvents for organic trace analysis were purchased form Merck (Germany).

Part	PVC cable (P) wt. %	Halogen free cable (H) wt. %
1 (Cover)	P1: PVC, 41 %	H1: Thermoplastic polyolefin (PE-TPE-ATH), 36 %
2 (Insulation)	P2: Reticulated polyethylene, 9 %	H2: Silicone rubber, 20 %
3 (Conductor)	P3: Copper, 50 %	H3: Copper, 44 %

Fig. 1. Scheme of the electrical cables, their composition (supplied by manufacturer) and % weight of each part.