



Effect of marine ambient in the production of pollutants from the pyrolysis and combustion of a mixture of plastic materials

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ABSTRACT

A mixture of polyethylene (PE), polyethylene-terephthalate (PET), polypropylene (PP) and Nylon was submerged in marine water during 12 months. The chlorine content of these plastics was measured through the passing time. Thermobalance was used to look for differences in the thermal decomposition of the plastics during in that time interval. Degradation of PET, PP and Nylon produced changes in the weight loss curve, but behaviour of PE is confusing. Pyrolysis and combustion at 850 °C was finally performed to get knowledge of the possible differences in the emission of main gases, volatiles and semivolatiles including polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes (ClBzs), polychlorinated phenols (ClPhs), polybrominated phenols (BrPhs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Results show that the emission of chlorinated species is somewhat not affected by the chlorine content of the plastics mix. The production of PCBs and PCDD/Fs was very low, under 4 pg WHO-TEQ/g.

1. Introduction

The presence of marine debris is a cause for concern due to several reasons. These debris have been identified as harmful to organisms and to human health (Rochman et al., 2013); also these debris have the potential to increase the transport of organic and inorganic contaminants (Avio et al., 2017; Gaylor et al., 2012; Iñiguez et al., 2017; Rochman et al., 2013).

The materials most commonly found in marine debris are glass, metal, paper and plastic (Cózar et al., 2014; OSPAR, 2007). The most commonly used plastics are polyethylene, polypropylene and polyethylene terephthalate, therefore, they are the most frequently found in the marine environment too (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Iñiguez et al., 2016; Ruiz-Orejón et al., 2016).

The annual input of plastics in the oceans increases every year. It is estimated that in 2015 around 9.1 million tons were accumulated (Jambeck et al., 2015).

One possible alternative for waste disposal is thermal decomposition through pyrolysis or combustion. These processes provide a reduction in waste volume and involve profitable energetic and/or chemical products. Nevertheless, the possible emission of pollutants during non-controlled plastic thermal degradation may create a serious hazard for human health and for the environment. In this way, it is important to control and reduce the emission of pollutants, and be aware of the chemical mechanisms involved in the thermal decomposition.

Different studies attempt to clarify the effects of chlorine content in waste on the formation mechanisms of polychlorinated pollutants, especially dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) (Gullett et al., 2000; Sablier et al., 2010; Wang et al., 2003; Wyrzykowska et al., 2009). The study done in 2003 by Wang et al. showed differences in the emission when the chlorine level in the waste is higher than 0.8–1.1%. If the level is lower than this threshold level, the formation of PCDDs dominates, probably because the chlorine is used to chlorinate the non-substituted phenol to produce chlorophenols, which are important precursors for PCDDs. In other cases, the PCDFs increase faster. Other authors (Gullett et al., 2000) pointed out a poor correlation between total chlorine in waste streams and formation of polychlorinated dibenzodioxin and polychlorinated dibenzofuran (PCDD/F) during waste combustion, because the active chlorine (Cl) species are strongly dependent upon combustion conditions. Nevertheless, Yasuhara et al. (Yasuhara et al., 2003) showed that the presence of NaCl during the combustion of newspapers increased more than 70 times the emission of PCDD/Fs. Accordingly, Ma et al. (Ma et al., 2010) revealed that the production of chlorinated compounds is affected both by organic and inorganic chlorine.

Regarding the environmental impacts, there are many studies that investigate the pollution associated with plastics combustion and/or pyrolysis (Devaraj et al., 2015; Font et al., 2011; Iñiguez et al., 2017; Poerschmann et al., 2015). However, there is no study investigating the effect of contacting marine water with plastic materials in the thermal

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decomposition of the wastes. Following this line, the aim of the present work is to study the changes that suffer plastic materials in contact with marine water, and the differences in the emission of pollutants comparing the pyrolysis and the combustion of materials before and after having passed one year in contact with marine water. Also, the chlorine content and the thermal behaviour are monitored during this time.

2. Materials and methods

2.1. Materials

Four main plastics components usually found in marine litter were studied for thermal decomposition. In this way, PE, PP, PET and Nylon were studied. The plastic components were submerged in marine water, in a 100 L drum, during a total period of one year. During this time, different samples were taken to measure the chemical composition and thermal behavior. Specifically, samples were taken at 2, 7 and 12 months, and were compared to the plastics before the treatment.

2.2. Determination of ions and NCV

The Net Calorific Value (NCV) was determined using a calorimetric bomb AC-350 Leco Instruments, and the inorganic anions content of the sample was measured by ionic chromatography following EPA methods 5050 and 9056 (US EPA, 1994a, 2007b).

2.3. TG runs

Runs for the TG analysis were carried out on a Mettler Toledo TGA/SDTA851e/SF/1100 Thermal Gravimetric Analyzer. The decomposition temperatures were measured under dynamic conditions in a mixture nitrogen:oxygen = 4:1 (20% oxygen, simulating air composition) with a total flow rate of 100 mL min⁻¹. Dynamic experiments were carried out at 20 K min⁻¹, from room temperature up to 1173 K. For each run, 4 ± 0.3 mg of sample were used.

2.4. Pyrolysis and combustion runs

The emissions from the thermal decomposition of marine plastic were studied comparing the decomposition before and after having the plastic submerged in the sea water. In this sense, a mixture of the four plastics was prepared in equal proportions, since it was representative of marine litter (Iñiguez et al., 2017). The pyrolysis and the combustion of this mixture were compared before and after passing one year in the marine water drum. During the rest of article, these samples will be named “MIX_original” and “MIX_12months”.

Combustion and pyrolysis runs of MIX_original and MIX_12months were carried out in a moving tubular reactor, which consists in a quartz tube (10 mm internal diameter) where the material was introduced in three quartz boats (70 mm long each) along the tube. Once the process programmed temperature was reached (850 °C in all runs) inside the horizontal furnace and with a constant flow of gas passing through, the boats were introduced in the furnace at constant speed using a horizontal actuator. This experimental system has been previously described in detail (Conesa et al., 2013). Synthetic air (combustion runs) or nitrogen (pyrolysis runs) was introduced in parallel to the sample, with a constant flow of 500 mL min⁻¹ (measured at 1 atm and 20 °C). The sample mass in each run was around 0.5 g. Before the decomposition runs, a control containing no sample was carried out using the same experimental conditions (blank). For the combustion runs, an oxygen ratio equal to 0.5 was selected, defined as the fraction between the actual and the stoichiometric air flow rate necessary for a complete combustion (Conesa et al., 2009).

The reproducibility of this type of experiments has been tackled in our laboratory. A previous study (Garrido et al., 2016) confirmed a good reproducibility for all compounds analyzed in the emissions from

combustion and pyrolysis runs of wastes using a similar laboratory scale horizontal reactor. The obtained standard deviations were small in comparison with the average values; only for some small average values, the standard deviations were somewhat greater, but with relative standard deviations around 5%.

The outlet gas stream of each run was sampled to analyze the following pollutants:

- Gases and volatile compounds were collected using Tedlar® bags (Restek, USA). CO₂ and CO were analyzed by gas chromatography with thermal conductivity detector (GC-TCD) (Agilent 7820). Light hydrocarbons were analyzed by gas chromatography with flame ionization detector (GC-FID) (Shimadzu GC-17A).
- PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs were collected in a polyaromatic Amberlite® XAD-2 resin (Supelco, Bellefonte, USA) placed at the exit of the furnace during the whole experiment. The Tedlar® bag was located after the resin.

Internal standards were employed to calculate the concentration of PAHs, ClPhs, ClBzs, BrPhs and PCDD/Fs in the samples. Dr. Ehrenstorfer-Schäfers (Augsburg, Germany) supplied the deuterated standards used for the analysis of the 16 priority PAHs and Wellington Laboratories (Ontario, Canada) supplied the ¹³C-labelled standards for ClPhs, ClBzs, BrPhs and PCDD/Fs. All the internal standards were added to the resin.

Next, the resin was successively extracted with a mixture of dichloromethane/acetone (1:1 vol) and toluene by Accelerated Solvent Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA) following the US EPA method 3545A (US EPA, 2000). The extract was divided into two fractions: approximately 30 wt% was used for the analysis of PAHs, ClPhs, ClBzs and BrPhs (US EPA, 2007a) and the remaining 70 wt% was employed for the analysis of PCDD/Fs (US EPA, 1994b).

PAHs, ClPhs, ClBzs and BrPhs were analyzed by GC–MS (Agilent GC 6890N/Agilent MS 5976N, Agilent Technologies, USA) following the US EPA method 8270D (US EPA, 2007a) as reference. ClBzs, ClPhs and BrPhs were analyzed in the SIR mode and the identification of each isomer was performed comparing the primary/secondary ion area ratio with that obtained in the calibration with the labelled compounds. For the analysis of PCBs and PCDD/Fs, a cleanup step was performed using the Power Prep automated system (FMS, Inc., Boston, MA) with three different columns: multilayer silica, basic alumina and activated carbon. The purified extract was analyzed by HRGC/HRMS. Regarding the analyses of PCBs and PCDD/Fs, the recoveries obtained for the labelled standards were within the ranges established by the reference standards (US EPA, 1994b).

3. Results and discussion

3.1. Inorganic anions analysis and net calorific value (NCV)

Fig. 1 shows the main results of the characterization of the plastic materials picked up at the different samplings. The main inorganic anions content and the NCV were measured in samples taken at 0 (original), 2, 7 and 12 months after introducing the plastics in the marine water.

As can be seen in the figure, plastics are quickly impregnated with the ions present in the water. In this sense, chloride is mainly incorporated to the plastics, especially PE that increases very quickly its chlorine content. Along time, the chloride content continues increasing, except in the case of PE that shows a high content from very early stages.

Respecting to the NCV (represented as “x” in the graph), is more or less constant for each sample, without being affected by the passage of time. As expected, NCV of PP and PE are much higher than those of PET or Nylon.

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