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# Mechanochemical pre-treatment for viable recycling of plastic waste containing haloorganics

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## ABSTRACT

Chemical recycling technologies are the most promising for a waste-to-energy/material recovery of plastic waste. However, 30% of such waste cannot be treated in this way due to the presence of halogenated organic compounds, which are often utilized as flame retardants. In fact, high quantities of hydrogen halides and dioxin would form. In order to enabling such huge amount of plastic waste as viable feedstock for recycling, an investigation on mechanochemical pre-treatment by high energy ball milling is carried out on polypropylene containing decabromodiphenyl ether. Results demonstrate that co-milling with zero valent iron and quartz sand ensures complete debromination and mineralization of the flame retardant. Furthermore, a comparative experiment demonstrates that the mechanochemical debromination kinetics is roughly proportional to the polymer-to-haloorganics mass ratio.

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## 1. Introduction

The technological improvement of plastic materials has brought to a significant increase in their use for production of a large number of commercial and industrial products. In 2014, the yearly global production of plastics was 311 Mt, with an increase of near 4% respect to the previous year (Worldwatch Institute, 2015). Consequently, the generation of plastic waste (PW) is growing up with similar rates. Currently, landfilling and incineration for energy recovery are the two major ways to dispose PW. But, these are unsustainable solutions because they do not allow material recovery and may be secondary sources of pollution (e.g., in leachate or flue gas) (Lee et al., 2014; Morin et al., 2015). It is noteworthy that 4% of petroleum world production is utilized for plastic (Worldwatch Institute, 2015), so PW recovery is relevant to reduce depletion of such limited resource. On contrary, re-use of plastic objects, mechanical recycling (by manufacture of other products from PW with homogeneous composition), chemical recycling by thermal treatments (e.g. pyrolysis and gasification to generate pyrolytic oil and syngas, respectively), are preferred ways. A more environmentally friendly way to treat such waste might be biolog-

ical treatment by recently discovered bacteria (Yoshida et al., 2016).

Chemical recycling (called also tertiary treatment) is the most promising way to beneficially utilize PW resource. Mechanical recycling necessitates of homogeneous feedstock, so it can be realized only with a specific and quite limited PW fraction (Al-Salem et al., 2009; Wu and Williams, 2010). Differently, pyrolysis and gasification allow the production of liquid (i.e. a mixture of oily more or less aromatic compounds) and gaseous (i.e. syngas) products, respectively, and can be applied to treat any mixture of PW (Al-Salem et al., 2009). If catalysts are employed in such processes, selectivity can be greatly enhanced to generate specific products such as methane (Onwudili and Williams, 2016) or hydrogen and carbon nanotubes (Nahil et al., 2015). Liquid and gaseous products of chemical recycling processes can be used either as energy source or as precursors for industrial processes. Hydrogen production is actually very interesting owing to its potential use as clean fuel with high calorific value (Bicer and Dincer, 2017). Opportunely blended PW can give origin to a pyrolytic oil with a chemical composition similar to diesel, thus it can be used as fuel for compression ignition engines (Mohanraj et al., 2017). Also, pyrolytic oil and syngas can be used to regenerate monomers (Ray and Thorpe, 2007).

Unfortunately, not all PW are suitable for chemical recycling. Plastics that are utilized for electronic devices or other special uses always contain significant amounts (near 15%w/w) of flame retar-

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dants. Such waste is estimated to be the 30% of the total amount of manufactured plastics (Bientinesi and Petarca, 2009). In general, flame retardants employed in plastics are halogenated organic compounds, which are soluble in plastics and do not alter their physicochemical properties and aspect. Their presence is a relevant issue for a viable chemical recycling. Firstly, during thermal treatment, high amounts of hydrogen halide gas is produced (Caballero et al., 2016; Shen et al., 2016), causing elevated risk for workers and damage to facility structure. Secondly, dioxin and dioxin-like compounds can be formed due to high temperature and presence of halogens, carbonaceous matter, and dioxin formation catalysts (Grause et al., 2011; Kawamoto and Miyata, 2015; Yang et al., 2013). Indeed, high content of haloorganics has been found in pyrolytic oil, as well as high concentration of hydrogen halides are always produced during gasification or pyrolysis of PW.

Brominated flame retardants in plastics deserve particular attention. They possess the higher compatibility with polymers and excellent flame retardancy, so they are largely present in plastics. But, in the last decades proofs for toxicity, persistence, and bioaccumulation of such compounds have been accumulating (Manzetti et al., 2014). These characteristics are typical of a class of pollutants, named persistent organic pollutants (POPs), that are recognized to be harmful to human health and the environment. In 2004, a global treaty, the Stockholm Convention, was signed to prevent release of POPs in the environment. Currently, several brominated flame retardants, e.g. hexabromocyclododecane and polybrominated diphenyl ethers (included the decabromo-congener), are listed as POPs, and thus are banned from production and use. As a consequence, polymers containing these brominated flame retardants cannot be commercialized and need adequate disposal, that is, destruction to a safe form (i.e. mineralization). Hence, debromination of PW before chemical recycling is highly required to avert their release into the environment of the formation of unintentional POPs, i.e. brominated dioxins (Shen et al., 2016).

In the last twenty years, the mechanochemical (MC) destruction has been demonstrated to be an effective methodology to mineralize halogenated organic pollutants (Cagnetta et al., 2016d). Chemical reactions take place thanks to the mechanical energy provided by special milling devices such as high energy ball mills (Baláž et al., 2013, 2014; Boldyrev, 2006). In this way, the haloorganic molecules, in presence of a co-milling reagent, are transformed into amorphous carbon and halides. Such technology has been found effective to destroy chlorinated (Birke et al., 2010; Wang et al., 2017; Yu et al., 2013; Zhang et al., 2001), brominated (Cagnetta et al., 2016c; Zhang et al., 2014, 2002), and fluorinated compounds (Cagnetta et al., 2017b; Yan et al., 2015; Zhang et al., 2016) at room temperature and in relatively rapid manner (few hour treatment). Very recently, it was demonstrated that possible formation of dioxins during the treatment, can be averted by choosing adequately long time of treatment (Cagnetta et al., 2016a; Chen et al., 2017b). Despite the promising results, MC methods have been rarely investigated as a possible pre-treatment for dehalogenation of PW. Grause et al. (2015) realized the complete debromination of decabromodiphenyl ethane (DecaBDE) in polystyrene by 24 h wet milling with a stirred ball mill. NaOH in ethylene glycol was utilized as dehalogenating reagent, at relatively high temperature (150–190 °C). The strong reagent, the high temperature, and long treatment highlight the poor reactivity of brominated compounds in polymer matrices. Yet, if adequate milling devices, operating conditions, and effective co-milling reagents are chosen, it is possible to realize the debromination in a more efficient way, also by a solvent-free process. The present study demonstrates that polypropylene (PP) containing DecaBDE can be debrominated by dry ball milling with cheap and largely available solid reagents (i.e. Fe and SiO<sub>2</sub>). This is

a further step forward in understanding the MC destruction of halogenated pollutants in waste materials, respect to the majority of previous studies that were dedicated to pure compound destruction.

## 2. Materials and methods

### 2.1. Materials

Commercially available polypropylene pellets (with a diameter of few millimeters) with DecaBDE as flame retardant were purchased from Jiangsu Jingliang Technology Ltd (China), while pure DecaBDE was obtained from J&K Scientific Ltd (China). PP was analyzed by X-ray Fluorescence (XRF) to identify the bromine content. Iron powder (Fe, 98% purity, ~300 μm average particle size), calcium hydroxide (Ca(OH)<sub>2</sub>, 99% purity), and quartz sand (SiO<sub>2</sub>, 98% purity, ~700 μm average particle size) were provided by Wako Pure Chemical Industries Ltd. Calcium oxide (CaO) was prepared in laboratory by heating Ca(OH)<sub>2</sub> at 1000 °C for 2 h, obtaining a powder with ~80 μm average particle size.

### 2.2. Milling experiments

A planetary ball mill (Pulverisette-7, Fritsch, Germany) was used for MC treatment with two zirconia jars (each of 45 cm<sup>3</sup> volume) in which 7 zirconia balls (Ø15 mm, total weight 70 g) were placed. 0.5 g quartz sands with 1.5 g iron or CaO (Fe-SiO<sub>2</sub> or CaO-SiO<sub>2</sub>) were mixed with 0.5 g PP and put into the mill jars. Rotational speed of the machine disk was set to 700 rpm for 15 min intervals, after which there was a 15 min rest period for cooling. After milling, samples were collected and then preserved in a hermetic and dry apparatus for further analysis. A portion (50 mg) of each ground samples was dissolved in deionized water by 30 min ultrasonic treatment. The solution was firstly filtered by 0.45 μm polyether sulfone (PES) filter and then analyzed by inductively coupled plasma (ICP) for bromide quantification. In order to classify the structural changes of the solids, milled samples were also analyzed by Fourier transform infrared (FTIR) spectrometry and microscopic confocal Raman spectrometry. Thermo-gravimetric analysis (TGA) was also performed using a TG/DTA analyzer.

Pure DecaBDE was also co-milled, using the same reagents and amounts used for the test with PP, in a planetary ball mill (QM-3SP2, Nanjing University Instrument Co., China), at 275 rpm rotation speed with a ball-to-powder ratio of 56. DecaBDE was extracted from milled samples by hexane:acetone 1:1 solvent and quantified by GC-MS. The detailed procedure was already described elsewhere (Cagnetta et al., 2016c).

## 3. Results and discussion

### 3.1. Debromination of PP by ball milling

Before experiments, the PP samples were analyzed by X-ray Fluorescence (XRF) to identify the bromine content. The average bromine content resulted to be 12.8%w/w and the calculated corresponding decabDE fraction was 15.4%w/w.

The MC debromination of PP was performed using Fe-SiO<sub>2</sub> and CaO-SiO<sub>2</sub> by high energy milling for various hours, during which soluble bromides were determined. Bromide recovery in Fig. 1 is expressed as ratio of soluble bromides to initial bromine content (determined by XRF). With the milling on going, soluble bromides increased rapidly in the first 2 h. Fe-SiO<sub>2</sub> shows a quicker debromination compared to CaO-SiO<sub>2</sub> because of the low reduction potential of Fe, which donates electrons to decabDE and facilitates the debromination/degradation of the latter. In detail, Fe-SiO<sub>2</sub> allows

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