



# 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.

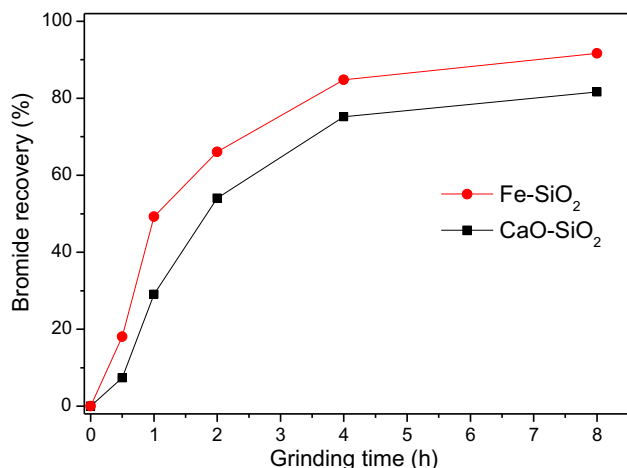
Pure DecaBDE was also co-milled, using the same reagents and amounts used for the test with PP, in a planetary ball mill (QM-3SP2, Nanjing University Instrument Co., China), at 275 rpm rotation speed with a ball-to-powder ratio of 56. DecaBDE was extracted from milled samples by hexane:acetone 1:1 solvent 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



**Fig. 1.** Bromide recovery respect to their maximum amount during milling test with the two co-milling mixtures.

bromide recovery of nearly 90% after 8 h milling, while the recovery was only 80% when using CaO-SiO<sub>2</sub>. Such result is consistent with our previous experiments, where faster degradation of pure decabDE was achieved with iron-based co-milling reagent, in comparison with sole CaO (Zhang et al., 2012). Moreover, it is demonstrated that addition of SiO<sub>2</sub> improves millability of Fe, thus enhancing the dehalogenation kinetics, but has no significant effect on reactivity or millability of CaO. This fact is due to the higher hardness of quartz (7 Mohs) that facilitates a finer comminution of iron, which is a plastic material with lower hardness (4–5 Mohs) (Baláž, 2008; Baláž et al., 2013). Specifically, iron is plastically deformed by ball hits, but the presence of SiO<sub>2</sub> induces its particle fracture and hampers agglomeration, thus augmenting iron specific surface. On contrary, CaO is a brittle material, so, in spite of SiO<sub>2</sub> presence, particle comminution rate is not improved in sensible manner.

Bromide significant recovery proves that the organic bromine contained in PP could be largely mineralized into soluble inorganic bromide. In this way, the concern of decabDE in PW could be eliminated, stating that the MC method can be an efficient choice for the destruction of brominated flame retardants in PW. In addition to this, the proposed MC process, realized in dry conditions at room temperature with cheap reagents, is sensibly faster than that previously studied (Grause et al., 2015).

To better understand the transformations of decabDE in milled plastic, FTIR spectroscopy was conducted on samples at various milling times (Fig. 2). The peak band around 500–700 cm<sup>-1</sup> is ascribed to C–Br stretching vibration in decabDE, which can be regarded as representative of organic bromine. During co-milling with Fe-SiO<sub>2</sub>, the peak around 500–700 cm<sup>-1</sup> (C–Br bonds) could be clearly observed in the sample of 0 h mixture and the intensity became weak after 2 h milling. After 8 h, the peak of C–Br completely disappeared, indicating that the organic bromine from decabDE in PP was entirely converted into inorganic bromide. This finding corroborates the effective mineralization of decabDE and, consequently, suggests that no organic by-products (in particular, dioxins or dioxin-like compounds) are formed during milling. When PP is co-milled with CaO-SiO<sub>2</sub>, presence of carbonates is detected, i.e. the band at 1500 cm<sup>-1</sup> in Fig. 2b attributed to C–O stretching (Zhang et al., 2002), conceivably owing to carbonation of the samples in air after milling. In addition, although the C–Br peak intensity becomes weaker during the MC treatment, small peaks are still observed in the 8 h sample. This fact is consistent with the better debromination achieved with Fe-SiO<sub>2</sub> (Fig. 1).

In order to obtain further information on the influence of PP on DecaBDE destruction by ball milling, two additional MC tests were

conducted with pure DecaBDE. These tests were executed using a milling device that is much less intensive than that employed for PP debromination. Such choice was done to have a finer control on the provided mechanical energy dose for the MC reaction. For the sake of comparison, the reaction progress of all MC treatment is expressed in terms of specific energy dose (Fig. 3). It was demonstrated that such quantity is invariant with the milling intensity (i.e. the mechanical power transferred from the mill to the material) (Delogu et al., 2001, 2004), also for organic-inorganic systems such as pollutant MC destruction reaction (Cagnetta et al., 2016b; Chen et al., 2017a). The specific energy dose ( $\hat{D}$ ) is defined as (Butyagin and Streletskii, 2005):

$$\hat{D} = \frac{1}{2} C_R v_i^2 F t \quad (1)$$

where  $C_R$  is the charge ratio (i.e. ball-to-powder ratio),  $v_i$  is the average impact velocity of balls,  $F$  is the hit frequency, and  $t$  is the milling time. A simplified procedure to calculate the specific energy dose is expounded in detail in our previous work (Cagnetta et al., 2016b). Experimental results clearly show that the MC destruction kinetic is more rapid for pure DecaBDE than for PP (Fig. 3). Reasonably, the polymer absorb a significant part of the kinetic energy transferred to the material by balls, resulting in a slower debromination rate. Utilizing a simplified kinetic model (Cagnetta et al., 2016b; Delogu et al., 2004), the kinetic constants can be estimated by data fitting:

$$\frac{[\text{DecaBDE}]}{[\text{DecaBDE}]_0} = (1 + KR\hat{D}) \exp(-KR\hat{D}) \quad (2)$$

where [DecaBDE] and [DecaBDE]<sub>0</sub> are the pollutant concentrations at a generic specific energy dose  $\hat{D}$  (or, equivalently, milling time) and at the beginning of the reaction, respectively;  $K$  is the kinetic constant; and  $R$  is the reagent-to-pollutant ratio. Kinetic constant values (Table 1) demonstrate numerically what is evident in Fig. 3: for both pure DecaBDE and PP, Fe-SiO<sub>2</sub> induces a roughly 1.4 time faster reaction than CaO-SiO<sub>2</sub>; MC destruction of pure DecaBDE is on average 4.4 times quicker than that of DecaBDE in PP, for both co-milling reagents. This latter number can be interpreted as the specific energy dose that is necessary to achieve a certain DecaBDE debromination percentage in PP respect to that required to obtain the same percentage in pure DecaBDE. In simple words, in order to attain debromination of PP, we need 4.4 times higher energy dose than for pure DecaBDE. It should be noted here that the PP-to-DecaBDE ratio in the polymer is 5.6. So, in a very first approximation, the total mechanical energy transferred by each ball hit is roughly divided among components of the milled material in equal manner. That is to say, PP absorb ~85% of the energy, while only the ~15% is used for effective debromination and destruction of DecaBDE. This consideration (although very rough) can be useful to estimate energy consumption and power costs for the MC treatment of POP polluted waste, taking advantage of the large literature on pure POP destruction by high energy ball milling. Nevertheless, such approximate estimation should be corroborated by suitable milling tests.

### 3.2. Milled residue characterization

Samples of PP co-milled with Fe-SiO<sub>2</sub> were further investigated by Raman and TGA to clarify the MC phenomena occurring during milling. In Raman spectra, the C–Br bonds also have a strong response around 500–700 cm<sup>-1</sup>, which is shown clearly in the 0.5 h milled sample (Fig. 4a). The C–Br peak became weak after 2 h milling, and then completely disappeared after 8 h treatment. This fact further corroborates the entire mineralization of decabDE. The peak at 1300 cm<sup>-1</sup> is probably due to milled PP. Its intensity

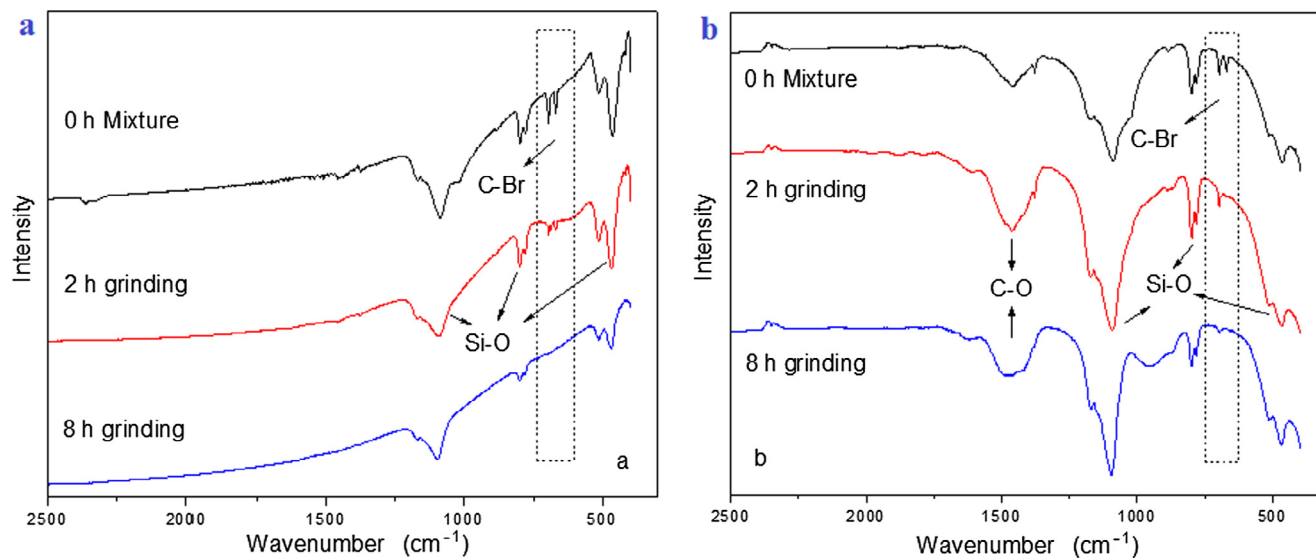


Fig. 2. FTIR spectra of the samples milled with Fe-SiO<sub>2</sub> (a) and CaO-SiO<sub>2</sub> (b).

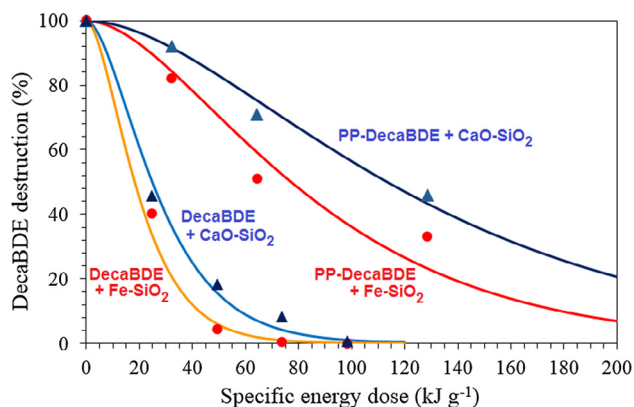


Fig. 3. DecaBDE degradation in PP or as pure compound by co-milling with Fe-SiO<sub>2</sub> or CaO-SiO<sub>2</sub>.

Table 1

DecaBDE destruction kinetic constants (calculated by interpolation of experimental data).

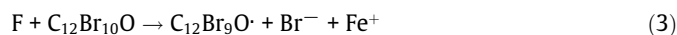
	Fe-SiO <sub>2</sub>	CaO-SiO <sub>2</sub>
PP-DecaBDE	0.005426	0.003703
DecaBDE	0.02285	0.01680

decreased along with milling time, suggesting that PP amorphization and partial degradation occur. Such peak, in the 8 h sample, is covered by one of the two bands that appear around 1350 cm<sup>-1</sup> and 1580 cm<sup>-1</sup>. These latter two peaks are usually identified as “D-band” (1330–1380 cm<sup>-1</sup>) and “G-band” (1540–1580 cm<sup>-1</sup>), which are recognized as the characteristic signals of the photon scattering from disordered carbon and graphite carbon, respectively. Their appearance in the Raman spectra reveals the generation of partially amorphized graphitic carbon. Carbonaceous matter is commonly found in products of MC destruction: under milling, co-milling reagents are MC activated and electron-rich crystalline defects are formed; organic molecules are then reduced by such electrons into carbon and halides (Cagnetta et al., 2016d, 2017a; Ikoma et al., 2001).

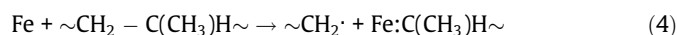
TGA of the milled samples was also carried out to confirm decabBDE degradation. Fig. 4b shows thermograms of samples milled

with Fe-SiO<sub>2</sub> for different MC treatment times. Concerning the 0 h mixture of the grinding materials, there were two phases of weight change that could be clearly observed in the temperature range from 300 to 400 °C and from 450 to 500 °C. The weight loss at 300–400 °C is identified as the decomposition of decabBDE in the samples, while the transition at 450–500 °C comes from the decomposition of PP. For the weight loss at 450–500 °C, it remained nearly unchanged in all samples, indicating that PP does not undergo significant transformation (e.g. oxidation, carbonization) during the MC process. On contrary, the weight loss of decabBDE (300–400 °C) decreased along with milling time, until no weight change was detected in the corresponding temperature range at 8 h grinding. This fact further demonstrates the destruction of decabBDE during the MC reaction, revealing that both the organic C and Br were transformed into inorganic form.

Overall, several processes occur during the high energy ball milling of PP containing DecaBDE with Fe-SiO<sub>2</sub>. Firstly, as mentioned in paragraph 3.1, the zero valent Fe is comminuted into fine particles, thanks to the presence of silica crystals, which improves millability of the plastic iron. It must be noted here that silica crystal crushing determines the generation of electron-rich surfaces (Delogu, 2011; Kaupp, 2009) that might contribute to the hereafter-mentioned reactions to a minor extent (because of the softer iron, which covers silica crystals). Fresh surfaces of the metal are then available for a more rapid electron transfer to DecaBDE (C<sub>12</sub>Br<sub>10</sub>O):



Such radical-anion couple formation after electron addition is typical of organic MC reactions (Todres, 2006). The process goes on until entire carbonization to amorphous and graphitic carbon of DecaBDE molecular skeleton, which was ascertained in our previous work (Zhang et al., 2012) and confirmed in the present one. Nonetheless, electrons from the iron particles are certainly captured also by the polymer chains, thus causing cleavage of the latter:



The gathered results confirm the effective decabBDE destruction in PP through the MC process with Fe-SiO<sub>2</sub>, suggesting that the milled residue can be utilized for further processing in safe manner. In addition, the polymer chains are shortened by the intensive milling, which reasonably facilitates a subsequent decomposition



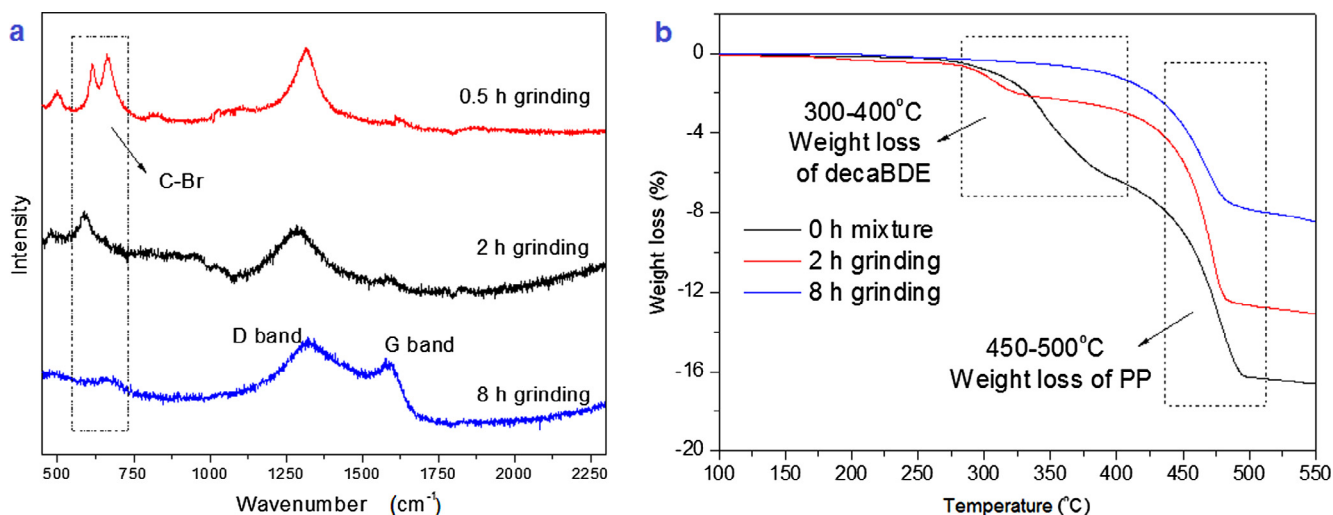


Fig. 4. Raman spectra (a) and TGA thermograms (b) of samples milled with Fe-SiO<sub>2</sub>.

by thermal treatments such as pyrolysis or gasification. Hence, the proposed MC process may be an effective pre-treatment for chemical recycling technologies to permit the beneficial use of the huge amount of PW containing halogenated organics.

#### 4. Conclusions

Chemical recycling technologies are among the most environmentally friendly and technologically viable processes that can realize the beneficial re-use of PW. However, being thermal treatments, the presence of halogenated flame retardants in the feedstock would cause gaseous hydrogen halide release (which would corrode reactor structure elements) and halogenated dioxin and dioxin-like compound emissions (which are toxic and strictly regulated in many countries). In order to enable chemical recycling of the massive amount in the world of PW containing haloorganics, a MC pre-treatment with cheap dehalogenating reagents was investigated. Results clearly shows that organic bromine in decaBDE-containing PP is substantially transformed into bromide after 8 h ball milling. Moreover, analyses corroborate the complete mineralization of the flame retardant. Comparative experiments with pure DecaBDE demonstrate that the required mechanical energy to obtain an efficacious and complete debromination is approximately proportional to the polymer-to-halogenated compound mass ratio. This is useful for preliminary feasibility assessment of the technology. In sum, high energy ball milling can be considered a valid pre-treatment for safe and viable recycling of PW containing haloorganics.

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GC, ZK, ZQ, and HJ designed and carried out the experiments; GC and ZK prepared the manuscript; HJ revised the manuscript; GY supervised the project.

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