Chapter 13
A Study on Fenton Technology for Polypropylene Waste Degradation and Recovery of High-Value Chemicals

Cheuk Fai Chow and Chung Sum Chan

Abstract Plastic waste management and handling are critical issues, and the development of breakthrough technology for these purposes is a challenging task. In this chapter, it will explore the feasibility of waste degradation and hopefully provide some insights and fundamental information for scientists and chemical engineers to address the issues of degradation and mineralization of inert plastic wastes, with polypropylene (PP) as an example, through effective chemical processes including surface activation and Fenton and photo-Fenton technology. To achieve a greener reaction process for practical use, commercially available hydrogen peroxide (H_2O_2) has been widely used as an oxidant. The Fenton reaction under ambient dark conditions was successful in converting the activated PP materials into water-soluble organic matter and carbon dioxide (CO_2) within 40 min, while the photo-Fenton reaction under UV-vis illumination was able to achieve complete mineralization within 80 min as determined by the analysis of the reaction solutions. In addition, the dissolved organic matter generated from the Fenton reaction was identified as belonging to three main classes: monocarboxylic acids, dicarboxylic acids, and diols. The study revealed that the concentration of H_2O_2 used in the Fenton reaction significantly affects the amount of diols and carboxylic acids recovered from the PP degradation, where the ratio could be tuned from 37.2 to 2.1% for diols and from 55.9 to 93.1% for carboxylic acids, under dark conditions. Moreover, under photo-Fenton degradation conditions, due to rapid decomposition, a positive pressure was observed (CO_2 gas: 550 kPa/g of material) from complete degradation of the activated PP. The gas pressure could potentially be converted into mechanical energy for further applications.

C. F. Chow (✉)
Department of Science and Environmental Studies and Centre for Education in Environmental Sustainability, The Education University of Hong Kong, 10 Lo Ping Road, Tai Po, Hong Kong SAR, China
e-mail: cfchow@eduhk.hk

C. S. Chan
Centre for Education in Environmental Sustainability, The Education University of Hong Kong, 10 Lo Ping Road, Tai Po, Hong Kong SAR, China

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13.1 Introduction

The wide range of applications of synthetic plastics in our daily life leads to extremely high consumption rates and significant waste handling problems. The ineffective treatment of plastic wastes adds to the threat of the limited supply of fossil fuel. According to the United States Environmental Protection Agency, 75.5% of the plastic material in the U.S. Municipal Solid Waste Stream was sent to landfills in 2014, with the remaining plastic material recycled (9.5%) or incinerated for energy generation (15%) (United States Environmental Protection Agency, 2016). The high cost of recycling (Wong, Ngadi, Abdullah, & Inuwa, 2015) and the problems associated with incineration such as generation of dioxins, polycyclic aromatic hydrocarbons (PAHs), and toxic ash (Siddique, Khatib, & Kaur, 2008) has resulted in landfills becoming increasingly stressed. Polypropylene (PP) constitutes 24.3% of the total plastic waste and is ranked second in worldwide plastic wastes. Its annual production currently exceeds 275 million metric tons (Jambeck et al., 2015). PP, a saturated and nonfunctional polymer that is "paraffinic" and extremely inert, was first discovered in 1951 by Hogan and Banks while attempting to convert propylene into gasoline (Sailors & Hogan, 1981) and is now widely produced using Ziegler-Natta catalysts for various applications (Sinn & Kaminsky, 1980). Current practices handle large amounts of inert PP wastes by disposal in landfills, which results in the loss of the high carbon content of these materials and their associated energy. However, effective technology for plastic waste treatment is limited. Several methods, such as photolysis, ozonolysis, ultrasound, biodegradation, pyrolysis, and catalytic degradation can be found in the literature for the mineralization of PP wastes or for their conversion into high-value chemicals/energy, to recover these energy-rich resources.

Photolysis involves the use of light to degrade materials. UV radiation can cleave the C–C and C–H bonds of PP at a wavelength of approximately 370 nm (Andrady, 1997). When PP film is exposed to the UV radiation, the polymer and oxygen react to form polymer peroxy radicals that can then cleave the C–C and C–H bonds of the tertiary carbon atoms of PP (Andrady, 1997). Photolysis of PP usually results in the loss of its mechanical properties, such as extensibility and strength, while decreasing its average molecular weight. The polymer breaks down into organic fragments such as CO_2, alcohols, ketones, and carboxylic acids (Fernando, Christensen, Egerton, & White, 2007). Ozonolysis is an oxidative process for the degradation of carbonaceous material by ozone. Saturated polymers such as PP react with ozone, resulting in the formation of polymer peroxy radicals that can oxidize PP into oxygen-containing materials such as carbonyls and unsaturated carbonyl polymers (Walzak et al., 1995). A study by MacManus et al. suggested that when PP film is exposed to UV radiation and ozone, insertion of oxygen atoms occurs on the surface of PP, resulting in ether linkage crosslinking as well as carbonyl and carboxyl acid containing polymeric materials (MacManus, Walzak, & McIntyre, 1999). Ultrasound can also be used to degrade plastic polymer when coupled with strong mechanical stress. Vibrational waves pass through the solution, resulting in a high shear gradient that leads to cavitation on the surface of the polymer chain and breakdown of the chemical bonds in the polymers (Chakraborty, Sarkar, Kumar, & Madras, 2004). The degradation of PP with ultrasound under different conditions has been studied (Chakraborty et al., 2004; Desai, Shenoy, & Gogate, 2008; Lin & Isayev, 2006). Chakraborty et al. reported that the degradation rate of PP in o-dichlorobenzene decreased with increase in the temperature (Chakraborty et al., 2004). Lin and Isayev monitored the degradation of PP and the associated changes in its mechanical properties under high-intensity ultrasound (Lin & Isayev, 2006). Desai et al. reported that using a low viscosity solvent in the ultrasound degradation of PP resulted in a higher extent of degradation (Desai et al., 2008). Biodegradation is a biochemical degradation process that results in the cracking of materials by microorganisms. The biodegradation of PP normally involves attaching microorganisms to the surface of the polymer, which acts as the carbon source that facilitates growth by the action of the enzymes in the microorganisms. The polymer is eventually degraded in this process (Arutchelvi et al., 2008). With careful selection of efficient microbial strains such as *Brevibacillus borstelensis* (Hadad, Geresh, & Sivan, 2005) and *Stenotrophomonas panacihumi* PA3-2 (Jeon & Kim, 2016), even the saturated PP polymer with strong and inert C–C and C–H bonds can be metabolized. Pyrolysis is the thermal degradation process of material by heat and pressure. Under reaction conditions involving intense heat and in the absence of oxygen, high-value materials for industrial applications like oil, gas, and char can be produced (Sharuddin, Abnisa, Daud, & Daud, 2016). The yield of oil, gas, and char by the pyrolysis of PP usually depends on the temperature. Ahmad et al. reported that the pyrolysis of PP at 300 °C using a micro-steel reactor yielded 69.82 wt% liquid oil, 28.84 wt% gaseous components, and 1.34 wt% solid residue (Ahmad et al., 2015). Fakhrhoseini and Dastanian obtained 82.12 wt% liquid oil, 17.76 wt% gaseous components, and 0.12 wt% solid residue at 500 °C from the pyrolysis of PP (FakhrHoseini & Dastanian, 2013). Catalytic degradation uses a catalyst to degrade synthetic polymers into hydrocarbons with higher commercial value. The advantages of using catalytic degradation include the relatively narrow distribution of hydrocarbon products and the lower operation temperatures when compared with pyrolysis (Hwang, Choi, Kim, Park, & Woo, 1998). Zeolites have been used for the catalytic degradation of PP, with the degradation temperature and the degraded hydrocarbon products being strongly governed by the nature and amount of the zeolite used (Zhao et al., 1996). The catalytic activity of zeolites also depends on their pore size and acidity, which affect the activation energy of C–C and C–H bond breakage (Durmuş, Naci Koç, Selda Pozan, & Kaşgöz, 2005). Other than zeolites, kaoline (Panda & Singh, 2014), silica, alumina (Ishihara et al., 1993; Lin & Yen, 2005), and activated carbon catalysts containing Pt and Fe (Uemichi, Makino, & Kanazuka, 1989) have also been reported for the catalytic degradation of PP.

Considering the aforementioned methods for degrading PP, most reported technologies require demanding operating conditions with high consumption of energy, uncontaminated single-type plastic waste, expensive catalysts, or dangerous ionizing radiation. Biodegradation methods are attractive and environmentally friendly, but require long periods of time for the microorganisms to completely degrade the plastics. These factors combine to hinder the development of plastic waste conversion. Therefore, it is necessary to develop a method to achieve rapid and low-cost degradation of PP with controllable mineralization and breakdown products under mild conditions. Fenton and photo-Fenton reactions are promising alternatives and the chemical reactions involved are advanced oxidation processes (AOPs), commonly employed in rapid degradation and mineralization techniques for chemical substances resistant to conventional technologies (Fenton, 1894; Litter, 2005). Both processes involve oxidative reactions that generate highly oxidizing species, such as hydroxyl radicals ($\cdot$OH, $E = 2.73$ V) from H_2O_2 in the presence of Fe(III) catalysts, for the destruction and ultimate mineralization of the targeted contaminants (Umar, Aziz, & Yusoff, 2010). Due to their high efficiency, simplicity, and ability to treat a wide range of organic pollutants, both reactions are powerful methods that are capable of destroying a wide range of hazardous organic pollutants (Barb, Baxendal, George, & Hargrave, 1949; Haber & Weiss, 1934; Umar et al., 2010). Although both processes can generate hydroxyl radicals, the photo-Fenton reaction can facilitate the reduction of Fe(III) to Fe(II) to produce more hydroxyl radicals via photolysis (Deng & Englehardt, 2006; Hermosilla, Cortijo, & Huang, 2009; Kavitha & Palanivelu, 2004), and the photo-decarboxylation of Fe(III)-carboxylates (Ollis, Pelizzetti, & Serpone, 1989; Pignatello, Oliveros, & MacKay, 2006). Depending on the operating parameters (pH, Fenton reagents, time, irradiation, etc.), the Fenton or photo-Fenton reactions may lead to either complete mineralization of the organic contaminants to CO_2, H_2O, and inorganic salts, or partial degradation of the contaminants to low molecular weight organic fragments (Umar et al., 2010). Despite the fact that the Fenton and photo-Fenton reactions have been widely used to degrade pollutants (Ollis et al., 1989; Pignatello et al. 2006), there have only been a few reports of plastic waste degradation, especially for saturated and nonfunctional inert polymers. In this work, the feasibility of applying Fenton and photo-Fenton reactions for the mineralization of PP wastes or for converting them into high-value chemicals are investigated. Our results showed that conversion and mineralization of PP into water-soluble organic matter and/or carbon dioxide can be achieved by grafting Fe(III)-sulfonated functionalities onto the polymer substrates, which undergo oxidation in the presence of H_2O_2 with suitable concentration, initial pH, and levels of irradiation. The degradation method described herein is applicable for most PP wastes, such as drinking bottles and microwave boxes.

13.2 Experimental

Materials and Methods Polypropylene (average Mw ~ 12,000) was purchased from Sigma-Aldrich. Chlorosulfonic acid (98%) was obtained from International Laboratory. Chloroform (ACS), Ferric chloride (Acros), hydrochloric acid (Sigma-

Aldrich), dichloromethane (ACS), and 30 wt% hydrogen peroxide (BDH) were obtained and used without further purification.

The dissolved organic carbon content of the degradation mixtures was determined by filtering through 1.0 μm pore size membrane filters (Pall Corporation) followed by the determination of their total organic carbon content using a Shimadzu TOC-L CSH high-sensitivity total organic analyzer. Infrared spectra in the range of 500–4000 cm^{-1} were recorded on a Perkin Elmer Model Frontier Fourier-transform infrared spectroscopy (FTIR) spectrometer. The elemental analyses were performed on a Vario EL CHNS analyzer. Analyses of the iron contents of the activated polymers were performed using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). The surface morphologies of the polymer particles were characterized using scanning electron microscopy (SEM) with a Philips XL30 ESEM-FEG coupled with energy dispersed spectroscopy (EDS). Characterization and quantification of the dissolved organic matter in the degradation studies were performed using an Agilent 1100 High-performance liquid chromatography (HPLC) coupled to a diode-array detector (DAD, G1315A system) and an electrospray ionization mass spectrometer (ESI-MS, PE SCIEX API 2000 LC/MS/MS system) with an Alltech Allsphere ODS-2 column (5 μm, 250 mm × 4.6 mm i.d.). The samples were injected using an autosampler with an injection volume of 5 μL. Eluents required for the liquid chromatography were prepared by dissolution of appropriate amounts of sulfuric acid (1 mM) and sodium sulfate (8 mM) in Milli-Q water. The solutions were then filtered through disposable 1 μm glass fiber membrane filters (Pall Corporation) and degassed in an ultrasonic bath prior to use. The mobile phase flow rate was 0.5 mL/min and the separation temperature was 25 °C. Peaks were recorded at 210 nm. Gas chromatograph–mass spectrometric (GC-MS) analyses were performed on a HP (Hewlett Packard) 6890 series gas chromatograph coupled with an HP 5973 mass selective detector. Injections were carried out with an HP 7683 autosampler. The capillary column used was an Agilent HP-5MS (30 m × 0.25 mm, 0.25 μm). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. The temperature program was: initial temperature, 60 °C for 2 min; ramp at 10 °C/min to 280 °C and held for 2 min; injection temperature, 280 °C; and transfer line, 280 °C. The sample injection volume was 2 μL. Split injection mode with a split ratio of 2:1 was used. The ionizing voltage was 70 eV. The source temperature was set at 250 °C. UV-visible spectroscopic analyses were performed on a Cary 50 UV-visible spectrophotometer.

Preparation of the Activated PP Materials (PPSO$_3$–Fe) PP beads were obtained from Sigma-Aldrich. PP beads and commercially available PP soymilk bottles and lunch bowls were ground to the size range of 125–250 μm prior to use. The PP material (1.00 g) was dissolved in 25 mL of 1,1,2,2-tetrachloroethane with stirring (200 rpm) under reflux at 65 °C (Chow et al., 2016, 2017; Dimov & Islam, 1991; Fischer & Eysel, 1994; Ihata, 1988; Kaneko et al., 2004). A mixture of concentrated chlorosulfuric acid and dichloromethane (15 mL, 1:2 v/v) was added dropwise over 30 min. The resulting mixture was allowed to react for an additional 2 h. The organic solvents were removed by distillation. FeCl$_3$ solution (0.75 M, 100 mL) was added to the mixture, which was then stirred overnight. A black precipitate was obtained by centrifugation and was washed with deionized water until the supernatant became almost colorless. The solids were then oven-dried at 80 °C for a total yield of 1.63 g. IR (KBr): $\nu_{\text{O–H}} = 3354\ \text{cm}^{-1}$; $\nu_{\text{C–H}} = 2954$, 2918, 2870, and $2839\ \text{cm}^{-1}$; $\nu_{\text{C=C}} = 1636\ \text{cm}^{-1}$; $\nu_{\text{S=O}} = 1151$ and $1033\ \text{cm}^{-1}$; $\nu_{\text{Fe–O}} = 528\ \text{cm}^{-1}$. The elemental analysis showed: C, 39.14; H, 5.21; N, 0.00; S, 7.87%.

Degradation of PPSO$_3$–Fe by Fenton Reaction In a typical degradation reaction, 0.15 g of **PPSO$_3$–Fe** powder (particle size in the range of 125–250 μm) was suspended in deionized water (85 mL) with ultrasonication for 10 min. Hydrochloric acid or NaOH was added to the reaction mixture to adjust the initial pH to 2.6. Hydrogen peroxide (30 wt%, 10.00 mL, i.e., 650.0 mmol/g of polymer used) was then added to the reaction mixture. The final volume of the reaction mixture was maintained at 100 mL, and hence the initial concentration of hydrogen peroxide was 3.0 wt%. The reaction was initiated by placing the reaction mixture in the dark under ambient conditions for 120 min. The dissolved organic carbon (DOC) in the reaction mixtures and the weight of the remaining suspended polymer were then recorded. The reaction was also studied using various initial hydrogen peroxide concentrations (81.25, 162.5, 325, and 650 mmol per gram of activated material).

Determination of Diols The crude products were extracted from the filtered reaction mixture (10.0 mL) by ethanol (4 mL) assisted by salting out with excess ammonium sulfate (5 g). The extract was further reacted with sodium periodate and acetylacetone. The diol content was then quantified by UV-visible spectroscopy.

Determination of Carboxylic Acids and Alkylsulfonic Acids The filtered reaction mixture was alkalized by NaOH to pH 11. The aqueous solution was then dried under vacuum and the crude product was extracted twice by methanol (3:4 v/v based on the aqueous content). The extracted organic matter was characterized and quantified by HPLC-DAD and GC-MS.

Mineralization of PPSO$_3$–Fe by Photo-Fenton Reaction

PPSO$_3$–Fe (125–250 μm) was suspended in deionized water (85 mL) using ultrasonication for 10 min. The initial pH of the mixture was adjusted to 2.5. Then, 30% H_2O_2 (10 mL, 650 mmol/g of activated plastic) was added to the suspension, and the final volume was adjusted to 100 mL with deionized water. The reaction was initiated by placing the reaction mixture 30 cm from a UV-vis lamp. The mixture was stirred under ambient conditions for 2 h. The light-triggered reaction was studied by varying the input light power ranging from 0 to 500 W. The reaction mixtures were filtered through 1.0 μm pore-size membrane filters (Pall Corporation). The carbon content of the reaction mixtures was determined using a Shimadzu TOC-L CSH high-sensitivity total organic analyzer. The amount of remaining solid plastic materials was recorded.

Three working conditions, (i) pH, (ii) amount of H_2O_2, and (iii) reaction time were studied. The effect of pH on the light-triggered reaction was studied by varying the pH from 1 to 7 by adding HCl or NaOH to the reaction mixture. While the effect of H_2O_2 on the light-triggered reaction was studied by adding 0–10 mL of H_2O_2

solution (0–650 mmol/g of activated plastic) to the reaction mixture. The effect of reaction time was studied by monitoring the light-triggered reaction over a period of 9 h. The final volume of each reaction mixture was adjusted to 100 mL with deionized water. All reactions were initiated by placing the reaction mixture 30 cm from the 500 W UV-vis lamp. The carbon content of the reaction mixture and the amount of remaining solid plastic materials were recorded.

Amount of CO_2 produced by the light–dark cycles in the light-triggered reaction of $PPSO_3$–Fe

$PPSO_3$–Fe, PP and activated commercial PP samples (0.005 g) were separately suspended in deionized water (1.4 mL) in 2 mL GC-vials, where they were ultrasonicated for 10 min and then placed in a 28.1 °C water bath for another 10 min. A solution of 30% H_2O_2 (0.008 mL, 100 mmol/g of activated plastic) was then added to the suspension and the final volume was adjusted to 1.5 mL with deionized water. The pressure of gas released was measured by manometer (density as 0.938 kg/m^3). The reaction was initiated by placing the reaction mixture 30 cm under light (400 W UV-vis lamp) and dark conditions with respect of reaction time. The pressure of gas recorded was calculated according to the equation $P = h{\cdot}g{\cdot}d$ where P is the calculated pressure (kPa), h is the height of the oil increased, g is the force of gravity (9.81 m/s^2) and d is the density of the oil (0.915 kg/m^3).

13.3 Results and Discussion

Activation of PP PP was activated by chlorosulfuric acid-mediated sulfonation of the carbon-hydrogen bonds followed by grafting Fe(III) onto the polymer chains. Recent studies demonstrated that the Fenton degradation of polyethylene (PE) and polyvinyl chloride (PVC) waste is feasible (Chow et al., 2017; Chow, Wong, Ho, Chan, & Gong, 2016), but the reaction with the more inert PP has not yet been explored. By applying similar activation conditions, the active PP material (**$PPSO_3$–Fe**) was prepared by reacting the virgin PP powder with 12.5 vol.% chlorosulfuric acid in chloroform in an open atmosphere under reflux at 65 °C, followed by grafting Fe(III) (Chow et al., 2016). **$PPSO_3$–Fe** was isolated as an air-stable black precipitate that was insoluble in water and common organic solvents. The sulfonation and grafting of Fe(III) onto the polymer chains was confirmed by IR spectroscopy, where two sets of new peaks at 1151 and 1033 cm^{-1} ($\nu_{S=O}$) and 528 cm^{-1} ($\nu_{Fe–O}$) were observed for **$PPSO_3$–Fe** (Fig. 13.1). Figure 13.2a shows the SEM image and EDS of the **$PPSO_3$–Fe** particles. The average size of the **$PPSO_3$–Fe** particles was found to be ~118 μm. It's chemical composition was determined using EDS where the peaks arising from C, O, S, and Fe were recorded (Fig. 13.2b). Elemental and ICP-MS analysis indicated that the material contained ~8.0 wt% sulfur and ~12.3 wt% iron. The S/Fe mole ratio in the **$PPSO_3$–Fe** was ~1, suggesting that every sulfonate group in the activated polymer chelated to one Fe(III) ion, while the carbon to sulfur (C/S) mole ratio in the **$PPSO_3$–Fe** was found to be 13 on average, indicating

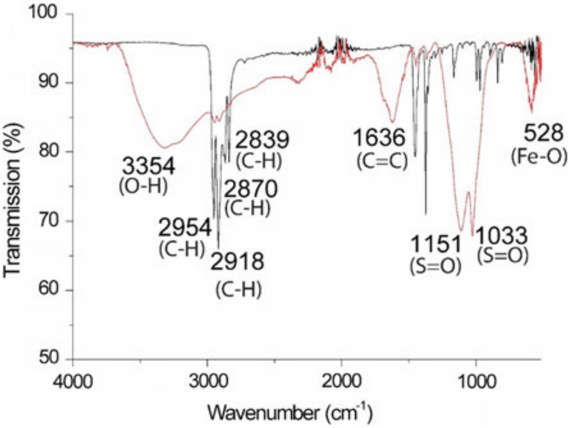


Fig. 13.1 FTIR characterization of the chemical nature of PP before (—) and after (—) treatment with chlorosulfonic acid, indicating the presence of sulfonate functional groups in the polymer material

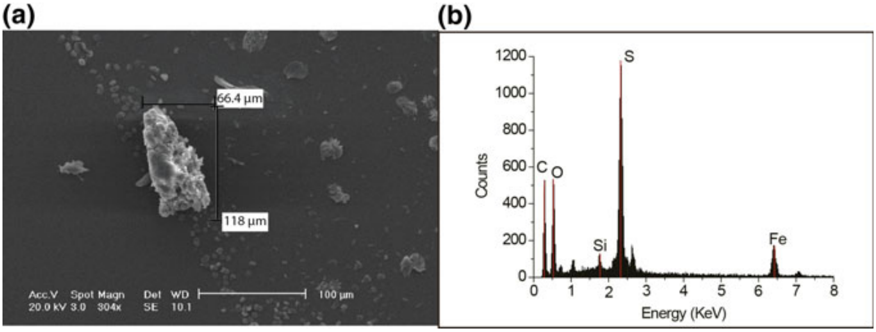


Fig. 13.2 **a** SEM images and **b** EDS of the **PPSO$_3$–Fe**

that every four propylene units in the activated polymer had one sulfonate group. It is also found that the generated **PPSO$_3$–Fe** contained alkene functionality by FTIR (Fig. 13.1).

Degradation of PPSO$_3$–Fe by the Fenton and Photo-Fenton Reactions Fenton and photo-Fenton reactions were conducted by suspending 150 mg of the polymer materials (PP and **PPSO$_3$–Fe**) in water with 650.0 mmol/g H_2O_2 at pH 2.5 under dark and ambient UV-vis conditions, respectively. Figure 13.3 shows the change in the organic and dry weight content during the course of the two treatments of **PPSO$_3$–Fe** and PP. Under the Fenton treatment, the DOC content of **PPSO$_3$–Fe** increased rapidly at the beginning and reached its maximum of ~390.0 mg/L at 50 min, while the content plateaued during the later stage of the degradation process (Fig. 13.3a). On the other hand, under the photo-Fenton treatment of **PPSO$_3$–Fe**, a different degradation pattern emerged with the DOC content of **PPSO$_3$–Fe** increasing rapidly at the beginning of the degradation and reaching its maximum of ~350.0 mg/L at 20 min, then decreasing to a minimum after 80 min (Fig. 13.3a). The increasing DOC content of the reaction mixtures of **$PPSO_3$–Fe** at the onset of both the Fenton and photo-Fenton processes can be explained by the oxidative breakage of the carbon-carbon polymer chains to produce water-soluble and lower molecular weight organic fragments in the reaction mixture. Under the Fenton treatment, the hydrophilic organic fragments remained intact without further degradation, while under the so-called strong photo-Fenton oxidative treatment, the small hydrophilic organic molecules are further oxidized to CO_2 (Fig. 13.3a). No evidence of any degradation or mineralization of the virgin PP polymer was observed after 9 h for either the Fenton or photo-Fenton treatments. With respect to the DOC changes, the degradation of **$PPSO_3$–Fe** in terms of dry weight loss was found to increase rapidly and leveled off at 95% degradation (i.e., 95% dry weight loss) in the first 50 and 20 min for the Fenton and photo-Fenton reaction treatments, respectively (Fig. 13.3b).

Degradation Products from the Fenton and Photo-Fenton Reactions Scheme 13.1 shows the production of organic products and/or carbon dioxide from PP polymers under the Fenton and photo-Fenton treatments with the 650.0 mmol/g H_2O_2. Through the photo-Fenton treatments, **$PPSO_3$–Fe** was completely mineralized into carbon dioxide and water. It is found that with 30 min of UV-Vis illumination (400 W) of **$PPSO_3$–Fe** (0.15 g) in neutral deionized water (15 mL) and H_2O_2 (100.0 mmol/g sample), 400 kPa/g of activated polymer of gas pressure (CO_2) was generated. On the other hand, through the Fenton treatment of **$PPSO_3$–Fe** under dark conditions, 64% of its carbon content was degraded into dissolved organic matter, while only 36% of its carbon content was mineralized in the form of carbon dioxide. The organic matter could be isolated from the reaction mixture through solvent extraction with alcohols. The extracts were then characterized and quantified by HPLC-DAD, GS-MS, and UV-visible spectroscopy. Through the Fenton treatment of **$PPSO_3$–Fe** under dark conditions with 650.0 mmol/g H_2O_2 at pH 2.5, carboxylic acid was the major component (93.0%) of the extract, while diols (2.7%) were a considerably smaller proportion. Approximately 4.3% of the organic molecules in the extracts could not be identified. Supplementary Information (SI) Fig. 13.1 shows the HPLC chromatograph of the extract of the dissolved organic matter of the degraded **$PPSO_3$–Fe**. Through HPLC analysis, it is found that the carboxylic acid component was mainly comprised of monocarboxylic acids (formic and acetic acid), dicarboxylic acids (oxalic, propanedioic, and butanedioic acid), and other carboxylic acids which constituted 32.2%, 13.7%, and 47.1%, respectively, of the total (Table 13.1, entry 4). 1,2-Diols were identified to contribute to 2.7% of total carbon content by UV-visible analysis (SI Fig. 13.2). It is envisioned that through the Fenton and photo-Fenton treatment of **$PPSO_3$–Fe**, there is potential to utilize their degradation products, i.e., pressure generated by CO_2 and the dissolved organic matter for mechanical and chemical energy, respectively.

Control of the Degradation Products of the Fenton and Photo-Fenton Reactions The composition of the organic products obtained from the Fenton degradation can be effectively controlled by varying the concentration of hydrogen peroxide. Table 13.1

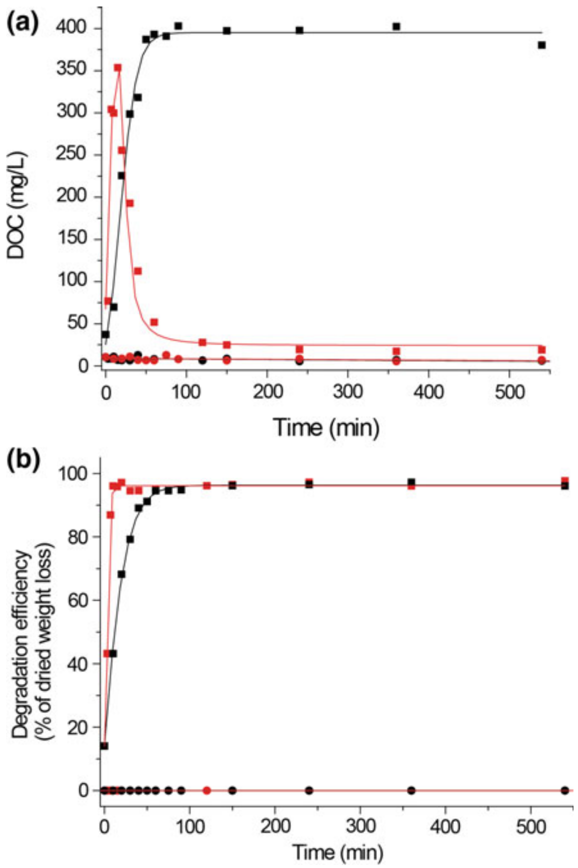
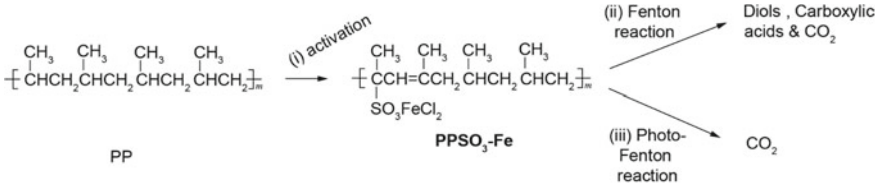


Fig. 13.3 Fenton treatment of **PPSO$_3$–Fe** (–■–) and PP (– ● –)and Photo-Fenton treatment of **PPSO$_3$–Fe** (–■–)and PP (– ● –) beads. The degradation efficiency was expressed as **a** the percentage of dry weight loss, and **b** the change in dissolved organic carbon (DOC) content over the course of the treatment. The initial polymer loading, pH, and H_2O_2 loading were 100 mg, 2.5, and 650 mmol/g, respectively. The photo-Fenton reactions were performed under 500 W UV-vis irradiation, while the Fenton reactions were performed under dark ambient conditions. Each data point is the mean value of three independent degradation runs



Scheme 13.1 Polymer activation, Fenton treatment, and photo-Fenton treatment of PP and the resulting degradation products. Reaction conditions: (i) chlorosulfuric acid and $FeCl_3$ in 1,1,2,2-tetrachloroethane; (ii) acidic conditions, dark, 650.0 mmol H_2O_2 per gram of **PPSO$_3$–Fe**; and (iii) acidic conditions, UV-Vis illumination, H_2O_2

Table 13.1 Degradation of the activated PP (**PPSO$_3$–Fe**) with Fenton treatment

H_2O_2 used (wt%)	Degradation efficiency (DOC (mg/L))	Yield of the degradation products (%)								
		Monocarboxylic acid		Dicarboxylic acid			Other carboxylic acids (%)	Diols (%)	Other organic matter (%)	Total (%)
		C1[a] (%)	C2[b] (%)	C2′[c] (%)	C3[d] (%)	C4[e] (%)				
0.5	89.1% (485.3)	6.7	15.7	0.7	0.7	4.4	27.7	31.2	12.8	100
0.75	99.6% (473.3)	8.1	21.4	1.2	1.7	5.3	28.6	15.2	18.5	100
1.5	99.7% (478.5)	9.6	22.6	2.1	2.0	7.1	37.0	11.6	8.0	100
3.0	98.4% (438.8)	8.9	23.3	3.2	2.4	8.2	47.1	2.7	4.3	100

[a] Formic acid. [b] Acetic acid. [c] Oxalic acid. [d] Propanedoic acid. [e] Butanedoic acid

shows the effect of the concentration of H_2O_2 on the distribution of degradation products recovered from the Fenton degradation of **$PPSO_3$–Fe**. In the system with low H_2O_2 concentration, for example, 108 mmol per gram of **$PPSO_3$–Fe**, 56.0% of the degradation products was found to be carboxylic acids (including mono-, di-, and other carboxylic acids), while 31.2% were diols. The diols were potentially oxidized to carbonyl compounds or carboxylic acids with excess oxidants. With increasing concentration of H_2O_2 from 108 to 650 mmol per gram of **$PPSO_3$–Fe**, the degradation efficiency in terms of dry weight loss was maximized to nearly 100% and the DOC decreased slightly from 485.3 to 438.8 mg/L. The decrease in DOC with nearly 100% complete degradation of the activated polymer suggested the degradation of the dissolved organic matter to carbon dioxide at higher concentrations of H_2O_2. Moreover, the proportion of diols was found to decrease significantly from 31.2 to 2.7% of the total carbon content in the dissolved organic matter, whereas carboxylic acids increased from 56.0 to 93.0%. Acetic acid became the major product and increased from 15.7 to 23.3% of the total carbon, while all other carboxylic acids increased dramatically from 27.7 to 47.1%. This suggested that the majority of degradation products, either diols or carboxylic acids, could be controlled by manipulating the concentration of H_2O_2 in the Fenton degradation.

Through the photo-Fenton treatment of **$PPSO_3$–Fe**, the mechanical energy, through the buildup of gas pressure, produced from the oxidation of the plastic material can be effectively controlled under several light-and-dark cycles. The crushed activated and nonactivated powder (0.005 g) were separately suspended in deionized water (1.5 mL) and H_2O_2 (100.0 mmol/g sample) in vials and irradiated with a UV-Vis lamp at 400 W. The reaction mixtures were cycled between illumination for 3 min and dark conditions for 5 min for four consecutive cycles. Figure 13.4 shows the light-controlled CO_2 gas release from the decomposition of the activated polymers. In each light/dark cycle, pressure was only generated during the illumination period indicating the mineralization of active PP to CO_2. Through 4 consecutive light-on/off cycles, the CO_2 gas generated built up a pressure (mechanical energy) of 550 kPa/g from the degradation of the activated polymer. It should be noted that there was no change in volume during the dark phases. The control experiment with nonactivated polymer only generated a small amount of pressure, which was due to the temperature increase caused by the UV-lamp.

Fenton and Photo-Fenton Reactions of Real PP Waste To test the application potential of this degradation protocol to treat PP waste from commercial and industrial sources, two of the most abundant PP wastes, soymilk bottles, and microwave lunch bowls, were selected for degradation investigation. The highest yield of organic products was achieved using 3 wt% of H_2O_2 in the Fenton degradation. Table 13.2 summarizes the degradation efficiencies of the collected plastic waste samples. In a 2 h reaction, 98.4 and 93.7% degradation was achieved for the soymilk bottles and microwave lunch bowls, respectively. The DOC content was found to be 432.2 mg/L for the soymilk bottles and 438.6 mg/L for the bowls. Greater than 90% degradation was achieved for both commercial PP samples, which suggests that the Fenton process could be applicable for the degradation of PP polymer matrix containing dyes

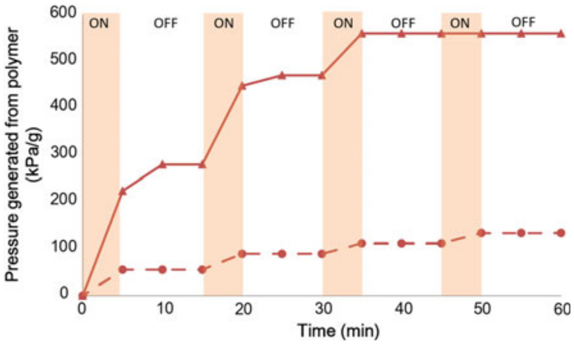


Fig. 13.4 The gas volume change generated by the degradation of (solid line) **$PPSO_3$–Fe**, (dashed line) PP + Fe under conditions of deionized water, 400 W UV-vis lamp, and 100.0 mmol/g H_2O_2 under 5 min light—10 min dark cycles

and plasticizers. The organic products recovered from the real samples were similar to that recovered from the virgin PP material. Over 95% of the carbon content in the dissolved organic matter extracted from the degraded solution of the real samples was determined to be carboxylic acids. The distribution of the monocarboxylic acids (formic and acetic acid) and the dicarboxylic acids (oxalic, propanedioic, and butanedioic acid) obtained from the degradation of the real samples were similar to that of the virgin PP. Acetic acid was found to be the most abundant single product (23.3–27.5%) from the recovery of both the virgin PP and real samples. Through the photo-Fenton degradation, CO_2 pressure of 350 and 430 kPa/g from the degradation of soymilk bottles and microwave lunch bowls were generated, respectively, with H_2O_2 (100.0 mmol/g sample) under a UV-vis lamp at 400 W.

13.4 Conclusion

In conclusion, this study successfully demonstrated the utility of Fenton technology with and without photo-assistance for the degradation of PP plastic waste into useful and recoverable resources under mild conditions. The Fenton process was found to be an efficient method for the breakdown of solid PP wastes after chemical activation into a number of water-soluble organic products such as carboxylic acids and diols, which are high-value industrial chemicals. In addition, for the degradation process under illumination, all the solid waste decomposed to CO_2 gas could build up a pressure that could be used as a mechanical energy source. The effectiveness of this method to degrade inert solid PP waste into small molecules and gas in a short period of time may be an alternative for the handling of the massive amount of domestic plastic waste currently disposed of in landfills.

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Table 13.2 Characteristics of the organic products recovered from the real PP plastic samples (soymilk bottles and lunch bowls) via the Fenton treatment

PP waste sample	Degradation efficiency (DOC (mg/L))	Yield of the degradation products (%)								
		Monocarboxylic acid		Dicarboxylic acid			Other carboxylic acids	Diols	Other organic matters	Total
		C1[a] (%)	C2[b] (%)	C2′[c] (%)	C3[d] (%)	C4[e] (%)				
Soymilk bottles	98.4% (432.2)	8.4	27.5	3.2	2.7	8.7	45.8	–[f]	3.7	100
Microwave Lunch bowls	93.7% (438.6)	8.4	27.3	2.9	2.4	8.4	46.0	–[f]	4.7	100

[a] Formic acid. [b] Acetic acid. [c] Oxalic acid. [d] Propanedoic acid. [e] Butanedoic acid. [f] Not determined

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Cheuk Fai Chow is an Associate Professor of Department of Science and Environmental Studies and the Director of Knowledge Transfer at the Education University of Hong Kong. He received his B.Sc. (Applied Chemistry) and Ph.D. from the City University of Hong Kong. He obtained a Croucher fellowship and did his postdoctoral training with Nobel laureate Jean Marie Lehn (The University of Strasbourg, France). His research interest lies in applying his environmental studies for energy, water resource, and plastic waste studies.

Chung Sum Chan is a Project Officer in the Centre for Education in Environmental Sustainability at The Education University of Hong Kong. He received his B.Sc. and M.Phil. degrees in Chemistry from The Chinese University of Hong Kong. He focuses his efforts on the study of plastic degradation, and the promotion of plastic resources education.