Separation and Purification Technology 173 (2017) 226–232

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Surface hydrophilization of acrylonitrile butadiene styrene by the mild heat treatment for its selective separation to recycling

Nguyen Thi Thanh Truc, Chi-Hyeon Lee, Byeong-Kyu Lee *, Srinivasa Reddy Mallampati

Department of Civil and Environmental Engineering, University of Ulsan, Daehak-ro 93, Nam-gu, Ulsan 680-749, Republic of Korea

A R T I C L E I N F O

Article history:
Received 25 November 2015
Received in revised form 22 September 2016
Accepted 22 September 2016
Available online 23 September 2016

Keywords:
ABS
Hydrophilic
Heat treatment
Froth flotation
Contact angle

A B S T R A C T

Acrylonitrile-butadiene-styrene (ABS) is one of hazardous halogenic plastics which containing brominated flame-retardants (BFRs) is considered as toxic wastes due to releasing hydrogen bromide and brominated dioxins through incineration or disposal activities. In present, recycling is aimed as a sustainable plastic waste management of ABS containing BFRs in ways that minimize the potential impact on human health and environment. This study was conducted to facilitate the separation of ABS plastics from heavy plastic mixture by froth flotation after surface rearrangement of ABS with mild heat treatment for its recycling. Hydrophilic moieties would be more likely to develop on the mild heat-treated ABS surfaces than on other plastics perhaps due to the difference of molecular mobility. This provides an excellent base for selective separation of ABS by froth flotation technique. As a result of froth flotation after mild heat treatment, about 97% of ABS with 100% purity was selectively separated from heavy plastics. The detailed mechanism for the selective separation of the ABS in the treatment (froth flotation after mild heat treatment) was discussed. Finally, this study facilities selective separation application effective and inexpensive method for of ABS from waste plastics.

1. Introduction

Plastic plays an important role in many industries and is used extensively in our daily lives. Thus, the generation volume of plastic waste has greatly increased. According to statistics from the Korea Environment Corporation, about 5.7 million tons of plastic waste was generated in Korea in the year 2013, with more than 63% from industry use and the rest from municipal use [1]. About 80% of the plastic waste generated in Korea consist of polypropylene (PP), polyethylene (PE), polycarbonate (PC), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), and acrylonitrile butadiene styrene (ABS). Proper management and control of plastic waste is highly important because incineration and landfill disposal of plastics cause numerous environmental contamination issues. A lot of plastic wastes are non-biodegradable and some plastics are also considered hazardous substances, particularly, those with halogenated functional groups such as brominated or chrominated atoms. Many of the ABS products that occupy around 20 wt% of the main resins used for electronic industries contain brominated flame-retardants (BFRs). BFRs are used as plastic additives to reduce fire damage by increasing the plastics' fire resistance. BFRs are applied in ABS at about 10 wt% and thus they are inevitable fractions in plastic waste flow, particular in Waste Electronic and Electrical Equipment (WEEE) and End of Life Vehicles (ELVs) [2]. During end-of-life management activities including incineration, heat utilization, the thermal energy recovery, disposal and chemical processing for plastic waste utilization or energy generation, bromines from plastic waste could be released as hazardous halogenated compounds such as hydrogen bromide, brominated dioxins and others [2]. Moreover, BFRs may become an overall environmental burden due to their contamination potential when disposed in landfills [3].

In general, technological developments for practical separation of brominated hydrocarbon plastics from mixed plastic waste are increasingly important because of the increased need for mechanical recycling for both economic and environmental purposes. According to a realistic estimate in Korea, about 34 wt% and 7 wt % of the generated plastic waste is sent to the incinerator and to landfills, respectively. The remaining 59 wt% is collected for recycling and the plastic recycling rate continues to grow in Korea [1]. However, the development of recycling processes for plastic waste is difficult because different types of plastic wastes have high incompatibility, with different chemical components, melting points, thermal stabilities and chemical interactions [4]. If recycled plastics have low purity or a low degree of separation, the application or value of the recycled plastic products is limited. In

* Corresponding author.
E-mail address: bklee@ulsan.ac.kr (B.-K. Lee).

http://dx.doi.org/10.1016/j.seppur.2016.09.042
1383-5866/

particular, the market prices of post-consumer products for recycled plastics are easily depreciated when fire retardant thermoplastics such as ABS are included with BFRs [5]. Therefore, it is necessary to develop practical or selective separation methods for each type of plastic from mixed plastic waste.

Several methods based on the plastic type or chemical structure are employed for plastic separation such as gravity separation [6,7], selective dissolution [8,9] and even manual sorting. Nevertheless, it is not easy to separate specific types of plastic from mixed plastic waste because there are only slight differences in their density and surface properties [4,5,10–13]. Plastic wastes can be divided into 3 groups based on their typical densities as follows: the heavy group with 1.33–1.42 g/cm^3 including PVC and PET, the intermediate density group with 1.03–1.19 g/cm^3 including PS, ABS, PC and PMMA, and the light group with 0.92–0.94 g/cm^3 including PE and PP [5,10,11,14]. If plastic mixture or waste is put into water, the light plastic group can be easily separated from others because their densities are lower than that of water and thus they float at the water level. However, separation of the remaining groups and/or ABS from others using the density difference of plastic waste is almost impossible. Thus, froth flotation can be considered an alternative method for the effective separation of plastics that have similar density or surface properties [15,16]. Separation of these plastics by froth flotation is required to modify the surface properties of one or several types of plastics by differentiating the chemical moiety on plastic surfaces. Properly treated plastic surfaces can be changed from hydrophobic to hydrophilic or vice versa. Several surface modification methods have been studied to facilitate plastics sorting using froth flotation [15,17–19]. However, each modification or treatment method had its own drawbacks. For example, the use of chemical reagents for surface modification [20,21] takes a relatively long time to complete and produces secondary pollution problems such as generating chemical contaminated wastewater. With ozonation modification [18], emission of the remaining ozone could happen, generating air pollution problems such as odor issues and requiring expensive control efforts. Other modification methods such as plasma treatment [4] and flame treatment [17] can physically modify the plastic surface by reaction or exposure to the generated corona discharge. In these methods, the plastic surfaces can be attacked by high-energy sources. Thus, hydrophilic or oxygen functional groups such as hydroxyls, carbonyls, and carboxylic groups are generated on the surfaces of plastics treated with flame or plasma. These hydrophilic moieties or oxygen containing functional groups may be water-wettable or miscible [17]. These physicochemical methods are difficult and relatively expensive because they require special or expensive facilities.

The purpose of the current study is to find an effective or economic physicochemical treatment or modification method for selective separation of hazardous brominated plastic such as ABS with BFRs from plastic wastes. This study combined mild heat treatment and froth flotation techniques to create different degrees of hydrophilic moieties on ABS surfaces from other plastics to selectively separate ABS from heavy plastics.

2. Materials and method

2.1. Materials

A mixture of four plastics (PC, PMMA, PS and ABS) with intermediate density ranging from 1.03 to 1.19 g/cm^3 was used as the target plastics for this study. PC and PMMA were purchased from the Kasai Sangyo Co., Ltd, Japan while PS and ABS were obtained from Hankook Resin Co. Ltd, Korea. Plastic samples were cut into a uniform size (10 × 10 × 2 mm). The particles generated during the sawing process using a vertical band saw and stainless steel pliers were attached to the surfaces of cut samples and cleaned using a clean tissue.

Ten pieces of each plastic sample were exposed to mild heat treatment for surface modification and then stirred in a glass reactor with tap water using froth flotation. The surface colors of plastic pieces were different, which helped with analyze the concentration of each plastic through manual sorting at the end of the flotation experiment. In froth flotation experiments, the frothing agent added to the flotation medium to get better floating plastic samples was MIBC (2-Methyl-4-pentanol) purchased from Daejung Chemicals and Metals Co., Ltd, Korea.

2.2. Mild heat treatment by a thermal oven

The prepared pieces of plastic (40 pieces of a plastic mixture including 4 types of plastic) were treated in a thermal oven machine (Model KT-1800H, Kitchen-Art Co., Ltd., Korea) to modify the surfaces of the plastic samples. Plastics samples were spread on the grille plate of the thermal oven for heat treatment at various times ranging from 0 to 100 s before analysis of the surface changes and froth flotation. The thermal heat treatment in this study generated 1.4 kW h, which was defined as a mild heat treatment at 100 °C during the given length of treatment.

2.3. Surface characterization tests

The effects of mild heat treatment on the plastic surfaces were investigated through contact angle measurements. A contact angle meter (FEMTOFAB Co., Ltd.) was applied to measure the contact angle of distilled water drops on the plastics' surface. All reported values for the measured contact angles were the average of at least five different samples measurements. The contact angle values were measured for each piece of plastic sample before and after the mild heat treatment in the thermal oven. To observe the changes in surface morphology and roughness associated with the mild heat treatment, scanning electron microscopy, SEM (JSM-6500F, JEOL, Japan) was employed. X-ray Photoelectron Spectroscopy (XPS) analyses were performed by using the XPS Spectrometer (K-Alpha, Thermo Scientific, USA) to identify the elemental states of carbons on the plastic surfaces before and after the mild heat treatment.

2.4. Floating application for ABS separation

The froth flotation experiments for heat-treated plastics were conducted using a flotation system with a glass reactor, a height of 150 cm and an inner diameter of 7 cm as shown Fig. 1. Air was supplied to the flotation system by an air-pump (MP-Σ300, Sibata, Japan) with a flow rate of 0.5 L/min. A controlled amount of dry air was provided to the glass reactor through a ceramic diffuser plate located at the bottom of the flotation system to produce gas bubbles for the experiment. Tap water (400 mL) was used for flotation tests with temperatures at 25–30 °C and MIBC 1 g/L was added into the mixture as a frother to enhance flotation efficiency. Ten pieces of each plastic per flotation experiment were put into the flotation reactor. The auto overhead stirrer (WiseStir, Daihan scientific Co., Ltd.) was employed to thoroughly mix the plastic, with air bubbles added at various steady mixing speeds (i.e., 50, 100, 150, 200, 250, 300 rpm). The flotation time was 2 min per experiment. Calculation of the recovery and purity of each plastic recovered was based on counting the number of each settled plastic after removing the settled plastics from the flotation reactor. The calculation was based on the average value of three results per condition. The froth flotation conditions, including the effects of airflow rate, water temperature used for the flotation and concentration of the