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Selective separation of ABS/PC containing BFRs from ABSs mixture of WEEE by developing hydrophilicity with ZnO coating under microwave treatment

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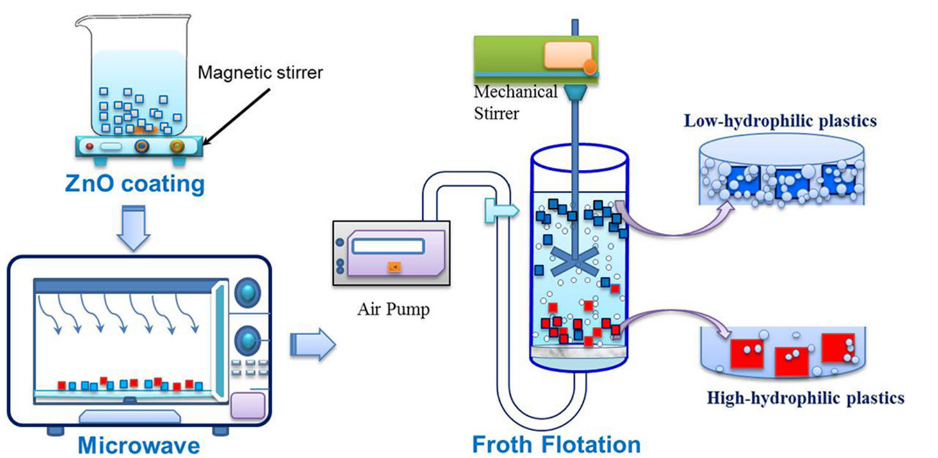
HIGHLIGHTS

- The combined ZnO coating and microwave treatments rearranged the ABS/PC surface.
- Selective development of hydrophilicity facilitated complete separation of ABS/PC.
- The combined treatments minimized the emission of hazardous brominated chemicals.
- Optimized froth flotation was crucial for selective separation of ABS/PC.

GRAPHICAL ABSTRACT



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ABSTRACT

This study reports a simple and facile method to separate plastic wastes of acrylonitrile–butadiene–styrene (ABS) and ABS-based plastics (blends of ABS) in waste electronic and electrical equipment (WEEE) by froth flotation after inducing hydrophilization by ZnO coating under microwave treatment. ABS-based plastics containing brominated flame retardants (BFRs) can release hazardous substances, such as hydrogen bromide and brominated dioxins, during disposal or recycling activities. ABS and ABS-based plastics are typical styrene plastics with similar properties and it is, therefore, difficult to separate them selectively for recycling. We used 2-min microwave treatment to rearrange and change the molecular mobility on the surface of the ZnO-coated ABS with increased hydrophilic surfaces, which eased the selective separation of the ABS/polycarbonate (PC) blend containing BFRs from the remaining plastics. Therefore, the combined ZnO coating and microwave treatments can facilitate the selective separation of ABS/PC blend plastics with a recovery and purity of 100% and 91.7%, respectively, in a short flotation time of 2 min. Based on these findings, the combination of ZnO coating-microwave treatment and froth flotation can be applied for the selective separation of ABS-based plastics, leading to improved plastic recycling quality.

1. Introduction

The estimated generation of total waste electrical and electronic equipment (WEEE) was 16, 11.7, 11.6, and 1.9 million tons in Asia,

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America, Europe and Africa in 2014, respectively [1]. In South Korea, about 19.2 kg/person of electrical and electronic equipment (EEE) was sold in 2012 and about 15.9 kg/person of WEEE was generated in 2014 [1,2]. The significant increase in WEEE generation has led to the establishment of many local recycling programs in Korea. About 2.5 kg/person of WEEE was recycled in Korea in 2010 [3]. The target of recycling and recovery in Korea is about 4.8 kg/person/year in 2017 [4]. The main recycled part in WEEE is plastic material which accounts for about 30–50% (w/w) of WEEE [5–8].

Acrylonitrile butadiene styrene (ABS), a copolymer [9,10], has been widely used in consumer electronics. In addition, ABS is frequently blended with other plastic types to increase physicochemical properties and mechanical strength and to decrease production expense. To increase the mechanical and thermal properties, ABS is blended with polycarbonate (PC), which helps to provide a stronger heat resistance and lowers the production cost. ABS is also mixed with other plastics such as polymethyl-methacrylate (PMMA), high impact polystyrene (HIPS), polybutylene terephthalate (PBT), styrene–acrylonitrile (SAN), and polyvinyl chloride (PVC) [11]. Nevertheless, blended plastics still retain some of the properties of each component. ABS and its blends, especially ABS/PC, have become widely used commercial plastics in EEE products. ABS and ABS/PC are also used in the production of cabinets for computer, telephones, television sets and some electrical appliances [5,10,12–14]. Thus, they constitute around 50 wt.% of total E-waste plastics [8,10]. Some E-waste can have an ABS fraction of 44%–69% of and an ABS/PC fraction of 20%–22% in CPUs and CRT monitors, respectively [5]. The keen attention on making more valuable products from plastic waste in WEEE streams has increased the need for efficient separation of ABS and ABS/PC blends from WEEE plastics [14].

Further, the addition of numerous hazardous additives into ABS blends or mixture, in particular flame retardants such as brominated flame retardants (BFRs), has introduced difficulties during recycling and disposal processes of WEEE plastics. Flame retardants are used to prevent damaging effects from the burning of EEE plastics. ABS plastics contain about 10% of BFRs and can reach up to 30% on printed circuit boards (with a main component of ABS/PC blend) [13,15]. In addition, when part of the waste flow for recycling or disposal activities, halogen-containing components affect not only recycled products but also environment pollution potential due to the formation of highly toxic brominated chemicals [8,12,16]. Therefore, in the end-of-life management of WEEE plastics, the BFR-containing plastics must be properly separated from the waste stream and recycled efficiently. The selective separation of BFR-containing plastics will help to eliminate the potential environment risk and obtain a high quality of recycled plastics.

Various studies have examined the separation of halogen-containing plastic from plastic mixtures [17,18]. Nevertheless, difficulties remain in the separation of BFR-containing plastics properly from a mixture with similar characteristics such as styrene-containing plastics – PS, HIPS, ABS, or ABS-based plastics. For those plastics, the effective separation method is to utilize infrared spectroscopy using near infrared (NIR) devices for efficient sorting of styrene plastics [10]. However, as NIR cannot identify BFRs in plastics, it is impossible to separate BFR-containing plastics from a mixture unless it is combined with an X-ray fluorescence device. These techniques require expensive instruments and the identification efficiency depends on the accuracy of the machines. Flotation is also an efficient method for ABS and PS separation based on differential wettability on the plastic surface after the surface treatments [19,20–22].

As the C═C bond in butadiene and the C≡N bond in polyacrylonitrile of abs are unstable, ABS is easily oxidized by free oxygen radicals or hydrogen peroxides that are produced during disposal or recycling processes [23]. This study hypothesizes that the ZnO coating in an alkaline solution will help to promote the hydrophilicity of the ABS surface under microwave energy, which is expected to be an effective method for building rapid surface interaction with ZnO [24,25]. Then, applying froth flotation can separate the treated ABS-based plastics from the mixture. This study also proposes a mechanism for the removal of Br in ABS plastic.

Table 1
Weight fraction (%) of the sorted plastic samples.

Plastics	d < 4.75 mm	d > 4.75 mm
ABS1	25.9	74.1
ABS2	17.5	82.5
ABS3	45.3	54.7

2. Materials and methods

2.1. Materials

Samples of ABS and ABS-based plastic wastes were obtained from Ulsan Resources Recycling Co., Ltd, Ulsan, Korea after dismantling of WEEE. Three types of ABS plastic wastes were identified with the analysis of Fourier Transform Infrared (FT-IR) transmittance spectra. Plastic waste samples were screened by using sieves of 4.75 mm, then sorted according to size (Table 1) (ABS1, AB2 and ABS3). The $Zn(CH_3COO)_2{\cdot}H_2O$ and NH_4OH were purchased from Samchun Pure Chemical Co., Ltd, Korea. To promote air bubbles in flotation, 2-methyl-4-pentanol (MIBC) purchased from Daejung Chemicals and Metals Co., Ltd, Korea was added in the flotation medium. The MIBC concentration was adjusted to 1 mL of MIBC per 1000 mL flotation medium to avoid any significant volume change of the test flotation medium (water).

2.2. ZnO coating and microwave treatment

The ZnO coating solution was prepared by dissolving a 0.2 M solution of $Zn(CH_3COO)\ _2{\cdot}H_2O$ in distilled water. NH_4OH was dropped into the solution at an approximate rate of 3–5 mL/min with stirring by a magnetic mixer until the precipitates disappeared. In the solution, the following reaction occurred:

$$Zn(CH_3COO)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4CH_3COO$$

The solution pH was maintained over 10 to get the ZnO phase. All of the ABS plastic samples were soaked in the prepared ZnO solution for 3 h and then dried in air at a room temperature at $20 \pm 1\,^{\circ}C$. After drying, microwave treatment was conducted in a microwave oven (Dongbu Daewoo Electronics Corp., Korea) at 1120 W with a frequency of 2450 MHz to modify the plastic surfaces for 2, 4, and 6 mins. Then, a froth flotation technique was used to determine the floating ability of the ABS-based plastics.

2.3. Flotation experiment

Flotation was performed using a flotation chamber (height of 155 mm and inner diameter of 95 mm) which contained 1000 mL tap water as the flotation medium. Airflow was supplied by an air pump (MP-Σ300, Sibata, Japan) through a 5mm-thick diffuser plate located at the bottom of the flotation chamber for making bubbles. To increase the mixing and interaction of plastics with air bubbles, an overhead stirrer (WiseStir, Daihan scientific Co., Ltd.) was employed with an adjustable mixing speed of 0–300 rpm.

2.4. Characterization methods

The scanning electron microphotographs were obtained by using FE-SEM (JSM-6500F, JEOL, Japan) to observe the changes in