

Separation of Hazardous Brominated Plastics from Waste Plastics by Froth Flotation after Surface Modification with Mild Heat-Treatment

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Abstract—This study evaluated to facilitate separation of ABS plastics from other waste plastics by froth flotation after surface hydrophilization of ABS with heat treatment. The mild heat treatment at 100°C for 60s could selectively increase the hydrophilicity of the ABS plastics surface (i.e., ABS contact angle decreased from 79° to 65.8°) among other plastics mixture. The SEM and XPS results of plastic samples sufficiently supported the increase in hydrophilic functional groups and decrease contact angle on ABS surface, after heat treatment. As a result of the froth flotation (at mixing speed 150 rpm and airflow rate 0.3 L/min) after heat treatment, about 85% of ABS was selectively separated from other heavy plastics with 100% of purity. The effect of optimum treatment condition and detailed mechanism onto separation efficiency in the froth flotation was also investigated. This research is successful in giving a simple, effective, and inexpensive method for ABS separation from waste plastics.

Keywords—ABS, hydrophilic, heat treatment, froth flotation, contact angle.

I. INTRODUCTION

ACRYLONITRILE-BUTADIENE-STYRENES (ABS) are non-biodegradable and are also considered hazardous substances because of containing brominated atoms as an flame retardants additive to reduce fire damage [1]. Many ABS products with brominated flame-retardants (BFRs) are mainly occupying around 20 wt% of the main resins used by in electronics such as electronic and electrical equipment [2]-[4]. 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 proper management, in particular, incineration or heating processing, bromines from ABS could be released as hazardous 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 [5].

In present, the sustainable plastic waste management have focused on plastic recovery and recycling rather than other disposal methods because of their economic and environmental advantages [6]-[9]. In a realistic estimate in

Korea, about 59 % of the generated plastic waste is sent to recycling and this rate continues to grow in Korea [10]. Moreover, the recycled plastic is qualitative and valuable when the components of plastics for recycling have high purity and high degree of separation. However, the plastic wastes have high incompatibility for example, differences of melting points, thermal stabilities, chemical interactions and chemical components [11]. In particular, some mixtures contain fire retardant thermoplastics such as ABS with BFRs maybe make the market prices of post-consumer products for recycled plastics are easily depreciated [1]. Therefore, the development of methods for selective plastic separation from the mixture is necessary.

There are many methods based on the difference of plastic specific gravity or density [12]-[15] and even manual sorting. Nevertheless, it is difficult to separate plastics which are only slight differences in their density and surface properties [1], [11], [16]-[19]. Numerous surface modification techniques, which base on hydrophobicity of plastic, have been also employed for the production of hydrophilic plastic surfaces by using chemical agents, physical treatment. These methods can increase the hydrophilic functional (ether, hydroxyl and carboxyl) groups on the plastic surfaces [20]. Then, using froth flotation technique separates the modified plastics [21]-[25]. This is a method was considered an effective method for the separation of plastics that have similar density or surface properties. However, modification or treatment of plastic surfaces had its own disadvantages. For example, using chemical reagent methods [24], [25] maybe have secondary pollution problem by wastewater. On the other hand, these methods usually take a long time to modify plastic surfaces. Using flame treatment [26] or ozonation [27] can modify the plastic surface by reaction or exposure to the generated corona discharge but need high-energy sources or special, expensive facilities.

In this study, an effective or economic modification method was developed for selective separation of hazardous brominated plastic such as ABS with BFRs from plastic wastes. The combination of mild heat treatment and froth flotation techniques can to create surface rearrangement of ABS. It makes a different degree of hydrophilic moieties on ABS surfaces from other plastics to selectively separate ABS from heavy plastics. The influence of mixing speed and airflow rate on flotation behavior of plastics was investigated.

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II. MATERIALS AND METHOD

A. Materials

A mixture of five plastics (PVC, PC, PMMA, PS and ABS) was cut into a uniform size ($10 \times 10 \times 2$ mm) was used in this study. PVC, PC, and PMMA were purchased from the Kasai Sangyo Co., Ltd, Japan while PS and ABS were obtained from Hankook Resin Co. Ltd, Korea. 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. 2-Methyl-4-pentanol (MIBC) (Daejung Chemicals and Metals Co., Ltd, Korea) used as the frothing agent added to the flotation medium (water) to get better floating plastic samples.

B. Mild Heat Treatment by a Thermal Oven

The plastic samples were treated in a thermal oven machine (Model KT-1800H, Kitchen-Art Co., LTD., Korea) for certain times (20, 40, 60, 80, 100 sec). The thermal heat treatment in this study generated 1.4 KWh, which was defined as a mild heat treatment at 100°C during the given length of treatment. After mild heat treatment, samples were cooled down at room temperature.

C. 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. Air was supplied to the flotation system by an air-pump with a flow rate of 0.5 L/min through a ceramic diffuser plate at the bottom of the reactor. Tap water was used for flotation tests. A certain amount of MIBC (1 g/L) was added into the reactor during the experiments. To thoroughly mix the plastic, The auto stirrer (WiseStir, Daihan scientific Co., Ltd.) was employed at various steady mixing speeds (i.e., 50, 100, 150, 200, 250, 300 rpm). The flotation time was 2 min per experiment. At the end of the flotation test, 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 counted on the average value of three results.

D. Surface Characterization Tests

A contact angle meter (FEMTOFAB Co., Ltd.) was used to measure contact angle of distilled water drops on the plastics' surface before and after the mild heat treatment. Scanning electron microscopy (SEM) (JSM-6500F, JEOL, Japan) was employed to observe the changes in surface morphology. X-ray Photoelectron Spectroscopy (XPS) analyses were performed by using the XPS Spectrometer (K-Alpha, Thermo Scientific, USA) to identify change of the elemental states on the plastic surfaces before and after the mild heat treatment.

III. RESULTS AND DISCUSSION

A. Change of Contact Angles by Mild Heat Treatment

The effects of mild heat treatment on the plastic surfaces were investigated through contact angle measurements are shown in Fig. 1. All values for the report were the average of at least five different samples measurements. For only the mild heat treatment at 20 sec, the contact angle of the PVC, PMMA and ABS slightly decreased but PC and PS increased. However, at treatments lasting 60 sec, there is a significant decrease in contact angle of ABS 79.5 to 63.8° . While the contact angles of PVC increased upto 89.8° and PC, PMMA, and PS decreased slightly by about 4.1 , 0.6 and 4.4° , respectively. The change in contact angle value depends on physical and chemical elements of the surface components, the surface roughness on the plastic surfaces [28]-[30]. The contact angle decrease indicates that the treated ABS surface maybe received more hydrophilic function groups such as hydroxyl groups and carboxyl groups [16], [28], [31]. Thus, after mild heat treatment, the ABS surfaces could be become more water wettable and hydrophilic than the untreated ABS samples and other plastics.

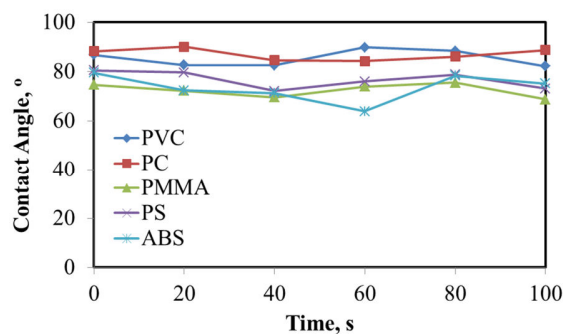


Fig. 1 Contact angle changes in the plastic surfaces before and after mild heat treatment at various times

B. Field Emission Scanning Electron Microscope (FE-SEM)

Field emission scanning electron microscope (FE-SEM) images were used to visualize the morphology and roughness changes on the surfaces of the heat-treated plastic samples. Fig. 3 shows the significant changes in morphology compared to the untreated samples of plastic surfaces. In particular, the ABS surfaces had larger pitted areas than the other treated plastic samples after heat treatment. ABS with BFRs showed a substantial decrease in the contact angle of water drops on the ABS surfaces after heat treatment, which can be subsequently used to facilitate the selective separation of ABS during froth flotation experiments.

C. X-Ray Photoelectron Spectroscopy (XPS)

A high-resolution XPS spectrum was further conducted to investigate the change of element content of the plastics' surfaces before and after heating at 100°C for 60 sec (Table I). As shown in Table I, after the mild heat treatment, the content of nitrogen elements on the ABS surface significantly increased from 2.75 to 4.90% after mild heat treatment. The

increase of the nitrogen element can be explained by the hydrophilic groups of ABS which is nitriles carbon (C≡N) greatly increased on ABS surface. This observation corresponds to the contact angle measurements. The increase of the hydrophilic groups can lead to a decrease in the contact angle of water drops on the heated plastic surfaces. This indicates that mild heat treatment can induce or develop more hydrophilic moieties on the ABS surfaces [24], [25] and facilitate easy or selective separation of ABS from the plastic mixture.

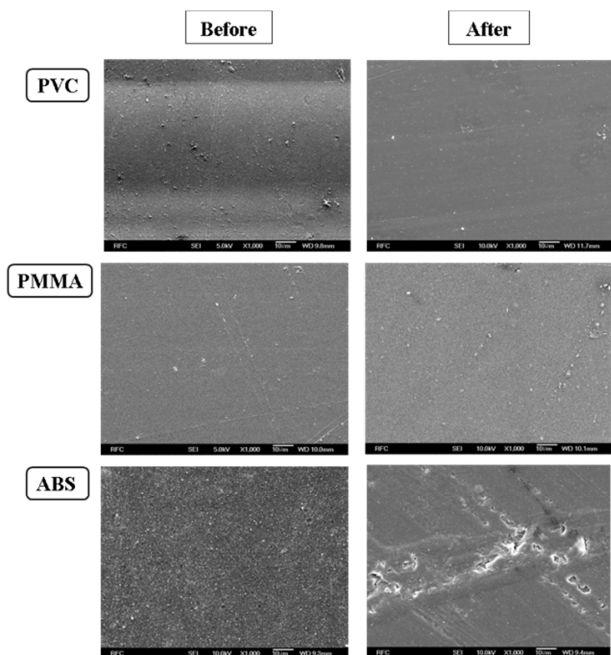


Fig. 2 SEM images of plastics before and after the mild heat treatment at 100°C for 60 sec

TABLE I
CHANGES IN THE ELEMENT CONTENT (WT%) OF THE ABS BEFORE AND AFTER MILD HEAT TREATMENT AT 100°C FOR 60 SEC

Plastics	C1s (%)	O1s (%)	N (%)
Before	69.10	21.11	2.75
After	74.79	16.79	4.90

D. Application of Froth Flotation for Separation of ABS

The froth flotation experiments were conducted at various mixing speeds, with temperatures of 25–30°C, flotation time of 2 min, and MIBC concentration of 1 mg/L. airflow rate also changed at certain level (0.1, 0.3, 0.5 L/m). Fig. 3 shows the change in floating behaviors with the application of froth flotation to plastic samples treated with mild heat at 100°C for 60 sec as the mixing speed was increased from 0 to 300 rpm.

Fig. 3 (a) shows the floating rate of the treated ABS decreased with increased mixing speed. However, the treated PVC is also settled down when the mixing speed increased. At a mixing speed of 200 rpm, the recovery rate of ABS reached 100% at a mixing speed of 200 rpm, but the purity of ABS was too low (50 %) due to contamination by PVC and PS.

Besides the mixing speed, the flow rate of the air was determined to be another important factor in froth flotation for the separation of plastics. When changing the air flowrate from 0.5 to 0.1 L/min and the lower mixing speed (150 rpm), the recovery rate of the treated ABS slightly decreased by 83.3 %, but the purity significantly increased up to 93 % even contaminating of some PVC (Fig. 3 (b)). Therefore, the selective separation of ABS by froth flotation was more effective at lower air flowrate and lower mixing speed.

When froth flotation was conducted at a mixing speed of 150 rpm, and airflow rate of 0.3 L/min, the settled or submerged heat-treated ABS showed 100% purity with a recovery rate of 85%, leaving only 15% of the ABS afloat (Fig. 3 (c)). Therefore, maximum purity can be achieved with a mixing speed of 150 rpm and airflow rate of 0.3 L/min. As the airflow rate decreased from 0.5 to 0.1 L/min, most of the remaining plastics (PVC, PC, PMMA, and PS) began to float. In addition, increasing the flow rate from 0.1 to 0.3 L/min produced helped to increase the purity of settling ABS up to maximum rate in compare with the remaining plastics. Thus, 150 rpm and 0.3 L/min are as the optimum condition for the highest purity while maintaining a high recovery rate for selective separation of ABS with BFRs from the plastic waste mixture.

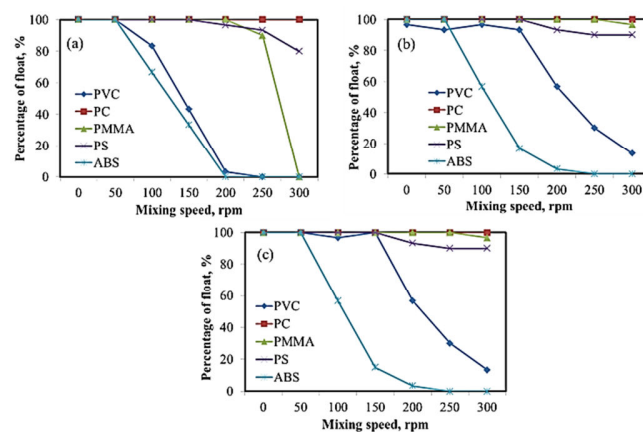


Fig. 3 The flotation rate of the mild heat-treated plastic as a function of mixing speed and airflow rate: 0.5 L/min (a), 0.1 L/min (b), 0.3 L/min (c) during froth flotation

IV. CONCLUSIONS

In the study on selective separation of the hazardous brominated plastic ABS from plastic waste mixtures (PVC, PC, PMMA, PS and ABS), the following conclusion was reached: mild heat treatment using a thermal oven at 100°C for 60 sec makes the surfaces of ABS plastics more hydrophilic than other plastics. The optimum flotation conditions for the highest recovery rate (85%) and the maximum purity (100 %) during selective separation of ABS from the plastic mixture were as follows: mixing speed 150 rpm, airflow rate 0.3 L/min, floating medium (water) temperature 25–30°C, floating agent (MIBC) 1 mg/L and floating time 2 min. Thus, the mild heat treatment by thermal oven shows effective selectivity of ABS

with BFRs. In addition, this combined technique can be a simple, effective, economic method for selective separation of ABS with BFRs from heavy plastic wastes.

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