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Development of hydrophobicity and selective separation of hazardous chlorinated plastics by mild heat treatment after PAC coating and froth flotation

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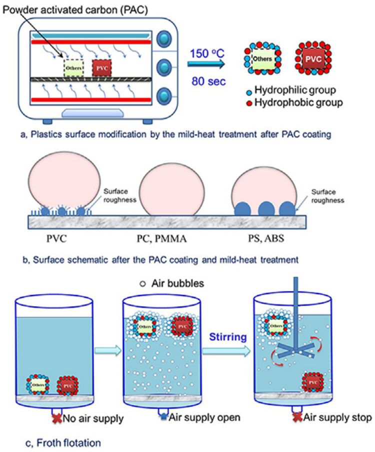
HIGHLIGHTS

- PAC coating and mild heat treatment were combined for selective wetting of PVC.
- The combined treatment rearranged the PVC surface and increased its hydrophobicity.
- Optimized froth flotation was crucial for selective separation of the treated PVC.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyvinyl chloride (PVC) containing chlorine can release highly toxic materials and persistent organic pollutants if improperly disposed of. The combined technique of powder activated carbon (PAC) coating and mild heat treatment has been found to selectively change the surface hydrophobicity of PVC, enhancing its wettability and thereby promoting its separation from heavy plastic mixtures included polycarbonate (PC), polymethyl methacrylate (PMMA), polystyrene (PS) and acrylonitrile butadiene styrene (ABS) by means of froth flotation. The combined treatments helped to rearrange the surface components and make PVC more hydrophobic, while the remaining plastics became more hydrophilic. After the treatments at 150 °C for 80 s the contact angle of the PVC was greatly increased from 90.5 to 97.9°. The SEM and AFM reveal that the surface morphology and roughness changes on the PVC surface. XPS and FT-IR results further confirmed an increase of hydrophobic functional groups on the PVC surface. At the optimized froth flotation and subsequent mixing at 150 rpm, 100% of PVC was recovered from the remaining plastic mixture with 93.8% purity. The combined technique can provide a simple and effective method for the selective separation of PVC from heavy plastics mixtures to facilitate easy industrial recycling.

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1. Introduction

Worldwide plastics production in 2010 was more than 300 million with an average annual growth rate of 5–6% [1–3]. Plastics are increasingly used in packaging, building, construction, transportation, electrical-electronic fields, etc. The expanded plastic consumption has consequently increased the generated plastic waste, which poses significant difficulties in proper management and disposal [3,4]. Plastic wastes account for about 9–30% by weight of municipal solid waste depending on the community or area [1,4]. As many plastics are non-biodegradable and hazardous, they cannot be disposed of to the natural environment. The options available for end-of-life management activities include landfilling, mechanical recycling, biological recycling and thermal chemical recycling such as heat utilization for energy recovery and pyrolysis [1,4,5].

During disposal activities, plastic can release hazardous compounds and some plastics such as polyvinyl chloride (PVC) that contains halogen elements are considered highly toxic materials [6]. Many PVC products with flame retardant properties are mainly used in electronic and electrical equipment [5,6]. PVC products containing chlorine are also applied to coating computer cables and wires [6]. According to statistics in the EU, PVC waste accounts for about 4.7 million tons in 2010 and could be increased to 6.2 million tons in 2020 [7]. Incineration of plastics containing chlorine can release toxic pollutants such as hydrochloric acid, polychlorinated benzo para dioxin, polychlorinated dibenzo furan, chlorofluorocarbon, polycyclic aromatic hydrocarbons and thus PVC incineration limits the application of waste-to-energy technologies for plastic mixtures containing PVC [4–6,8].

Many viable strategies for sustainable plastic waste management have aimed to promote plastic waste recovery and recycling rather than other disposal methods because of their economic and environmental advantages [3,4,9–12]. About 1.1 million tons of plastics are also reused in Korea annually [13] and the recycling target rate of plastic waste has continued to grow [14]. However, plastic wastes have different physicochemical properties such as melting points, chemical components, thermal stabilities and chemical interactions [10,12,15,16]. Some plastics contain fire retardants, such as hazardous chlorine (PVC), which renders the components of plastic waste mixtures highly incompatible. Therefore, they need to be separated into different types to upgrade value or market price of the secondary plastic products for their recycling [17]. However, the separation of each plastic type from mixed plastics is challenging.

The many methods that been applied to plastic separation based on the plastic type, chemical structure or their typical densities include gravity separation [18,19], air tabling (dry gravity method) [20], triboelectric separation [20–24], selective dissolution [25,26], hyperspectral imagery [27,28] and even manual sorting. Numerous surface modification techniques have also been used to produce hydrophilic plastic surfaces that selectively facilitate plastics separation using froth flotation techniques combined with plasma treatment, chemical reagent [16,29–32], ozonation modification [33–35], boiling treatment [36], and flame treatment [37,38]. Generally, all plastics have naturally hydrophobic surfaces and readily float with the aid of air bubbles. The selected treatment system must render at least one plastic hydrophilic, resulting in no air attachment. This can be achieved by the addition of a reagent that reacts with the surface layer of the plastic [39,40]. The hydrophobicity and gravitation are two main factors that are applied in flotation techniques for plastic separation [41]. Therefore, most of these methods have tried to modify the plastic surfaces to produce hydrophilic species on the surface and modify water-based coatings to be more suitable for flotation processing. However, using chemical reagents for surface modification is time consuming and produces additional wastewater issues such as secondary pollution or ozone by-produce in ozonation modification.

Physical modification techniques provide potential alternative methods for selectively wetting plastic surfaces. Plasma treatment and flame treatment method are effective to modify the PVC surface by hydrophobic recovery prior to the second stage of flotation. Besides, hydrophilic or oxygen functional groups such as hydroxyls, carbonyls, and carboxylic groups are generated on the surfaces of plastics with some oxidation techniques such as ozonation, plasma or flame treatment (PET, PC) [37,38]. However, these methods require special or expensive facilities.

PVC has a higher dielectric-loss coefficient than the other plastics do [42,43]. Exposure to mild heating may not be effective for PVC, which is relatively unaffected, whereas other plastics selectively melted with sufficiently high efficiency may be hydrophilized thermally even in a mixture [44]. PVC's resistance is due to the scission of the C—C main chain of plastics followed by the vaporization of fragment molecules (probably small hydrocarbons) [6]. These variations influence the surface reactions, especially for other plastics (except PVC), which increases the hydrophilic functional (ether, hydroxyl and carboxyl) groups [30]. In the current study, a mild heat treatment with lower energy consumption was used as an alternative surface treatment technique. Mild heat treatment was used to change the physical or chemical property of thermoplastic surfaces quickly. Then, the froth flotation technique was investigated for the selective separation of hazardous chlorinated plastics such as PVC from heavy plastic mixtures.

2. Materials and methods

2.1. Materials and chemicals

The mixture of plastics investigated included polycarbonate (PC), PVC, polymethyl methacrylate (PMMA), polystyrene (PS) and acrylonitrile butadiene styrene (ABS) with densities of 1.14, 1.43, 1.19, 1.04, and 1.05 g/cm^3, respectively. PC, PVC and PMMA were obtained from Kasai Sangyo Co., Ltd, Japan. PS, and ABS from Hankook Resin Co. Ltd, Korea were cut into cubes sized 10 × 10 × 2 mm using stainless scissors. These plastics were selected because they have densities above 1 g/cm^3 (i.e., higher than that of water). The pictures of the original plastic samples are shown in Fig. 1. The plastics used for this study have different colors that can help to calculate the concentration of each plastic by manual sorting at the end of flotation experiment.

Powder activated carbon (PAC; Activated Charcoal Norit®, Sigma-Aldrich, Co., Ltd), 10 g, was used as a heat absorbent agent to coat the plastics surface. The frother, methyl isobutyl carbinol (MIBC), was obtained from Daejung Chemicals and Metals Co., Ltd and was used to promote cavitation in the flotation medium.

2.2. Mild heat treatment of PAC-coated plastics

One hundred pieces of each plastic were prepared for pretreatment by mild heat, and then for froth flotation. Twenty-five pieces of each plastic were mixed and shaken with PAC (2 g) manually for 15 min in such a way that the PAC covered the whole surface of the plastic sample. The PAC-coated plastics were spread on the grill plate of a thermal oven machine (Model KT-1800H, Kitchen-Art Co., LTD., Korea) at 150 °C to modify their surfaces. Five pieces of each type of these plastic samples with and without the PAC coating were used for the heat treatment. The plastic samples were treated by mild heat at five different times (i.e., 20, 40, 60, 80, and 100 s) and then cooled down to room temperature of 25 ± 1 °C. The treated plastics were analyzed for their surface changes according to the methods described in the following section. Based on