

Separation of Chlorinated Plastics and Immobilization of Heavy Metals in Hazardous Automotive Shredder Residue

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

Abstract—In the present study, feasibility of the selective surface hydrophilization of polyvinyl chloride (PVC) by microwave treatment was evaluated to facilitate the separation from automotive shredder residue (ASR), by the froth flotation. The combination of 60 sec microwave treatment with PAC, a sharp and significant decrease about 16.5° contact angle of PVC was observed in ASR plastic compared with other plastics. The microwave treatment with the addition of PAC resulted in a synergetic effect for the froth flotation, which may be a result of the 90% selective separation of PVC from ASR plastics, with 82% purity. While, simple mixing with a nanometallic Ca/CaO/PO₄ dispersion mixture immobilized 95-100% of heavy metals in ASR soil/residues. The quantity of heavy metals leached from thermal residues after treatment by nanometallic Ca/CaO/PO₄ was lower than the Korean standard regulatory limit for hazardous waste landfills. Microwave treatment can be a simple and effective method for PVC separation from ASR plastics.

Keywords—Automotive shredder residue, microwave treatment, chlorinated plastics, separation, heavy metals, Immobilization, separation.

I. INTRODUCTION

ELV (End of Life Vehicles) are increasingly important secondary source of ferrous, nonferrous metals and plastics. About 1 million ELVs are generated every year in Korea [1], [2]. The most problematic fractions of ELV recycling treatments which have been mainly landfilled/incinerated in the past are shredding residues (SR, automobile shredder residue (ASR) from ELV composed of plastics, small metals, wires, rubber, textiles etc [3]. ASR can be classified as ‘‘hazardous waste’’, on the basis of the presence of hazardous substances, such as chlorinate/brominated plastics (PVC/BFRs), persistent organic pollutants (POPs), heavy metals etc. [2], [3]. The Korea directive set the recycling target including thermal recycling as 95% by 2015 [4]. However, during thermal recycling, PVC can lead to the generation of environmentally hazardous chlorinated compounds (HCl and dioxins). As a consequence, the amount of heavy metals and chloride ions in the residues obtained from the ASR can be remarkably high. Therefore, it is so important to effectively separate PVC/or safely dispose ASR residues.

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Although the microwave techniques are developing, little work is currently available in published literatures on surface hydrophilicity of PVC [5]-[7]. PVC is known to have a higher dielectric-loss coefficient than the other plastics [8]. Exposed to radio-microwave frequency, PVC may be selectively heated with sufficiently high efficiency even in a mixture and may hydrophilized/decomposed [9]. This is due to the scission of the C-C main chain of PVC followed by the vaporization of fragment molecules (probably small hydrocarbons) [9]. These variations will influence the surface reactions especially for PVC, which increases the hydrophilic functional (ether, hydroxyl and carboxyl) groups (i.e. C-Cl (ether carbon)) increases. Further, carbon materials are, in general, very good absorbents of microwaves, i.e., they are easily heated by microwave radiation [10]. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties, to be used as microwave receptors, in order to heat other materials indirectly, or to act as a catalyst and microwave receptor in different heterogeneous reactions.

Our recent investigations showed that the nanometallic Ca/CaO mixture being the most effective reagent for efficient hydrodechlorination of polychlorinated biphenyl (PCB) (up to 98%) in contaminated soil [11]. When the targeted heavy metal was cesium, soil immobilization (even pozzolanic cement) could be achieved with supplementary additives, such as sodium phosphate (NaH₂PO₄)/[PO₄], in a moisturized atmosphere, with cesium being trapped into the immobile Ca/PO₄ salts [12].

In this research, first we evaluated the selective surface modification of PVC by microwave treatment, as a method for separating PVC from hazardous ASR and second, heavy metals immobilization in ASR soil/residue with novel nanometallic Ca/CaO/PO₄ composite to reduce the risk of environmental emissions and the landfilling leaching.

II. MATERIALS AND METHODS

A. ASR Plastics and Soil/Residues Sample Collection Characterization and Treatment

The ASR polymer samples and ASR soil/residue were collected at automobile recycling/shredding plants in Pohang, Korea (Fig. 1). Each polymer composition in ASR was identified by recording their IR spectra using with FT-IR Spectrometer (Perkin-Elmer, Spectrum one). The individual polymer compositions in ASR were quantified. The samples used for each test for microwave treatments and froth flotation

experiments consist 10 pieces of each ASR plastics. The microwave radiation was produced with the help of a microwave oven (Dongbu Daewoo Electronics Corp., KR-G20EW), producing a frequency of 2,450 MHz with 1,120 W as the rated microwave input. For the powder activated carbon (PAC) pretreatment as a heat absorbent, we used the commercial product of PAC. Mixtures of ASR plastic samples and the PAC (10 g) were shaken by hand in 50 ml centrifuge tubes for 10 min, in order to completely coat the plastic samples by PAC. Ten pieces of each plastic sample, both untreated (control) and pretreated with PAC, were heated in the microwave oven on glass plate for the specified time intervals (i.e., 60 sec).

To selectively separate PVC from plastic samples, froth flotation experiments were conducted with different conditions. Main glass reactor which had 14cm of height, 7cm of inner diameter and 0.54dm³ of volume, was connected with the mini air pump (MP-Σ300, Sibata, Japan) and ceramic bubble diffuser was equipped at the bottom of glass reactor to generate small size of air bubble that enhanced the flotation efficiency of plastic samples. The auto overhead stirrer (WiseStir, Daihan scientific Co., Ltd.) was installed to mix the floated plastic samples after bubbling with steady mixing speed and specific time. For the froth flotation experiment, 400ml of tap water was used and as a frother a little amount (0.5ml/L) of Methyl isobutyl carbinol (MIBC) was added into the water to make easy flotation of plastic samples. Ten pieces of the each of plastic samples, PMMA, PC and PVC, were put into the glass reactor and air bubbles were provided into the glass reactor through the ceramic bubble diffuser at the bottom of reactor by operating mini air pump with 0.5L/min for 1min to be floated all of plastic samples. After being floated all of plastic samples, auto overhead stirrer was operated with various mixing speed (0 and 1500rpm) for 1min and the number of floated and settled each of plastic samples at the each mixing speed were counted to decide optimum PVC separation condition.

The quantitative analyses of the main inorganic components in the samples of ASR soil/residues were analyzed using an X-ray fluorescence spectrometer (EDX-720; Shimadzu Corp.). Solvent-free production of the reagent, a dispersed mixture of nano-metallic Ca and CaO, was prepared through a planetary ball-milling process [13]. The heavy metal-contaminated ASR soil/residue samples (10 g) were blended with 0.5g nanometallic Ca/CaO and 0.5 g NaH₂PO₄ ([PO₄]). Simultaneously, a blank experiment with only 10 g of heavy metal-contaminated ASR dust/thermal residue was carried out. The individual mixtures were blended/ground with a Vortex Mixer (WiseMix, VM-10) (250 mL plastic bottle along with 10 iron balls of 10 mm diameter) for 30 min at 2500–3000 rpm. At the end of each treatment interval, both the treated and untreated ASR thermal residues were sampled for analysis. Heavy metal concentrations in content and eluted solutions were analyzed using atomic absorption spectroscopy (AAS) (Varian, SpectRAA, 55).

III. RESULTS AND DISCUSSIONS

A. ASR Plastics Characterization

The compositions of main polymers in the ASR samples were identified with FT-IR and quantified and presented in Fig. 2. In ASR, rubber and other plastics is major portion about 45.6%, “others” also include in heavy fraction. The FT-IR results further indicated that the PVC plastics in ASR were about 4.6. In wet gravity separation heavy plastics of specific density >1.0 g/cm³ (including PVC, PET, PS, PA, PC and PMMA) were separated from light plastics of specific density <1.0 g/cm³ (including PP and PE) in ASR [14]. The ASR consisted about 74.2 of heavy polymers.

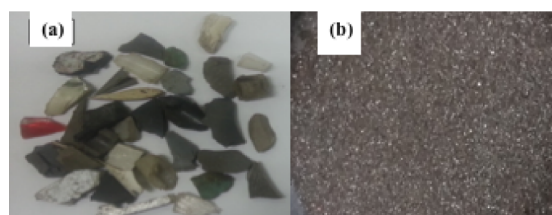


Fig. 1 Homogenized (a) ASR plastic samples (for PVC separation) and (b) ASR soil/residues (for heavy metals immobilization) used for this study

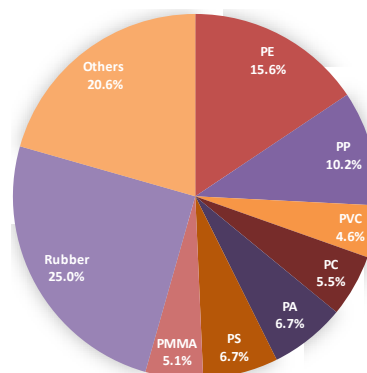


Fig. 2 Quantified polymer compositions in ASR

B. The Effect of Microwave Treatment on the Hydrophobicity of ASR Polymers

The combination of 60 sec microwave treatment with PAC decreased the contact angle of PVC in significantly about 16.5°, whereas the contact angles of other polymers slightly decreased (Fig. 3). This could be due to the chloride groups on the surface of PVC being replaced with hydrophilic functional groups, e.g., hydroxyl groups and carboxyl groups [15]. If a PVC surface has a high hydrophilicity, a PVC would be the first to settle on the bottom during the froth flotation experiment. Therefore, to selectively separate the PVC from the plastic samples using the froth flotation method, it is necessary to determine the lowest contact angle for the PVC surface compared to other plastics.

C. Froth Flotation Separation of PVC from ASR

As presented in Table I, by only 60 sec, microwave treatment about 20% of PVC observed to be settled along with 20% and 30% of PC and PMMA at 150 rpm mixing speed in ASR polymers. While, when the plastic samples treated 60 sec, by microwave with PAC were mixed at a speed of 150 rpm, 90% of the PVC was separated in settled fraction from the other plastic samples, with 10% of each PC and PMMA contamination (Table I). The purity ratios of the PVC that was recovered about 29% for ASR plastic samples by only microwave treatment. The highest purity, about 82% of PVC was recovered from ASR plastics by microwave treatment with PAC. The combined treatment of the froth flotation and microwave treatment is, therefore, a simple and effective technology for separating PVC from plastic waste.

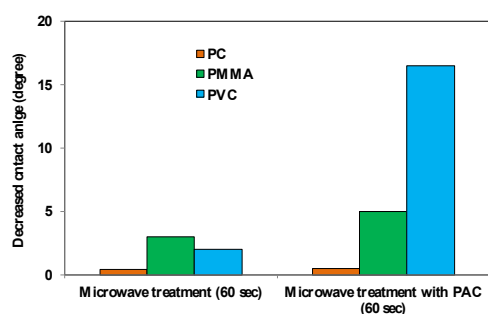


Fig. 3 The contact angle of decrease of PC, PVC and PMMA in ASR polymers after microwave treatment with PAC

TABLE I

THE FLOTATION PERCENTAGES OF PC, PMMA AND PVC POLYMERS AT OPTIMIZED MIXING SPEED DURING FROTH FLOTATION AT DIFFERENT TREATMENT CONDITIONS

| Treatment | Polymers | ASR | |
|------------------------------|----------|----------------------|------------------------|
| | | Mixing speed (0 rpm) | Mixing speed (150 rpm) |
| No treatment | PC | 100 | 100 |
| | PMMA | 100 | 80 |
| | PVC | 100 | 70 |
| Microwave treatment | PC | 100 | 80 |
| | PMMA | 100 | 70 |
| | PVC | 100 | 80 |
| Microwave treatment with PAC | PC | 100 | 90 |
| | PMMA | 100 | 90 |
| | PVC | 100 | 10 |

D. Heavy Metals Immobilization

Compared to the concentrations of untreated heavy metals eluted after simple mixing, the concentrations of heavy metals released in the leachate from the samples treated by nanometallic Ca/CaO/PO₄ were markedly decreased. These concentrations of eluted heavy metals in the ASR soil/residues corresponded to an intrinsic heavy metals immobilization efficiency of about 95–100% after treatment with nanometallic Ca/CaO/PO₄ (Fig. 4). The eluted/leachable heavy metal concentrations were substantially decreased after treatment by nanometallic Ca/CaO/PO₄ to a lower level than the leachate regulatory limits (i.e., Cd 0.3 mg L⁻¹, Cr 1.5 mg L⁻¹, Pb and Zn

3.0 mg L⁻¹, and Cu 1 mg L⁻¹) proposed by the Korean hazardous waste elution standard regulatory threshold [16]. Generally, CaO increases soil pH and favors the formation of oxides, metal carbonate precipitates, and complexes that decrease metal solubility. Particularly, nanometallic Ca/CaO generates a high pH when mixed with ASR residues in the presence of moisture. Therefore, it is more difficult to mobilize heavy metals in ASR residues at high pH. On the other hand, nanometallic calcium and NaH₂PO₄ can also react with moisture and CO₂ to yield insoluble pozzolanic cements that can enclose or bound heavy metals. When combined with the formation of Ca-associated (CaCO₃/Ca(OH)₂)/Ca₁₀(PO₄)₆(OH)₂ salts, this leads to an almost impenetrable shell layer [12], [13]. As a result, immobile Ca salts remarkably inhibit the desorption of heavy metals from ASR residues, suggesting that their addition can significantly reduce the mobilization of heavy metals.

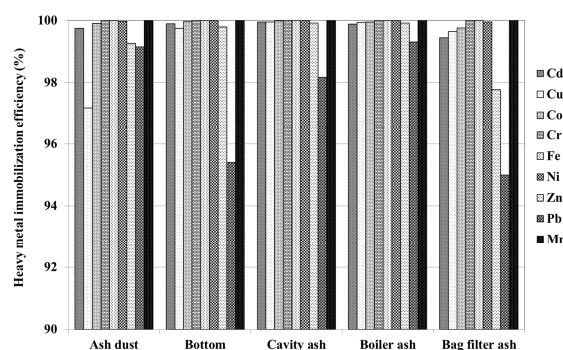


Fig. 4 Heavy metals immobilization efficiency in different ASR residues after treatment with nanometallic Ca/CaO/PO₄

IV. CONCLUSIONS

In this research, first we evaluated the selective surface modification of PVC by microwave treatment, as a method for separating PVC from hazardous ASR and second, heavy metals immobilization in ASR soil/residue with novel nanometallic Ca/CaO/PO₄ composite to reduce the risk of environmental emissions and the landfilling leaching.

- The combination of 60 sec microwave treatment with PAC, a sharp and significant decrease about 19° contact angle of PVC was observed.
- The microwave treatment with the addition of PAC resulted in a synergetic effect for the froth flotation, which may be a result of the 90% selective separation of PVC from ASR plastics, with 82% purity.
- Simple mixing with a nanometallic Ca/CaO/PO₄ dispersion mixture immobilized 95-100% of heavy metals in ASR soil/residues.
- The quantity of heavy metals leached from thermal residues after treatment by nanometallic Ca/CaO/PO₄ was lower than the Korean standard regulatory limit for hazardous waste landfills.
- Combined treatment by microwave and froth flotation can be a simple and effective method for PVC separation from ASR plastic wastes.

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