2015 International Conference on Advances in Environment Research
Volume 87 of IPCBEE (2015)
DOI: 10.7763/IPCBEE. 2015. V87. 11

Hazardous PVC Plastics Separation from ASR by Froth Floatation after Microwave Assisted Surface Modification

Srinivasa Reddy Mallampati [1 +], Chi-Hyeonlee [1], Nguyenthithanhtruc [1] and Byeong-Kyulee [1]

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

Abstract. One of the major problems in incineration for thermal recycling or heat melting for material recycling is the polyvinyl chloride (PVC) contained in automobile shredder residue (ASR) plastics. This is due to the production of hydrogen chloride, chlorine gas, dioxins, and furans originated from PVC. Therefore, the separation of PVC from ASR plastics is necessary before recycling. The separation of heavy polymers (PVC 1.42, PMMA 1.12, PC 1.22 and PET 1.27 g/cm^3) from light ones (PE and PP 0.99 g/cm^3) can be achieved on the basis of their density. However it is difficult to separate PVC from other heavy polymers basis of density. There are no simple and inexpensive techniques to separate PVC from others. If hydrophobic the PVC surface is selectively changed into hydrophilic, where other polymers still have hydrophobic surface, flotation process can separate PVC from others. In the present study, the selective surface hydrophilization of polyvinyl chloride (PVC) by microwave treatment after alkaline/acid washing and with activated carbon was studied as the pre-treatment of its separation by the following froth flotation. In presence of activated carbon as absorbent, the microwave treatment could selectively increase the hydrophilicity of the PVC surface (i.e. PVC contact angle decreased about 19^o) among other plastics mixture. At this stage, 100% PVC separation from other plastics could be achieved by the combination of the pre-microwave treatment with activated carbon and the following froth floatation. The hydrophilization of PVC by surface analysis would be due to the hydrophilic groups produced by microwave treatment with activated carbon. The effect of optimum condition and detailed mechanism onto separation efficiency in the froth floatation was also investigated.

Keywords: Hydrophilic, PVC, contact angle, additive, microwave, froth floatation, waste plastics

1. Introduction

ELV (End of Life Vehicles) and WEEE (Waste Electric and Electronic Equipment) or (e-waste), are increasingly important secondary source of ferrous, nonferrous metals and plastics. About 1 million ELVs are generated every year in Korea [1], [2]. On the other hand, In Korea, generation of WEEE, or electronic waste (E-waste), has rapidly increased in recent years [3]. Recycling of WEEE and ELV can comprise of a great number of physical/mechanical treatments: manual dismantling, disassembling, shredding, crushing, grinding, and separation (of different size fractions) by mechanical and physical properties [4]. The most problematic fractions of WEEE and ELV recycling treatments which have been mainly landfilled/incinerated in the past are shredding residues (SR, Automobile Shredder Residue (ASR) from ELV and Electronic Shredder Residue (ESR) from WEEE) composed of plastics, rubber and textiles etc. An estimate for the annual amount of ASR is about 20 to 25% from total ELVs. The ASR/ESR recovery as a heat resource has been considered using methods such as pyrolysis, gasification and injection to blast furnace, which are mostly recent developments, however, the contamination with PVC and BFRs contributes the production of highly toxic and persistent chlorinated dioxins, hydrogen bromide and brominated dioxins [5]. In landfills, some of the chemical additives contained in PVC may leach out, adding to the overall contaminant burden of

+ Corresponding author. Tel. +82 52-259-1412; Fax. +82 52-259-2629.
E-mail address: srireddys@ulsan.ac.kr.

landfill leachate. Therefore, before any recovery of the plastics content of ASR/ESR, for example by mechanical recycling or energy recovery, the BFR and PVC fraction must be efficiently separated out.

Major plastics are in ASR/ESR having normally hydrophobic surface characters. Specific gravity and contact angle of Polyethylene (PE) 0.93 g/cm^3, 90°, Polypropylene (PP) 0.90 g/cm^3, 92°, Polypropylene (*flame retarden*) (PP-FR) 1.25 g/cm^3, 86°, Polyvinylchloride (PVC) 1.3g/cm^3, 87°, polystyrene (PS) 1.05g/cm^3, 89°, Acrylonitrile butadiene styrene (ABS) 1.05g/cm^3, 77°, *ABS (flame retardant)* (ABS-FR), 1.21g/cm^3, 84°, polycarbonate (PC) 1.20g/cm^3, 80°, Polyacetal (PA) 1.4g/cm^3, 82° and polyethylene terephthalate (PET) 1.4g/cm^3, 80° respectively [6]. In wet gravity separation of PVC, PP-FR, ABS-FR, plastics as well as PET, PS and PA with more than 1.0 g/cm^3 of specific gravity are fractionated as heavy plastics and separated from light plastics like PP and PE. However, further separation of chlorinated and brominated flame retardant plastics (PVC, PP-FR and ABS-FR), from other heavy plastics is difficult due to the similar densities, and therefore heavy plastic fraction separation cannot be applied for material and chemical recycling even if the fraction is mainly composed of non-chlorinated plastics. As an alternative technology to solve the problems of previous technologies and to provide more advantages, microwave treatment that requires simple system and less energy consumption was suggested in this study. The objective of this study was to effectively separate PVC from mixed plastic wastes by applying froth flotation with microwave treatment to utilize these plastic wastes as an incineration fuel for heat utilization with minimum adverse environmental and health effects.

2. Materials and Methods

2.1. ASR and ESR Samples Collection

The ASR polymer samples were collected at two different automobile recycling/shredding plants one is Pohang, Korea (Sample A), and another one at Yamaguchi, Japan (Sample B). The each polymer composition in ASR were identified by recording their IR spectra using with FT-IR Spectrometer (Perkin-Elmer, Spectrum one). The individual polymer compositions in ASR samples were identified and quantified.

2.2. The Effect of Microwave Treatment on the Hydrophobicity of Virgin Polymers

Initially, in present study we studied with virgin plastics, in this regard virgin plastic sheets, PMMA, PC and PVC were obtained from the Kasai Sangyo Co., Ltd, Japan. These virgin plastic sheets had rectangular shape with 1,500mm of length, 1,200mm of width and 2mm of thickness. Each of the plastics was cut to small and uniform size (10mm x 10mm x 2mm) by saw and nipper and the four edges of cut plastics were sandpapered to remove attached particles which is generated after sawing. Ten pieces of the each of plastic samples were used for microwave treatments and froth flotation experiments. A microwave oven (Dongbu Daewoo Electronics Corp., KR-G20EW, 2,450MHz, 1,120W) which is generally used as an electric home appliance in kitchens was used to modify surfaces of plastic samples. Ten pieces of the each of plastic samples before and after acid or base treatment were put on the glass plate that was equipped in the microwave oven. These plastic samples were treated by microwave oven for different time periods (30, 60, 90 and 120sec). To identify the formation of functional group on the plastic surfaces after microwave treatment, the FT-IR analyses were done. The morphology and roughness changes of plastic surfaces after microwave treatments were analyzed by using the Field Emission Scanning Electron Microscope (FE-SEM, JSM-6500F, JEOL, Japan). To check the hydrophilic characteristic of plastic surfaces, the contact angles of plastic surfaces with water drops were analyzed by using contact angle analyzer (Smartdrop, Femtofab, Korea).

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 0.54d㎥ 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 (50, 100, 150, 200, 250, 300, 350, and 400rpm) 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.

3. Results and Discussion

3.1. Quantification of ASR Plastics Composition

The polymer composition in both ASR samples were identified with FT-IR and the values were presented in (Fig. 1). Major polymers are in ASR/ESR having normally hydrophobic surface characters. Specific gravity and contact angle of PE 0.93 g/cm^3, 90°, PP 0.90 g/cm^3, 92°, PVC 1.3g/cm^3, 87°, PS 1.05g/cm^3, 89°, ABS 1.21g/cm^3, 84°, PC 1.20g/cm^3, 80°, PA 1.4g/cm^3, 82° and PET 1.4g/cm^3, 80° respectively [6]. The FT-IR results indicated that the PVC plastics in ASR were about 4.6% and 4.0% in Sample A and Sample B respectively. In wet gravity separation of PVC, ABS, plastics as well as PET, PS and PA with more than 1.0 g/cm^3 of specific gravity are fractionated as heavy plastics and separated from light plastics like PP and PE. The ASR consisted of 74.2% and 77.6% of heavy plastics in sample A and sample B respectively. While, in ESR about 80.8% of heavy polymers were quantified. On the other hand, in ASR and ESR polymer composition "others" also include in heavy fraction.

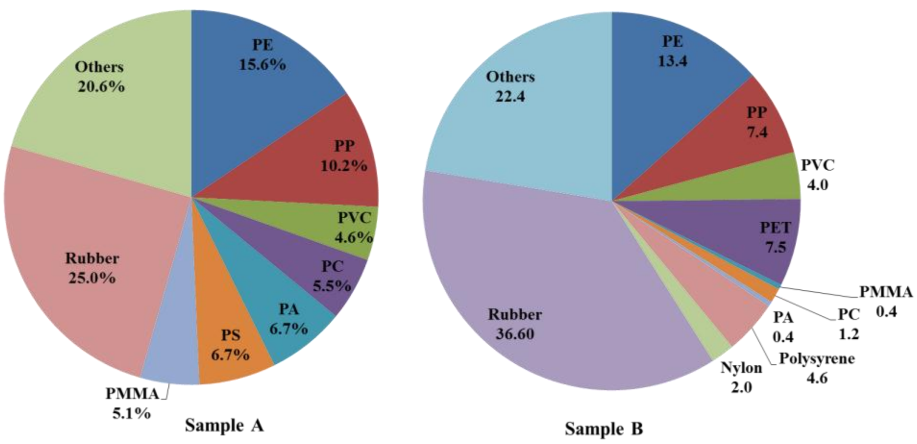

Fig. 1: Polymer compositions in ASR (Sample A and B).

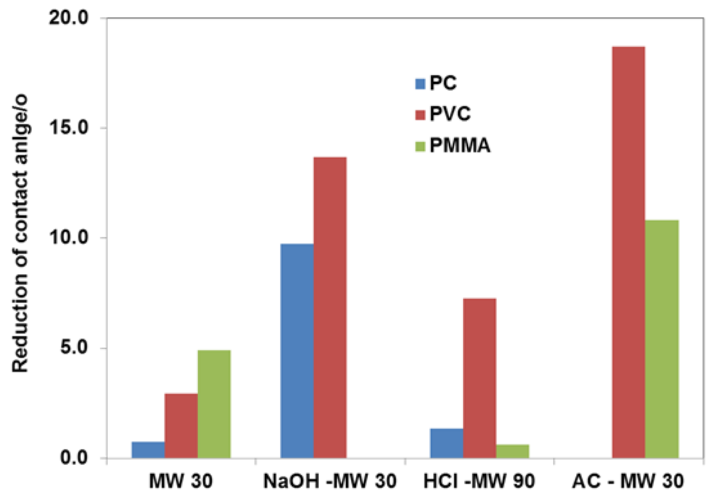

Fig. 2: The contact angle of PC, PVC and PMMA after microwave treatment combined with washing by NaOH, HCl and activated carbon as absorbent agent.

The contact angles results of PVC, PMMA and PC after microwave treatment with alkaline/acid washing and with activated carbon was presented in Fig. 2. A sharp and significant decrease of the contact angle of PVC was observed for microwave treatment with activated carbon. After 30 sec microwave treatment with activated carbon, the contact angles of PVCs had decreased by about 18.7°, PMMA about 10.8°, whereas PC contact angle not decreased. The results shown here indicate that microwave treatment with activated carbon can selectively decrease the contact angles of PVCs, meaning an increase of hydrophilicity of the PVC surface. 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 [7], [8].

3.2. Froth Flotation Separation of PVC

In next step, we tried to separate PVC from PMMA and PC by froth flotation based on the different hydrophilicity produced by microwave treatment. Fig. 3a-c shows, the flotation percentages of PC, PVC and PMMA were treated by microwave after alkaline/acid washing and activated carbon at each mixing speed. By increasing the mixing speed, the sedimentation of PVCs was promoted by preventing bubbles attaching and removing bubbles already attached on the surface of PVCs. After microwave treatment with activated carbon, the PVCs settled more easily than those of microwave treatment combined with washing by NaOH and HCl washing. In presence of activated carbon as absorbent, the microwave treatment could selectively increase the hydrophilicity of the PVC surface (i.e. PVC contact angle decreased about 19^{o}) among other plastics mixture. At this stage, 100% PVC separation from other plastics could be achieved by the combination of the pre- microwave treatment with activated carbon and the following froth floatation. The hydrophilization of PVC by surface analysis would be due to the hydrophilic groups produced by microwave treatment with activated carbon. Although chemical reactions occur on the PVC surface, microwave treatment has little influence on the bulk characteristics of PVC, since only a few nanometers of PVC surface were destroyed during the treatment process. Therefore, microwave treatment does not affect the post-recycling process by froth flotation. As a result of this research effort, the selective surface modification of PVC with microwave treatment can be efficiently useful to separate the PVC from other similar density mixed plastic waste including ASR. Therefore, we are in progress to apply this technology to real above quantified ASR plastics composition in order to separate PVC form other plastics.

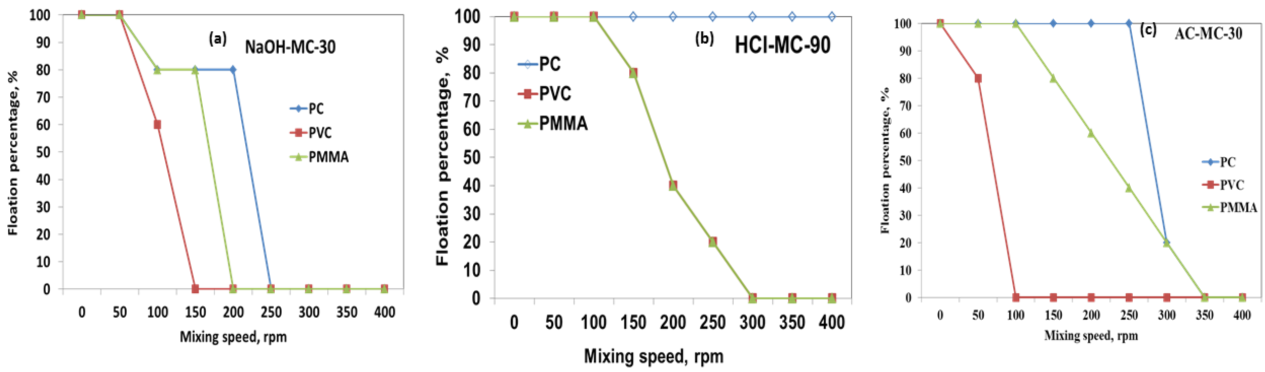

Fig. 3: The flotation percentages of PC, PVC and PMMA were treated by microwave after (a) alkaline, (b) acid washing and (c) activated carbon at each mixing speed.

4. Conclusion

In the present study, the selective surface hydrophilization of polyvinyl chloride (PVC) by microwave treatment after alkaline/acid washing and with activated carbon was studied as the pre-treatment of its separation by the following froth flotation. In presence of activated carbon as absorbent, the microwave treatment could selectively increase the hydrophilicity of the PVC surface (i.e. PVC contact angle decreased about 19^{o}) among other plastics mixture. At this stage, 100% PVC separation from other plastics could be achieved by the combination of the pre- microwave treatment with activated carbon and the following froth floatation. The hydrophilization of PVC by surface analysis would be due to the hydrophilic groups produced by microwave treatment with activated carbon. The combined treatment of the froth flotation and microwave treatment is, therefore, a simple and effective technology for separating PVC from plastic waste.

Furthermore, this work facilitates the industrial application of plastics flotation and provides technical insights into the process of waste plastics recycling including ASR.

5. Acknowledgement

The authors are grateful to the National Research Foundation of Korea (NRF) for providing financial support for this study through Basic Science Research Program funded by the Ministry of Education (2014R1A1A2055487).

6. References

[1] KAMA, 2003. Available from <http://www.kama.or.kr/eng/K_eng_main.jsp>, Seoul, Korea.

[2] KASA, 2003. Available from <http://www.kasa.or.kr/bbs_board_file/ statistics/statistics_list.asp>, Seoul, Korea.

[3] Kim IS (2004) E-waste issues and measures in Korea. In: Proceedings of The Third Workshop on Material Cycles and Waste Management in Asia (NIES E-waste Workshop), December 14–15, NIES, Tsukuba, Japan.

[4] Zevenhoven R., Sayeed L.: Automotive Shredder Residue (ASR) and Compact Disc (CD): Waste:Options for Recovery of Materials and Energy. TKK Eny 14, Espoo 2003

[5] Srinivasa Reddy, M., Okuda, T., Kurose, K., Tsai, TY., Nakai, S., Nishijima, W., Okada, M. (2010) Surface ozonation of polyvinyl chloride for its separation from waste plastic mixture by froth floatation. *Journal of Material Cycles and Waste Management.* 2010 12:326–331.

[6] Hwang, J. Y., Mich, H. Separation of normally hydrophobic plastic materials by froth flotation. US patent, 5377844, 1995.

[7] Okuda T, Kurose K, Nishijima W, Okada M (2007) Separation of polyvinyl chloride from plastic mixture by froth fl otation after surface modifi cation with ozone. Ozone Sci Eng 29:373–377.

[8] Kaczmarek H, Szalla A, Chaberska H, Kowalonek J (2004) Changes of surface morphology in UV-irradiated poly(acrylic acid)/poly(ethylene oxide) blends. Surface Sci 566–568:560–565.