

Separation of polyvinyl chloride (PVC) from automobile shredder residue (ASR) by froth flotation with ozonation

Mallampati Srinivasa Reddy^{a,*}, Keisuke Kurose^a, Tetsuji Okuda^b,
Wataru Nishijima^b, Mitsumasa Okada^a

^a Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University,
1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

^b Environmental Research and Management Center, Hiroshima University, 1-5-3 Kagamiyama,
Higashi-Hiroshima, Hiroshima 739-8513, Japan

Received 6 December 2006; received in revised form 26 January 2007; accepted 26 January 2007
Available online 6 February 2007

Abstract

The purpose of this study is to develop froth flotation to separate polyvinyl chloride (PVC) from automobile shredder residue (ASR) plastic mixtures of variable composition. Some polymers in ASR polymer mixtures have similar density and hydrophobicity with PVC and thus selective flotation of PVC from ASR polymer mixtures cannot be achieved. The present study focused on the surface modification of PVC with ozonation, and then the modified PVC can be separated from other polymers by the following froth flotation. The results of this study indicate that the selective recovery of PVC from real ASR polyethylene tetra pethelate (PET), polymethyl methacrylate (PMMA), polybutyl methacralate (PBMA), ethyl acrylate (EA), polycarbonate (PC) and rubber mixtures can be accomplished in a three-step process involving a gravity separation, ozonation and froth flotation. The rubber was removed from other heavy ASR (PVC, PET, PMMA, PBMA, EA and PC) polymers by froth flotation without mixing. It was found that ozonation process produced the desired difference in contact angle required (from 89.5 to 73.0°) for separation of PVC from other heavy ASR polymers, whereas the contact angles of other polymers was slightly decreased. The most of the load ASR, i.e. about 72.4% is floated away and 27.6% was settled down. The highest component 96.7% of PVC was recovered in the settled fraction. As a result of this research effort, the surface modification of PVC with ozonation can be efficiently useful to separate the PVC from other similar density ASR mixed polymers.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Automobile shredder residue (ASR); Polymers; Polyvinyl chloride (PVC); Froth flotation; Ozonation; Surface modification

1. Introduction

Today's automobiles contain more polymers and less metal than older ones [1,2]. Metals have been recovered for its re-use [3]. The remaining non-metallic portion, called automobile shredder residue (ASR), has been generally hauled to landfills for disposal even though it contains recyclable materials like polymers [4–8]. ASR was estimated to be produced 550,000–800,000 tonnes in Japan annually. Minister of Economy, Trade and Industry (METI), Japan drew up a set of quantified targets for the recycling rate for end of life vehicles to

95% by 2015 from the current recycling rate of 75% on average. The demand for comprehensive, sustainable and environmentally friendly treatment methods becomes therefore increasingly higher [4–8].

The recovery of polymers from ASR as a heat resource has been considered using pyrolysis, gasification and injection to blast furnace. ASR consists of several kinds of polymers viz. polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polyethylene tetra pethelate (PET), acrylonitrile–butadiene–styrene resin (ABS), polymethyl methacrylate (PMMA), polybutyl methacralate (PBMA), ethyl acrylate (EA), polycarbonate (PC), nylon, rubber, etc., in which PVC leads to generation of environmental hazardous chlorinated compounds such as hydrogen chloride and dioxins during the treatments with heat [9–15]. Therefore, PVC should be removed from ASR. PVC can be generally

* Corresponding author. Tel.: +81 82 424 6197; fax: +81 82 424 6195.

E-mail addresses: srreddys@hiroshima-u.ac.jp, srreddys@hotmail.com (M.S. Reddy).

removed from polymer mixtures by a gravity separation. The densities are approximately 0.9 PE and PP, 1.42 PVC, 1.41 POM, 1.03 PS, 1.27 PET, 1.05 ABS, 1.12 PMMA, 1.19 nylon and rubber 1.51 g/cm³, respectively [15–18]. PVC is removed as a heavy polymer with more than 1.0 g/cm³ of density with POM, PET, PS, ABS, PMMA, PC, nylon and rubber from ASR. However, further separation of heavy polymers by density is difficult.

Novel separation technologies have been proposed for the removal of PVC from other polymers based on the electrostatic property, X-ray spectrum, infrared radiation (IR) spectrum and solubility for solvent [16–18]. However, there is no simple and inexpensive technique to separate the heavy polymers into one another. If PVC surface is selectively changed into hydrophilic one, where other polymers still have hydrophobic surface, the flotation process can be applied for the separation of PVC from other polymers [19–21]. One of the commonly methods for the wetting is a chemical conditioning with wetting agents, e.g. the selective adsorption of surfactant onto plastic. There are also some researches about physical selective surface modification, e.g. flame, heating and plasma treatments [22–24]. However, the use of chemicals makes a problem in waste water treatment and it is difficult to apply the flame and plasma treatments after wet gravity separation, which may be applied for separation of heavy polymers from light polymers before separation of PVC. Hence, the alternative surface modification technique, which can be conducted in wet condition, should be developed.

It is well known that chlorinated organic compounds are dechlorinated by ozone in water treatment field [25]. If ozone can dechlorinate the surface of PVC particles, the hydrophilicity of PVC would increase. Our recent study in virgin polymers revealed that the ozonation could selectively increase the hydrophilicity of the PVC surface among polymer mixture including PET, PC and PMMA [26]. The PVC was successfully separated from the other polymers by the froth flotation based

on the selective increase of hydrophilicity on the surface of PVC by ozonation.

In this study, we applied ozonation following the froth flotation for the separation of PVC from ASR after removing light polymers by the wet gravity separation.

2. Materials and Methods

2.1. ASR samples

The ASR sample was collected at an automobile shredding plant in Hiroshima, Japan. The ASR sample was cut with continuous universal cutter (ASONE, RBK-01) to be particles in a diameter of 5.0 mm. Each particle was identified by recording their IR spectra using with FT-IR Spectrometer (Perkin-Elmer, Spectrum one).

2.2. The effect of ozonation on the hydrophobicity of ASR polymers

To study the effectiveness of ozonation on the selective surface modification of the PVC, the contact angle of each ASR polymer (PVC, PET, PMMA, PBMA, EA and PC) separated from the ASR was measured before and after ozonation. Light polymers (i.e. PP and PE) with less than 1.0 g/cm³ of density in the ASR were not evaluated for ozonation because they could be easily removed by the wet gravity separation. Ten pieces of heavy polymers were prepared for evaluation after washing with deionized water. They were submerged in ultra pure water at around pH 7 and ozone was supplied using the equipment shown in Fig. 1. Ozonation was conducted for 10 min in a glass reactor, 18 cm height and 5.0 cm inner diameter giving a volumetric capacity of 0.35 dm³, with a glass bubble diffuser plate at the bottom (pore diameter of 10–16 μm). Ozone gas (90–150 mg O₃/l) was produced by ozonizer (POX- Fuji-electric 10) and intro-

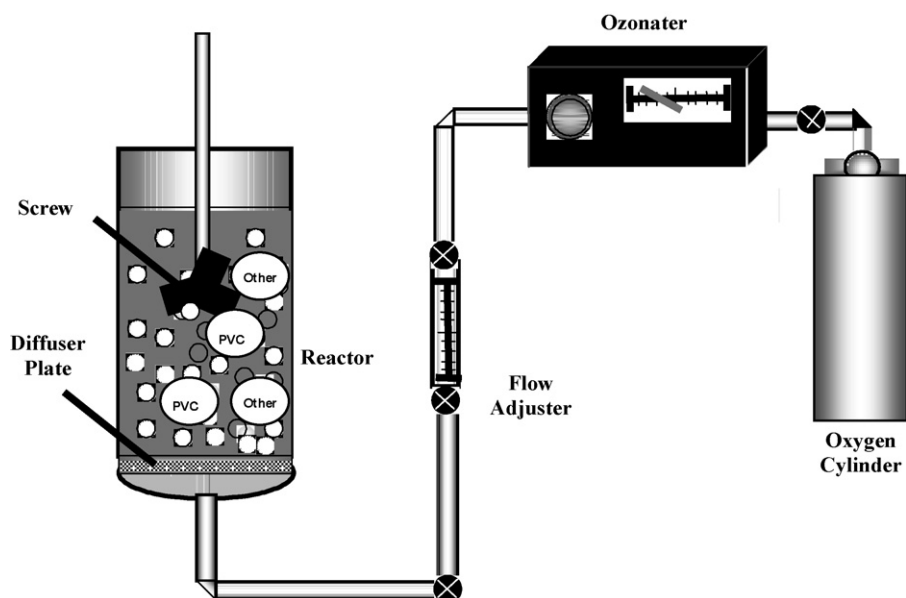


Fig. 1. Shows apparatus used and scheme of the experimental method.

duced into the reactor through the diffuser at a flow rate of 100 ml/min at 250–300 rpm mixing speed. Contact angle meter (CA-XP Kyowa Interface Science) was used for the analysis. The procedure was repeated three times for each sample giving a standard error for the mean value of 0.1°.

2.3. Selective removal of PVC from ASR

The selective separation of PVC from the heavy polymers by the ASR by ozonation followed by the froth flotation was evaluated for two samples. Ten pieces of each polymer were collected from the ASR and were applied for the froth flotation after ozonation. Then real weight (3.4 g) of the heavy ASR polymers was also applied for the froth flotation after ozonation. The polymers were washed by deionized water before use. MIBC (methyl isobutyl carbinol, 4-methyl-2-pentanol) was added to be 36 µg/l as a frother [15] in pure water and then 10 pieces or 3.4 g of the heavy polymers were introduced into the equipment shown in Fig. 1. The ozone was supplied for 10 min at the condition as described in 2.2 and then the polymers in the reactor were agitated at 100 rpm for 1–5 min. The floated and settled fractions were identified and counted.

3. Results and discussion

3.1. Quantification of ASR composition

The polymer composition of the ASR is shown in Fig. 2. The FT-IR results indicated that the following polymers were found in the ASR: polypropylene 45%, polyethylene 17%, polyvinyl chloride 3%, polyethylene tetra pethelate 8%, polymethyl methacrylate 6%, polybutyl methacralate 9%, ethyl acrylate 4%, polycarbonate 4% and rubber 4 wt%. The ASR consisted of 38% of heavy polymers and 62% of light polymers, which could be removed by the gravity separation.

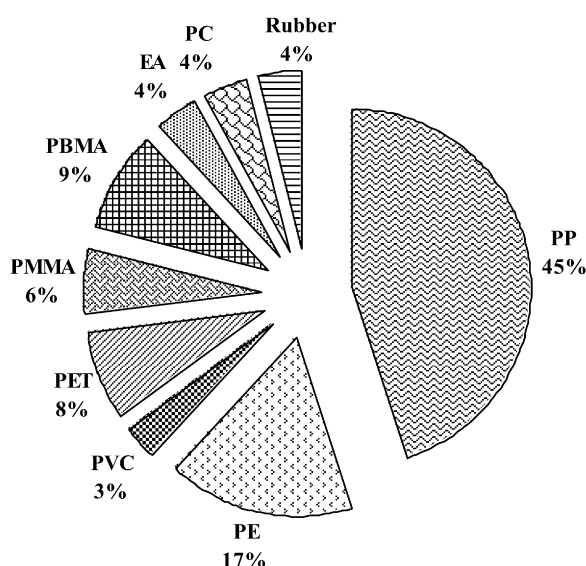


Fig. 2. Polymer composition in the ASR (wt%).

Table 1
Contact angles of virgin polymers before and after 10 min ozonation

	Contact angle (°)	
	Before ozonation	After ozonation
PVC	90.3	68.4
PC	87.4	84.9
PMMA	88.1	87.3
PET	88.8	86.9

3.2. The effect of the ozonation on the hydrophobicity of ASR polymers

The contact angles were measured for virgin polymers and polymers collected from the ASR before and after ozonation. The result for virgin polymers is presented in Table 1. Ten-minutes ozonation clearly decreased the contact angle of PVC from 90.3° to 68.4°, whereas almost no decrease was observed at other polymers, which still showed high contact angles of more than 86.0°.

For the polymers in the ASR as presented in Table 2, 10 min ozonation decreased the contact angle of PVC from 89.5° to 73.0°, whereas the contact angles of other polymers slightly decreased; PET from 88.8° to 83.4°, EA 85.2° to 80.6°, PBMA 80.5° to 77.0°, PMMA 80.2° to 76.7° and PC 79.7° to 76.3°. It was confirmed that the contact angle significantly decreased even for PVC in the ASR. However, slight decrease in the contact angle was observed for other polymers in the ASR, which showed no difference in the contact angle by ozonation. Moreover, initial values before ozonation were found to be a smaller in polymers in the ASR than those in the virgin polymers. The polymers collected from ASR would have attached contaminants such as paint and oil even though those were washed by water before experiment. These contaminants on the polymers would change the contact angles of the polymers. The slight decreases in the contact angles of polymers would be caused by the oxidation of contaminants on the polymers during ozonation.

These results indicate that the ozonation can selectively decrease the contact angle of PVC even in the real ASR. This would be due to the change of the chloride groups on the surface of PVC into hydrophilic functional groups; hydroxyl group and carboxyl group [25–27]. In some other surface modification methods, e.g. plasma and ultraviolet treatments, there is generally no selectivity for PVC [23–25].

Table 2
Contact angles of ASR polymers before and after 10 min ozonation

	Contact angle (°)	
	Before ozonation	After ozonation
PVC	89.58	73.06
PC	79.72	76.36
PET	88.88	83.42
EA	85.24	80.66
PBMA	80.58	77.02
PMMA	80.22	76.78

3.3. Floating and settling behavior of each polymer from ASR in froth flotation

The selective decrease of the contact angle of PVC in the real ASR samples would be able to cause the separation of PVC from other similar density polymers. Therefore, the froth flotation was conducted for each 10 piece of PVC, PET, PMMA, PBMA, EA, PC and rubber collected from the ASR at several mixing speeds after 10 min ozonation. The all ASR samples were submerged in ultra pure water before ozonation. After the 10 min ozonation, all polymers except for rubber were floated away with bubbles. Therefore, rubber could be separated from other polymers as a settling fraction after ozonation.

The percentage float for each heavy ASR polymer except for rubber at 50–350 rpm mixing speed after 10 min ozonation during froth flotation is shown in Fig. 3. The PVC settled down at lower mixing speed than other polymers. At 100 rpm, 90% of PVC was settled down with 20% of PBMA, whereas PET, PMMA, EA and PC were perfectly floated. The highest PVC separation from other polymers was achieved at 100 rpm. At the higher mixing speed, 200–300 rpm, although all PVC particles could be settled down, the other polymers were also settled down. The best mixing speed for separation was observed to be lower in polymers from real ASR, compared to virgin polymers (330–366 rpm) [23]. This may be due to the smaller difference in hydrophilicity after ozonation as shown in (Table 2).

3.4. Floating and settling behavior of ASR polymers in froth flotation

The froth flotation test after 10 min ozonation was also conducted at 100 rpm mixing speed for the heavy fractions of

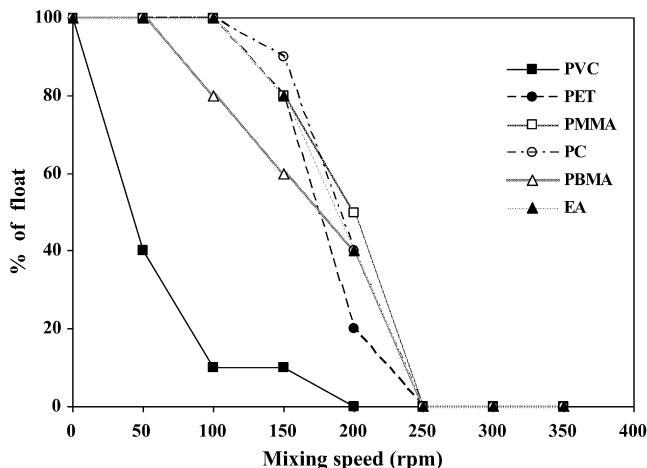


Fig. 3. The floating/settling behaviors for 10 pieces of each heavy ASR polymers at each mixing speed after 10 min ozonation during froth flotation.

ASR 3.4 g, separated from the gravity separation. The effectiveness of the froth flotation was determined by the weight percentage of floated/settled fraction for each polymer after 10 min of froth flotation was presented in Table 3. The result indicates that about 72.4% of polymers were floated away and 27.6% were settled down. As shown in Table 3, the settled fraction of PVC reached 97%. On the other hand, 10% of PET, 10% of PMMA, 19% of PBMA, 45.0% of EA and 47.5% of PC were also settled down. This result shows that PVC was successfully removed from the ASR and concentrated to be 30% in the settled fraction from 3% in the original ASR and 70% in the heavy polymers except for rubber. The 93.7% PVC free polymers (less than 0.41% of PVC) were

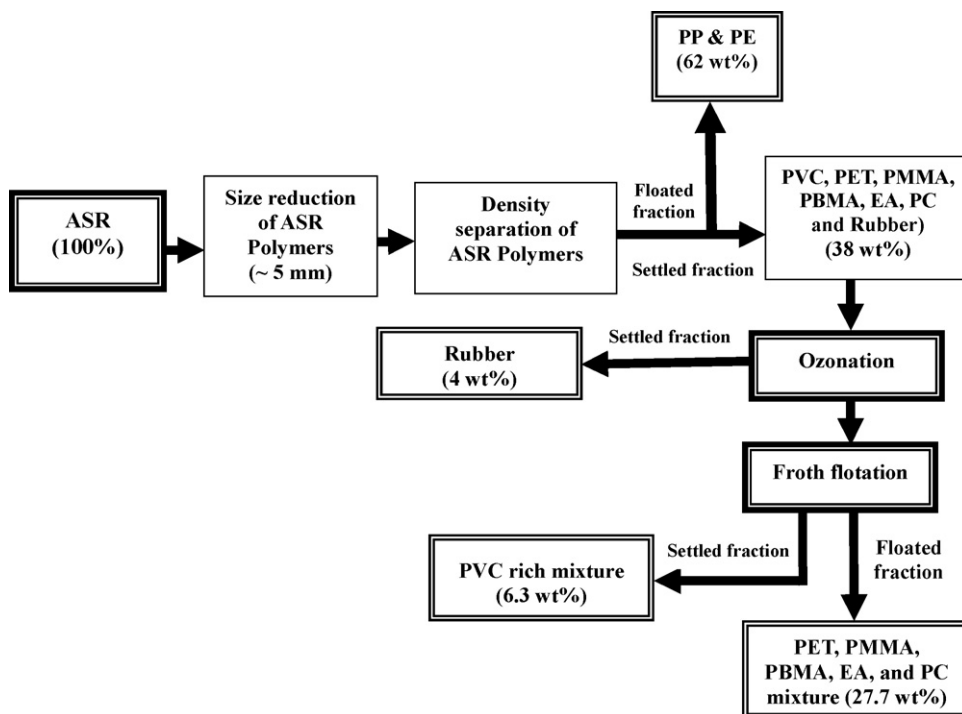


Fig. 4. A simplified flow sheet for the selective removal of PVC from ASR (wt%).

Table 3

The percentage of float/settled fraction of heavy ASR polymers after froth flotation

ASR	Floated (wt%)	Settled (wt%)
PVC	97	3
PET	10	90
PMMA	7	93
PBMA	19	81
EA	45	55
PC	45	55

obtained from the ASR by the froth flotation after ozonation.

The results of this study indicate that the selective recovery of PVC and rubber from ASR polymers can be accomplished in a three-step process involving a gravity separation, ozonation and froth flotation. A simplified flow sheet for the separation of PVC is shown in Fig. 4. The 62 wt% PP and PE can be recovered by a simple gravity separation from heavy ASR polymers as a floated fraction. Subsequently, the 4 wt% rubber can be recovered from other heavy ASR (PVC, PET, PMMA, PBMA, EA and PC) polymers during ozonation as a settled fraction. The polymers ozonated are then applied to froth flotation process and finally 6.3 wt% PVC rich polymers are separated from 34 wt% of PVC free polymers as a settled fraction. Total recovery of polymers without PVC reaches 93.7 wt%, which is significantly improved from 62 wt% by a conventional gravity separation.

4. Conclusions

Ozonation was applied for selective modification of the PVC surface among polymers with almost the same density and hydrophobicity. It was found that ozonation could change contact angle of PVC collected from ASR from 89.5° to 73.0°, whereas those of other heavy ASR polymers after ozonation ranged from 83.4° to 76.3°. Rubber could be removed from the ASR polymers with PVC during ozonation as a settled fraction. In the froth flotation following to ozonation, PVC was successfully removed from the heavy ASR polymers and concentrated to be 30% in the settled fraction from 3% in the original ASR. As a result, 93.7 wt% of polymers with little PVC (less than 0.41%) were obtained from the ASR.

Acknowledgements

Authors would like to thank Mr. Yamaguchi Takefumi (Master student), for his kind assistance during the experiments. M.S. Reddy thanks Monbukagakusho (MEXT), Japan for providing financial support in the form of a Research Fellowship during this study.

References

- [1] B.J. Jody, E.J. Daniels, A.P.S. Teotia, Recycling of polymers from automobile shredder residue (opening chapter), in: Conversion and Utilization of Waste Materials, Taylor and Frances for the American Chemical Society, 1995.
- [2] B.J. Jody, E.J. Daniels, P.V. Bonsignore, N.F. Brockmeier, A process to recover plastics from obsolete automobiles using solvents at ambient pressure, in: Presented at and published in the proceeding of the 206th American Chemical Society National Meeting, 1993, pp. 22–27.
- [3] B.J. Jody, E.J. Daniels, P.V. Bonsignore, N.F. Brockmeier, Recovering recyclable material from shredder residue, *J. Metals* 46 (1993) 40–43.
- [4] B.J. Jody, E.J. Daniels, Automobile shredder residue: treatment options, *Hazard. Waste Hazard. Mater.* 8 (1992) 219–230.
- [5] P.V. Bonsignore, B.J. Jody, E. Daniels, Separation Techniques for Auto Shredder Residue in Designing for Recyclability and Reuse of Automotive Polymers SP-867, Society of Automotive Engineers, Warrendale, Pennsylvania, 1991, pp. 59–63.
- [6] H. Hock, M.A. Maten, A Preliminary Study of the Recycling and Recovery of Automotive Polymers, Automobile Life Cycle Tools and Recycling Technologies SP-966, Society of Automotive Engineers, 1993, pp. 59–71.
- [7] B.J. Jody, E.J. Daniels, P.V. Bonsignore, Alternatives for recycling of auto shredder residue, *J. Resource Manag. Technol.* 20 (1992) 14–26.
- [8] B. J. Jody, E. J. Daniels, P. V. Bonsignore, A process to recycle shredder residue, DOE case No. S-76, 923, Patent Application S. N. 972, 426 (2001).
- [9] B. Andricic, T. Kovacoc, Non-isothermal degradation of poly (vinyl chloride)/methylmethacrylate-butadiene-styrene blends, *Polymer Degrad. Stabil.* 65 (1999) 59–64.
- [10] E.J. Anthony, L. Jia, D.L. Granatstein, Dioxin Furan formation in FBC boilers, *Environ. Sci. Technol.* 35 (2001) 3002–3007.
- [11] B. Baum, L.H. Wartman, Structure and mechanism of dehydrochlorination of polyvinyl chloride, *J. Polym. Sci.* 28 (1958) 537–546.
- [12] T. Hjertberg, Degradation of PVC in landfills: a theoretical evaluation, Report R23981.000, Norsk Hydro Research Centre, Porsgrunn, 1995.
- [13] J. Bernard, H. Ole, V. Jürgen, The influence of PVC on the quantity and hazardousness of flue gas residues from incineration, Released by Bertin Technologies Tarnos (F), Contract Number: B4-3040/98/000101/MAR/EE, 2000.
- [14] J. Balg, Recycling fly ash from incinerators, in: Proceedings of Recycle'96, Davos, Switzerland, 1995.
- [15] A.M. Gisela, J.A.S. Tenorio, Use of froth flotation to separate PVC/PET mixtures, *Waste Manag.* 20 (2000) 265–269.
- [16] H. Shen, E. Forsberg, R.J. Pugh, Selective flotation separation of polymers by particle control, *Resources Conserv. Recycl.* 33 (2001) 37–50.
- [17] G. W. Espiridion, J. Wayne, Separation of polymers by flotation, Patent Application S. N. 870,161 (1979).
- [18] E.S. Huiting, R.J. Pugh, Selective flotation separation of polymers by chemical conditioning with methyl cellulose, *Resour. Conserv. Recycl.* 35 (2002) 229–241.
- [19] J. Drelich, T. Payne, J.H. Kim, J.D. Miller, R.W. Kobler, S. Christiansen, Selective froth flotation of PVC from PVC/PET mixtures for the polymers recycling industry, *Polym. Eng. Sci.* 38 (1998) 1378–1386.
- [20] J. Drelich, J.H. Kim, T. Payne, J.D. Miller, R.W. Kobler, Purification of polyethylene terephthalate from poly (vinyl chloride) by froth flotation for the polymers (soft-drink bottle) recycling industry, *Sep. Pur. Technol.* 5 (1999) 9–17.
- [21] T. Takoungsakdakun, S. Pongstabodee, Separation of mixed post-consumer PET-POM-PVC plastic waste using selective flotation, *Sep. Pur. Technol.* (2006).
- [22] X. Hu, J.M. Calo, Enhancement of liquid-fluidized bed classification of palstic particle mixtures via selective thermal particle modification, *Powder Technol.* 151 (2005) 44–53.
- [23] G.L. Hearn, J.R. Ballard, The use of electrostatic techenics for the identification and sorting of waste packing materials, *Resour. Conserv. Recycl.* 44 (2005) 91–98.
- [24] R.J. Ehring, Plastic Recycling: Productes and Processes, Hanser, New York, 1992.
- [25] N. Graham, W. Chi, C. Lau, Observations of 2,4,6-trichlorophenol degradation by ozone, *Chemosphere* 51 (2003) 237–243.
- [26] T. Okuda, K. Kurose, W. Nishigima, M. Okada, Separation of Poly Vinyl Chloride (PVC) from plastic mixture by froth flotation with ozonation by surface modification, *Ozone Sci. Eng.* (2007).
- [27] E.M. Sanders, S.H. Zeronian, An analysis of the moisture-related properties of hydrolyzed polyester, *J. Appl. Polym. Sci.* 27 (1982) 4477–4491.