SELECTIVE SURFACE OZONATION OF POLYVINYL CHLORIDE FOR ITS SEPARATION FROM WASTE PLASTIC MIXTURE BY FROTH FLOATATION

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Abstract: The separation of waste plastics is important for its feedstock and mechanical recycling. The selective surface hydrophilization of polyvinyl chloride (PVC) by ozonation was studied as the pre-treatment of its separation by the following froth flotation. The ozonation could selectively increase the hydrophilicity of the surface of PVC among plastic mixture with three other plastics. The hydrophilization of PVC by surface analysis would be due to the hydrophilic groups produced by ozonation. XPS and AFM analysis revealed that the increase was due to the structural change in chlorine group in PVC to hydroxylic acid, ketone and carboxylic groups by ozonation. The separation of PVC from other plastics could be achieved by the combination of the pre-ozonation and the following froth floatation. The effect of some condition onto separation efficiency in the froth floatation was also investigated.

Keywords: Froth floatation; hydrophilization; ozonation; PVC

1. Introduction

Synthetic organic polymeric materials (plastics) are widely used in our daily life and various industrial fields. Therefore, large amounts of waste plastics were produced and reached about 9.9 million tons/y in Japan [1,2]. Before, the most of waste plastics were disposed to landfill site directly or after incineration, because many kind of plastics was mix in the waste plastics. However, the recycle is recently desired, and several kinds of low promoting plastic recycle had been established in Japan. One of them was the Containers and Packaging Recycling Law, and it was established in Japan and came into effect in 2000 to impel recycling of the containers and packaging waste[3]. The problems associated with each recycling method, including the thermal, chemical or material recycling, of waste plastics are the productions of hydrogen chloride and chlorine gas in addition to the formation of dioxins and furans[4,5]. These problems caused by chlorine in the waste plastics can be avoided by the removal of PVC from waste plastics.

About 75% of polymer produced in Japan consists of six polymers, i.e. polyethylene (PE), polypropylene (PP), acrylonitrile-butadiene-styrene resin (ABS), polystyrene (PS), poly(ethylene terephthalate) (PET) and PVC. These typical densities are approximately 0.9, 0.9, 1.1, 1.1, 1.3 and 1.4 g/cm^3, respectively [1,6,7]. Therefore, the separation of heavy polymers (PVC and PET) from light ones (PE and PP) can be achieved on the basis of their density. However it is difficult to separate the heavy polymers from middle density polymers (PS and ABS). Especially, the separation of PVC from PET would be practically impossible on the 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[8,9]. One of the commonly used methods for the hydrophilization is a chemical conditioning with hydrophilization agents, e.g. the selective adsorption of a surfactant onto polymer. Another method is physical modification, such as flame, heating and plasma treatments [7,11,12]. It is well known that chlorinated organic compounds are dechlorinated by ozone in water and wastewater treatment processes. The separation of PVC from mix waste plastics would be possible by froth flotation, if ozone can dechlorinate PVC and produce hydroxyl and carboxyl groups in the surface and the hydrophilicity of the PVC surface would be selectively increased. Therefore, the selective surface modification of PVC surface by ozone was confirmed and its mechanism was studied in this research. The separation of PVC from other plastics was also studied by the combination of the pre-ozonation and the following froth floatation, and the effect of floatation condition onto separation efficiency was investigated.

2. Materials and methods

2.1 Materials

Three types of virgin PVC plates (Takiron Ltd, 10×10mm with 2 mm thickness) were used for the separation study. The rigid and flexible PVC plates contained 8 and 36wt% of additives, respectively (Tab.1). Although rigid PVCs are known to have the smaller amount of plasticizers, rigid PVCs without plasticizers were used to confirm the correlation between hydrophilization and plasticizers as additives. The plasticizer was Dioctyl phthalate (DOP) and its double bond could react with ozone. Colorant and stabilizer are titanium dioxide and lead compounds ($3PbO \cdot PbSO_4 \cdot H_2O$), respectively, and these inorganic oxides are expected to be less-reactive with ozone.

Tab. 1 Properties of three PVCs[12,13]

		Rigid PVC	⟷	Flexible PVC
Content (wt%)	Vinyl chloride	92	90	64
	Additives	8	11	36
	Plasticizer	0	4	27
	Colorant and stabilizer	8	7	9
Density (g/cm^3)		1.43	1.40	1.24

2.2 Contact angles and ozonation

To evaluate the effectiveness of ozonation on the increase of hydrophilization for PVCs, the contact angles of plastic plates were measured before and after ozonation. Contact angle meter (Kyowa Interface Science, CA-XP) was used for the analysis. Sessile bubble method was used to analyze the contact angles.

Surface modification of plastics by ozonation was conducted in a glass reactor, 18 cm high with 5.0 cm inner diameter, giving a volumetric capacity of 0.35 dm^3, with a glass bubble diffuser plate at the bottom (pore diameter of 10-16 μm). Ozone gas (90-150 mg-O_3/L) was produced by a ozonaizer (POX-10, Fuji-electric) and introduced into the cell through the diffuser at a flow rate of 50 mL/min in ultra pure water at around pH 7.

2.3 Surface analysis

The changes of chemical and physical structure on surface were observed by XPS (X-ray Photoelectron Spectrometer) and AFM (Atomic Force Microscopy) analysis, respectively. Nano Scope Ⅲ multimode (Veeco Instruments Inc.) was used for AFM analysis with scan size of 20×20 μm^2, x-range of 2 m/div and y- and z- range of 700 nm/div. A S-Probe ESCA (Surface Science Instrument) was used for XPS analysis, each binding energies at 288.5, 531.8, 533.3 and the sum of 200.0 and 201.6eV were used for the analysis of O=C-O, C=O, C-O and -CHCl-CH_2-, respectively.

2.4 Froth flotation

Flotation experiments were conducted in the same equipment as the ozonation and a glass cylinder with 15.0 cm inner diameter. Nitrogen gas was used for the flotation experiments. A paddle was installed into the cell for mixing. MIBC (Methyl Isobutyl Carbinol, 4-Methyl-2-pentanol) was added to be 36 μg/L as a frother.[3] The nitrogen gas was supplied to the reactor for 15 seconds.

3. Results and Discussion

3.1 Hydrophilicity change of surface by ozonation

The contact angles in sessile bubble method of PVCs with 8-36% of additives at 0-60 minutes of ozonation are shown in Fig. 1. The increase in the contact angle indicates the increase of surface hydrophilicity, rapid increase was observed until 15 minutes in every PVC. The contact angle change during 15 minutes ozonation was summarized in Fig 2, and highest increase was observed in the rigid PVC with 8% of additives, its contact angles was increased from 108 deg to 157 deg. The results confirm the hydrophilization on the surface of PVCs as shown in previous repot [14], and it was found that rigid PVC containing low additives was easily modified in comparison with flexible PVC containing high additives. This would be due to the replacement of the chloride groups on the surface of PVC into hydrophilic functional groups.

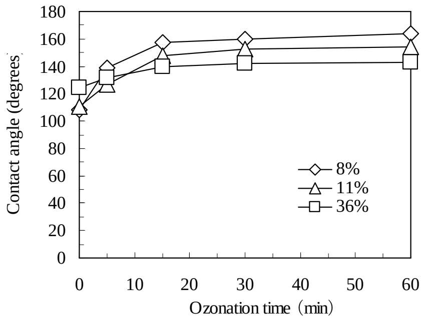


Fig. 1 Contact angles of PVCs with different additive ratio during ozonation.

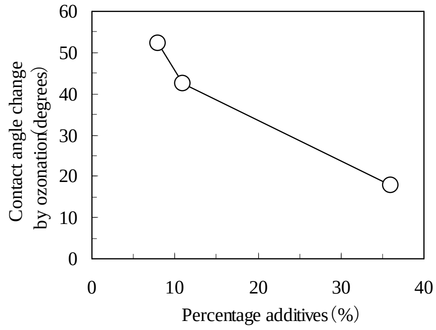
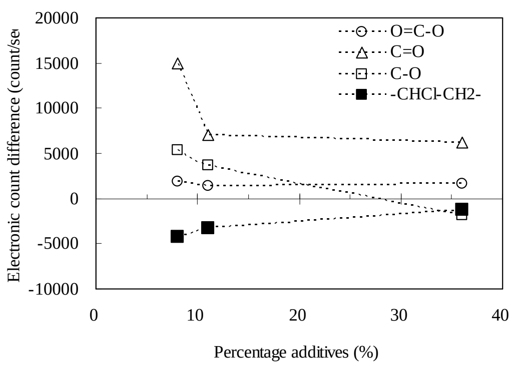


Fig. 2 Contact angles change of PVCs with different additive ratio during ozonation.

3.2 Chemical and physical structure change

The changes of electron counts of each functional groups carbonyl, as like carboxyl and chlorine groups, in XPS analysis before and after ozonation are summarized in Fig.3 . It is clear that the hydrophilic groups on PVC surfaces, especially ketone group including a part of carboxylic groups, increased by ozonation, whereas the vinyl chloride group decreased. The changes were more significant in the rigid PVC with low additives coincident with the higher hydrophilization in the rigid PVC surface (Fig. 1 and Fig. 2). These results suggest that the hydrophilization of PVC was not caused by the oxidation of additives but the oxidation of vinyl chloride itself because the vinyl chloride group decreased with the increase in the hydrophilic groups.

AFM was conducted to study the physical surface change by ozonation. The surface hydrophilicity may increased by the decrease in surface roughness.[15] The surface roughness expressed by the root mean square (RMS) of AFM height images of PVC before and after ozonation (Fig. 4) indicated that the hydrophilization of PVC surface was not caused by the change in the surface roughness in both rigid and flexible PVC.



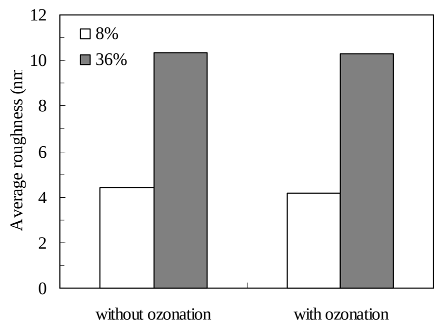


Fig. 3 Changes of electron counts associated with each functional groups in XPS before and after ozonation

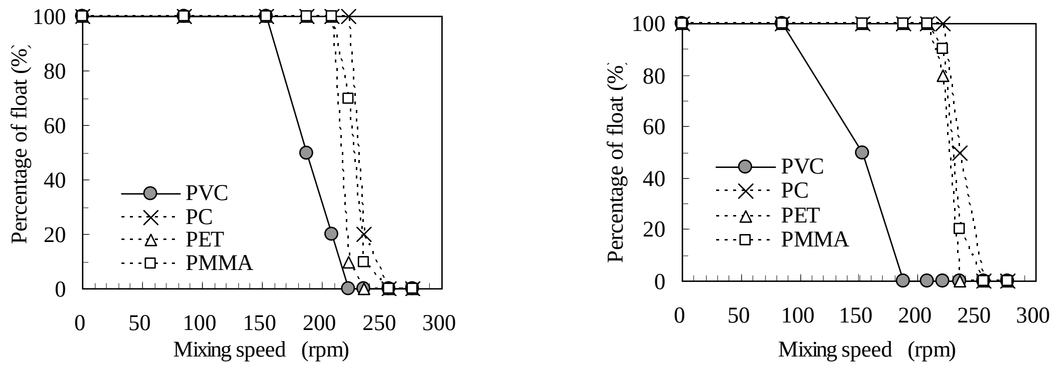
Fig. 4 Average roughness of PVC before and after ozonation

3.3 Selectivity of ozonation

Fig. 5a shows the comparison of froth floatation among 4 plastics include rigid PVC with 8% additives without ozonation. Each plastic can be settled at certain mixing speed in the froth floatation, and the mixing speed depends on surface hydrophilicity. We could not find any specific mixing speed where PVC could be separated from other three plastics, that is, all PVC tubes settled down and all other plastic tubes floated. On the other hand, the perfect removal of PVC from other three plastics could be achieved at 190-210 rpm of mixing speed in case of pre-ozonation as shown in Fig. 5b. The separation was summarized in Fig. 6 which shows the floatation percentage of three other plastics when all PVC pieces was settled down. It indicates that selective surface hydrophilization could be happen on PVC, and the separation could be achieved in froth floatation.

3.4 Effect of conditions of froth floatation

The condition of froth floatation could affect on the separation efficiency, therefore the effects of reactor size, pellet size, water temperature and mixing time onto the separation efficiency was investigated. The results were summarized in Fig. 7, and the result of PET was shown. The increase of cylinder reactor size from 5 cm (Fig. 6) to 15 cm (Fig. 7) of diameter was not affect on the separation efficiency for 5×5×5mm pellets. The increase of pellet size from 5×5×5mm to 5×15×15mm was dramatically decrease the separation efficiency. It would be caused by the difficulty of keeping floatation on the balance of bubbling and mixing when the relative surface area of plastic was increased. However, it was found that the increase of temperature and mixing time could improve the balance, and could improve the separation efficiency.



(a) without pre-ozonation (b) with 10 minutes pre-ozonation

Fig. 5 The effect of ozonation on the selective separation of PVC in the froth floatation.[14]

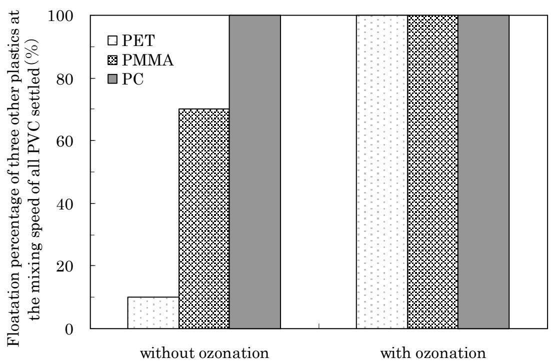


Fig. 6 Separation efficiency of three plastics when all PVC pieces was settled (5×5×5mm pellets in 5cm cylinder)

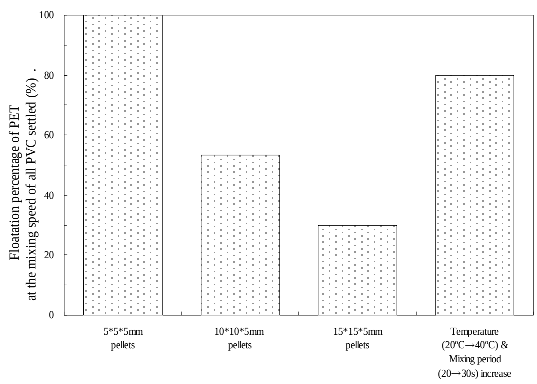


Fig. 7 Effects of pellets size and floatation condition on the separation efficiencies. (15cm cylinder)

4. Conclusions

The increase was due to the structural change in chlorine group in PVC to hydroxylic acid, ketone and carboxylic groups by ozonation. The separation of PVC from other plastics could be achieved by the combination of the pre-ozonation and the following froth floatation. The increase of temperature and mixing time could improve the separation efficiency.

References

[1] H. Shen, E. Forssberg and R. J. Pugh, *Resour. Conserv. Recycl.***2001,** *33*,37-50.

[2] Plastic Waste Management Institute, http://www.pwmi.or.jp/ei/ **2004**.

[3] Japan Containerand Package Recycling Association (JCPRA), http://www.jcpra.or.jp/eng /jcpra_eng05.html **2005**.

[4] G. A. Marques, J. A. Soares Tenório, *Waste Management*, **2000**,*20(4)*, 265-269.

[5] H. Shen, E. Forssberg, R. J. Pugh, Resour. *Conserv. Recycl.* **2002**,*35*,229-241.

[6] H. Shent, R. J. Pugh, E. Forssberg, Resour. *Conserv. Recycl.* **1999**,*25*,85-109.

[7] X. Hu and J. M. Calo, *Powder Technol.***2005**,*151*,44-53.

[8] J. Drelich, J. H. Kim, T. Payne, J. D. Miller, R. W. Kobler, *Separation Pur. Technol.* **1999**,*5*,9-17.

[9] T.Takoungsakdakun, S. Pongstabodee, *Separation. Pur. Technol* .**2007**, *54*, 248-252.

[10] R. J. Ehring. Plastic Recycling: Products and processes,**1992**.

[11] G. L. Hearn, J.R. Ballard, Resource. Conservation and Recycling.**2005**,*44*,91-98.

[12] Material safety date sheet (MSDS), 112-787.

[13] Material safety date sheet (MSDS), 113-168.

[14] T. Okyda, K. Kurose, W. Nishijima, M. Okada, *Ozone Science & Engineering.* **2007**,*29(5)*, 373-377.

[15] O. Attila, H. Henrik, G. J. Vancso, *Applied Surface Scienc.* **2005**,*239*,410-423.