

Catalytic Degradation of PVC Mixed Plastics into Fuel Oil and Dechlorination of the Derived Oil

Yusaku Sakata*

Department of Applied Chemistry, Okayama University, Okayama 700-8530, Japan

E-mail: yssakata@cc.okayama-u.ac.jp Fax: +81-86-251-8082

The thermal and catalytic degradation of mixed plastics containing poly(vinyl chloride) (PVC) was carried out at 360~430°C under atmospheric pressure by semi-batch operation both in liquid phase contact and vapor phase contact. The thermal degradation (380 °C) oil from PVC and PP (in 20:80 weight ratio) contains about 12,7000 ppm of organic chlorine compounds containing mainly 2-chloro-2-methylpropane and 2-chloro-2-methylpentane. When iron hydrous oxide (α -FeOOH) particles were used as a catalyst for the dechlorination of PVC/PP degradation oil in vapor phase contact at 380 °C, the amount of organic chlorine compounds decreased to 3200 ppm. The crystalline phase of α -FeOOH had changed to mainly Fe₃O₄ and it lost the mechanical strength, which is undesirable for practical purposes. When the iron oxide carbon composite catalysts (TR97305) prepared from α -FeOOH and phenol resin was used for the dechlorination of PVC/PP degradation, the organic chlorine compounds were removed from the liquid product to levels as low as 200 ppm and the Fe₃O₄ phase was changed to FeCl₂. The details of the mechanism of dechlorination reaction over iron oxide carbon composite catalysts are discussed in detail.

Introduction

Recently, the study of the waste plastic degradation into fuel oil has been carried out frequently as a means of reutilization petroleum resources [1,2]. We have proposed a catalytic process for plastic degradation using solid acid catalysts in melted plastic (liquid) phase in contrast to thermal degradation. We have already reported that this process was effective for increasing the degradation rate and yield of oil product in the case of degradation of PE and PP into fuel oil using silica-alumina catalyst [3,4] and also using non-acidic mesopore silica catalyst (FSM) [5].

Waste plastic is a mixture of many kinds of plastics such as PE, PP, PS, PVC-containing chlorine and ABS-containing nitrogen, etc. The harmful substances produced by the simple incineration of waste plastics have caused serious socio-environmental problems. In the case of the degradation of these plastic polymers into fuel oil, chlorine compounds and nitrogen compounds are contained in the product oil [6]. When we use the product oil for fuel oil, these become a cause of corrosion of instruments and produce harmful substances and it is necessary to decrease the chlorine and nitrogen contents in oil as much as possible. In this study, the degradation of PVC mixed plastic into fuel oil was carried out and the boiling point distributions and identification of organic chlorine compounds were performed. The effect of solid acid catalyst for degradation of mixed plastics and the effect of iron oxides as chlorine sorbent of dechlorination from products was investigated.

Materials and Methods

The solid acid catalyst employed in this study, silica-alumina (SA1) was supplied by Mizusawa Chemical Industries Co. Ltd., Japan. SA1 has a surface area of 420m²g⁻¹ and its SiO₂/Al₂O₃ mole ratio is 4.99. The chlorine sorbents such as goethite (α -FeOOH), goethite calcined at 400 °C in air (TR-96103), hematite (α -Fe₂O₃) and magnetite (Fe₃O₄) were supplied

by Toda Industries Co. Ltd., Hiroshima, Japan. These iron oxides have a surface area of 72, 64, 5 and $4\text{m}^2\text{g}^{-1}$, respectively. Particle size of SA1 and all chlorine sorbents is 1mm. High density polyethylene (PE) was obtained from Mitsui Chemical Co. Ltd., Japan; Polypropylene (PP) from Ube Chemical Industries Co. Ltd., Japan; Polystyrene (PS) from Asahi Kasei Industries Co. Ltd., Japan; Poly (vinyl chloride) (PVC) from Geon Chemical Co. Ltd.. Chlorine content of PVC was 52.8wt% (analytical data).

Thermal and catalytic degradation of plastic was carried out in a glass reactor under atmospheric pressure by semi-batch operation. Experimental details and product analyses were described previously [7]. In brief, 10g of sample plastic (in a weight ratio: PE or PP or PS/PVC=8/2) was loaded into the reactor, for thermal degradation. In the case of degradation using both catalyst and sorbent, 1g of acid solid catalyst and 2g of sorbent were added to 10g of plastic. For catalytic degradation in vapor phase contact, catalysts or sorbents were placed on a stainless steel net located 12cm from the bottom of the reactor. In typical run, after the reactor was set, air remaining in the reactor was purged with N_2 at a flow rate of 30ml/min. The reactor was then heated with an electric furnace from room temperature to 120°C at $3^\circ\text{C}/\text{min}$ and held at 120°C for 60min in order to remove the physically absorbed water from the catalyst and plastic sample. Nitrogen flow was then cut off and the reactor temperature was increased to the degradation temperature at a heating rate of $3^\circ\text{C}/\text{min}$. The hydrogen chloride evolved from the degradation of PVC was trapped in a flask containing an aqueous solution of NaOH. The products of degradation were classified into three groups viz., liquid products, which are condensable at room temperature; gaseous products; and residue, which refers to both carbonaceous species and waxy compounds. The liquid and gaseous products were analyzed by two gas chromatographs with a thermal conductivity detector (TCD) (YANACO: G180) and a flame ionization detector (FID) (YANACO: G6800), respectively. Organic chlorine in the liquid product were analyzed by two gas chromatographs with an atomic emission detector (AED: HP G2350A) and a mass selective detector (MSD: HP 5973), respectively.

Results and Discussion

The dechlorination ability and the effect of contact mode [liquid phase contact (LP), vapor phase contact (VP)] were investigated using goethite ($\alpha\text{-FeOOH}$) as a chlorine sorbent and silica-alumina as solid acid catalyst. Yields of all products, chlorine content and chlorine distribution to degradation products, catalyst and chlorine sorbent after degradation are shown Table 1. When SA1 was used as a chlorine sorbent, the distribution of chlorine was 92 % in

Table 1. Product Yields and Cl Distribution in Products and Catalysts for Degradation of a PP/PVC^a (8/2) Mixture (10 g) Using SA1 and $\alpha\text{-FeOOH}$ into Fuel Oil at 380°C

contact mode	catalyst	product yield (wt %)			d^c (g/mL)	Cnp ^d	Cl content in oil (ppm)		Cl distribution (wt %)		
		liquid (L)	gas (G) ^b	residue (R)			inorg.	org.	liquid	gas	residue and catalyst
1	thermal	73.2	12.8	14.0	0.78	13.0	4900	12700	12.2	89.4	0.1
2	LP SA1	59.2	21.0	19.8	0.71	8.6	1600	7000	4.8	92.0	0.6
4	LP $\alpha\text{-FeOOH}$	73.4	9.7	16.9	0.78	12.9	1300	4100	3.7	16.8	70.9
6	LP $\alpha\text{-FeOOH}$, SA1	60.6	17.0	22.4	0.73	8.7	5000	18100	13.1	18.0	66.4
3	VP SA1	68.4	14.5	17.1	0.74	10.1	2500	11400	9.0	87.4	1.1
5	VP $\alpha\text{-FeOOH}$	62.6	8.9	28.5	0.75	10.9	900	3200	2.4	6.2	90.5
7	VP $\alpha\text{-FeOOH}$, SA1	63.9	16.4	19.7	0.73	9.8	600	1100	1.0	2.4	78.9

^a Cl content of PVC polymer is 52.8 wt %. ^b $G = 100 - (L + R)$. ^c Liquid density. ^d Average carbon number of liquid based on C-NP gram. LP: liquid-phase contact. VP: vapor-phase contact.

gas and 0.6 % in the catalyst for liquid phase contact (No. 2), and 87.4 % in gas and 1.1 % in the catalyst for vapor phase contact (No. 3). For liquid phase contact, organic chlorine content in liquid product decreased from 12700 ppm to 7000 ppm. However, it is suggested that as SA1 increased the rate of degradation the residence time of the products derived from

PP degradation in the reactor is shorter than the thermal degradation and hence there is less chance to react with HCl. The above results imply that SA1 does neither fix chlorine, nor is it effective for the removal of chlorine from the liquid product. The curve of cumulative volume, composition of liquid products and organic chlorine compounds in the product oil are shown Figures 1, 2 and 3. In Figure 1, the slope of the cumulative curve is equivalent to

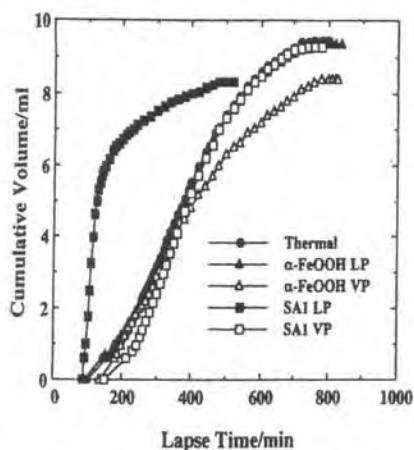


Figure 1. Cumulative volume of liquid products from thermal and catalytic degradation using SA1 and α -FeOOH of a PP/PVC (8/2) (10 g) at 380 °C.

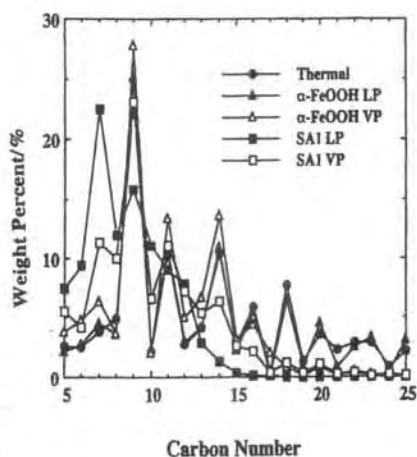


Figure 2. C-NP gram of liquid products from thermal and catalytic degradation using SA1 and α -FeOOH of a PP/PVC (8/2) (10 g) at 380 °C.

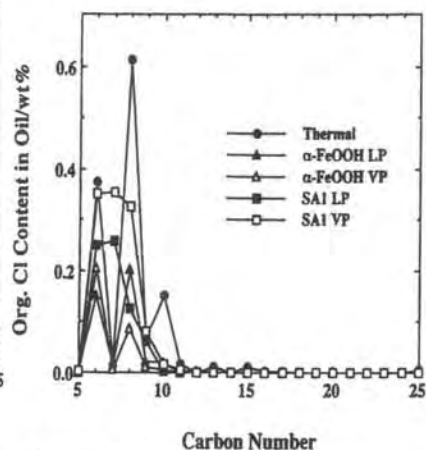


Figure 3. Cl-NP gram of liquid products from thermal and catalytic degradation using SA1 and α -FeOOH of a PP/PVC (8/2) (10 g) at 380 °C.

initial degradation rate. Figure 1 demonstrates that the degradation of PP/PVC mixture using silica-alumina (SA1) was effective for increasing the degradation rate and Figure 2 demonstrate that the weight percent of lower molecular weight components increased with the use of SA1 catalyst. Solid acid catalyst SA1 had a similar catalytic effect for the degradation of single component plastics such as PE, PP [5]. Figure 3 shows the composition of the chlorine containing liquid products: the C₆ component contains mostly 2-chloro-2-methylpropane, C₇ mostly 2-chloro-2-methylbutane and C₈ mostly 2-chloro-2-methyl pentane. The products derived from non-catalytic thermal and catalytic degradation of PP are consisted of many branched olefins. From the structure of organic chlorine compounds in liquid products derived from PP/PVC degradation, it is strongly suggested that organic chlorine compounds in liquid products was formed by reaction of HCl derived from PVC degradation to the tertiary carbon of branched olefins derived from PP degradation. Organic chlorine compounds of C₇ component was formed over SA1 catalyst only. This is thought that degradation mechanism using solid acid catalyst (SA1) differs from non-catalytic thermal one. Silica-alumina (SA1) acts as solid acid catalyst for plastic degradation, however, it does not have the ability to remove chlorine, thus a suitable sorbent is necessary to remove chlorine from the products.

The chlorine removal from the products using goethite (α -FeOOH) as chlorine sorbent was carried out. Distribution (in wt%) of chlorine derived from PVC after degradation in the liquid, gas and residues/catalyst is shown in Table 1. When goethite was used as a chlorine sorbent in liquid phase contact, 70.9% of the chlorine derived from PVC was distributed (or fixed) in goethite and 16.8% in gaseous products. We have verified that the crystalline structure of goethite was changed to magnetite by reduction during the degradation of mixed plastics. A comparison of liquid phase contact (No.4) with vapor phase contact (No.5) for dechlorination using goethite, shows that vapor phase contact was more effective for chlorine removal from products than vapor phase contact. From Figure 1, degradation rate using goethite in liquid phase contact and vapor phase contact was almost the same as the non-catalytic thermal degradation. Figure 3 shows that the distribution of organic chlorine

compounds derived from PP/PVC degradation using goethite was very similar to the thermal degradation, but the content of organic chlorine compounds decreases significantly. The fact that the chlorine content in product oil was 17600ppm for non-catalytic thermal degradation and 5400ppm for the degradation using goethite demonstrates that goethite removes chlorine from the liquid product. Furthermore when silica-alumina and goethite coexisted in vapor phase (No.7), chlorine content in liquid product decreased to 1700ppm.

The above results clarify that goethite and vapor phase contact is effective for chlorine removal from the products. Next, the chlorine removal from the products derived from PP/PVC degradation was carried out in vapor phase contact using other iron oxides (goethite calcined at 400 °C in air (TR-96103), α -Fe₂O₃ and Fe₃O₄). Table 2 compares the dechlorination ability of different types of iron oxides. Goethite calcined at 400 °C in air (TR-96103) and Fe₃O₄ also possessed dechlorination ability, but α -Fe₂O₃ did not.

Table 2. Product Yields and Cl Distribution in Products and Catalysts for Degradation of a PP/PVC^a (8/2) Mixture (10 g) Using Iron Oxides in Vapor-Phase Contact into Fuel Oil at 380 °C

Cl sorbent	product yield (wt %)			<i>d</i> ^c (g/mL)	Cnp ^d	Cl content in oil (ppm)		Cl distribution (wt %)		
	liquid (L)	gas (G) ^b	residue (R)			org.	total ^e	liquid	gas	residue
		73.2	12.8			14.0	0.78	13.0	12700	17600
α -FeOOH	62.6	8.9	28.5	0.75	10.9	3200	4100	2.4	6.2	90.5
TR-96103	65.5	9.8	24.7	0.76	11.0	3000	4300	2.7	11.3	80.0
α -Fe ₂ O ₃	62.2	11.9	25.9	0.75	11.3	15500	20800	12.3	34.9	49.7
Fe ₃ O ₄	60.4	8.0	31.6	0.75	11.0	3100	4600	2.7	1.2	96.5

^a Cl content of PVC polymer is 52.8 wt %. ^b $G = 100 - (L + R)$. ^c Liquid density. ^d Average carbon number of liquid based on C-NP gram. ^e Organic Cl + Inorganic Cl (Cl stands for chlorine).

Although chlorine was fixed to solid iron oxides, the crystalline structure of iron chlorides was not observed in the XRD pattern of the spent iron oxides. But when dechlorination using the iron oxide (Fe₃O₄) supported on active carbon as a chlorine sorbent was carried out, the crystalline structure of chlorine sorbent changed as follows: Fe₃O₄ → Fe₃O₄, FeCl₂·2H₂O, FeCl₂·4H₂O. From this result, it is thought that the crystalline structures of the sorbents may have changed partially to FeCl₂.

Conclusions

Organic chlorine compounds were produced by the addition of HCl deriving from PVC to the products obtained from the degradation of PE, PP and PS. Solid acid catalyst (silica-alumina) was effective for the degradation of PVC mixed plastic. Iron oxides were efficient chlorine sorbents for the dechlorination of degradation products. Vapor phase contact was more effective for chlorine removal from products than liquid phase contact. Although the data of chlorine removal from PE/PVC and PS/PVC degradation using solid sorbents are not shown, we have verified similar effects of sorbents in PE/PVC and PS/PVC degradation as PP/PVC degradation i.e. the content of chlorine in the oil was decreased by the use of chlorine sorbents.

References

- Mordi, R.C.; Field, R.; Dwyer, J. *J. Anal. Appl. Pyrolysis*, 1994, **29**, 45-55.
- McCaffrey, W. C.; Kamal, M. R.; Cooper, D. G. *Polym. Degrad. Stab.*, 1995, **47**, 133-139.
- Sakata, Y.; Uddin, M. A.; Koizumi, K.; Murata, K. *Chem. Lett.*, 1996, **3**, 245-246.
- Uddin, M.A.; Koizumi, K.; Murata, K.; Sakata, Y.; *Polym. Degrad. Stab.*, 1997, **56(1)**, 37-44.
- Sakata, Y.; Uddin, M. A.; Muto, A.; Kanada, Y.; Koizumi, K.; Murata, K. *J. Anal. Appl. Pyrolysis*, 1997, **43**, 15-25.
- Blazso, M.; Zelei, B.; Jakab, E.; *J. Anal. Appl. Pyrolysis*, 1995, **35**, 221-235.
- Uddin, M. A.; Sakata, Y.; Shiraga, Y.; Muto, A. *Ind. Eng. Chem. Res.*, 1999, **38**, 1406-1410.