# Influence of Metal Oxide on the Fixation of Chlorine in Thermal Decomposition of Poly (vinylidene chloride co vinyl chloride)

O. Terakado*, Y. Takahashi and M. Hirasawa

*Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, 464-8603 Nagoya, Japan*

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## ABSTRACT

The chlorine-fixation ability of various metal oxides (ZnO, $Fe_2O_3$, $La_2O_3$, $Nd_2O_3$, CaO) has been examined in thermal decomposition of copolymer of poly(vinylidene chloride) and poly(vinyl chloride), denoted hereafter as PVDCcp, at 1073 K under inert atmosphere. The addition of metal oxide gives rise to the suppression of HCl gas owing to the chlorination of oxides. The formation of main chlorinated organic compounds in the process of thermal decomposition has also been investigated for the mixture of the PVDCcp and metal oxides.

**Keywords:** poly(vinylidene chloride); metal oxides; chlorine fixation

## 1. INTRODUCTION

Thermal treatment of waste plastics including chlorine-containing polymers, e.g. poly(vinyl chloride), PVC, and poly(vinylidene chloride), PVDC, gives rise to the emission of harmful compounds, such as hydrogen chloride and chlorinated organic compounds. The fixation of chlorine is, therefore, an important issue for the feedstock recycling of waste polymers and the environment-friendly chlorine circulation. We have so far carried out pyrolysis study of PVC-metal oxide mixtures in order to examine the simultaneous recycling treatment of PVC and waste oxides discharged extensively as metallurgical dust, sludge and so forth /1-3/. One of the typical waste oxides is the electric arc furnace dusts, ca. 500 thousand tons of which being discharged annually in Japan, consisting mainly of $Fe_2O_3$ and ZnO. Recycling of rare earth magnet sludge is becoming important because of the rapid increase in their usage in various electronic equipments. It has been found that pyrolysis of PVC - metal oxide mixture leads to the suppression of hydrogen chloride and chlorinated organic compounds resulting from the formation of metal chloride or oxychloride.

In the present work we have studied the influence of metal oxide on the thermal decomposition of copolymer of PVDC and PVC, PVDCcp. The polymer is used as packaging film because of its high oxygen barrier ability as well as good water vapor permeability, and, as a consequence, is abundant chlorine containing polymer in municipal waste plastics. As known in literature, the de-chlorination behavior of PVDC is different from that of PVC /4/. The comparison was made between the pyrolysis behavior of PVDCcp – metal oxide mixture and that of the PVC – oxide systems.

## 2. EXPERIMENTAL PROCEDURE

PVDCcp, supplied from Aldrich, with the nominal

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* Corresponding author. Tel.: +81 52 789 3250; fax: +81 52 789 3250.
*E-mail address:* teramon@numse.nagoya-u.ac.jp (O. Terakado).

unit composition of $C_4H_5Cl_3$ (Particle size: 0.2mm; Melt viscosity: 530 Pa·s at 448 K) was used in the present study. Pyrolysis samples were prepared by mechanical mixing of the co polymer and metal oxide of reagent grade and the consequent pelletization with the load of ca. $2.5\times10^8$ Pa. The oxides have the particle diameter of 1-10 μm, and the BET surface area of the order of 1 $m^2/g$. Detailed physical properties of the oxides are summarized in Ref. /3/. It was previously found that pyrolysis behavior of polymer is not affected significantly by the physical properties. The composition of [polymer unit]:[oxide] = 2:3 and 2:1 in molar ratio was examined on the basis of the stoichiometry of the corresponding metal chlorides.

The pyrolysis set up is similar to that described elsewhere /3/. A sample pellet was placed on an alumina boat which was inserted in a quartz tube of 700 mm in length and 30 mm in i.d. Pyrolysis was performed under helium atmosphere with the flow rate of 100 ml/min. The sample was quickly inserted into the hot zone of the quartz reaction tube placed in a horizontal electric furnace. The reaction time was 10 min. Evolved gas was passed through a water trap followed by a hexane trap. Volatile organic compounds captured at the hexane trap were analyzed by a chromatography – mass spectrum (GC/MS) analyzer (GC/MS 6890/5973, Hewlett-Packard). After the pyrolysis run, the reaction products adhered on the reaction tube were carefully collected with tetrahydrofuran (THF), and analyzed by GC/MS. We have used DB-5 column for the GC/MS analysis.

The amount of chloride ion, $Cl^-$, in the water trap was determined after pyrolysis run by an ion meter (IM-40S, TOA Electronics). A chloride ion-selective electrode (TOA CL-125B) was used as the working electrode, and the reference electrode (TOA HS-305DS) was a double junction-type Ag/AgCl electrode with saturated KCl solution as an inner solution and 0.1 M $KNO_3$ solution as an outer solution adjacent to the sample solution. Typical experimental error was within 10%.

For the PVDCcp – ZnO and – $Fe_2O_3$ systems the deposition of metallic compounds was observed at the cold part of the quartz reaction tube. We have carefully collected them with distilled water and analyzed the solution with ICP spectrometer (SPS 1500VR, Seiko Instruments). The characterization of pyrolysis residues in alumina reaction boat was performed with X-ray diffractometer (XRD-6100, Shimadzu) and scanning electron mictroscopy with EDS analyzer (JSM-6330F&JED-2140, JOEL).

The thermal decomposition behavior of the sample was studied also by a thermogravimetric (TG) analyzer (TGA 2050, TA Instruments). A piece of sample pellet (~20 mg) prepared with the load of ca. $9.8\times10^7$ Pa was heated up to 1073 K with the heating rate of 10 K/min under helium atmosphere (flow rate: 100 ml/min).

## 3. RESULTS AND DISCUSSION

### 3.1 TG analysis

Figure 1 shows typical results of TG for various PVDCcp – metal oxide mixtures. The degradation behavior of pure PVDCcp is similar to that reported by Akama *et al.* /4/ for PVDC where the dechlorination starts at about 473 K.

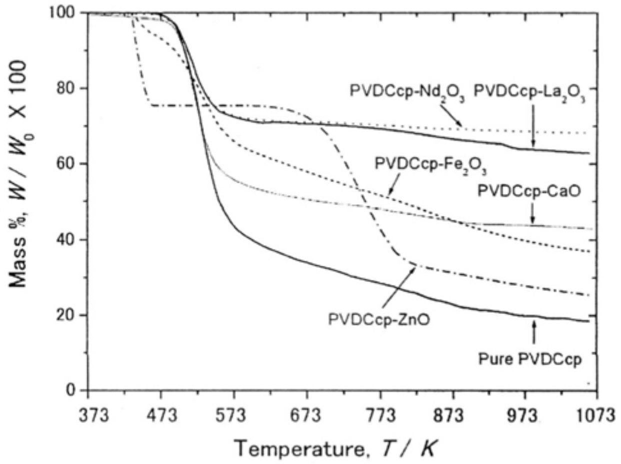

**Fig. 1:** TG curve of the PVDCcp – metal oxide mixtures under helium atmosphere with the heating rate of 10 K/min. The molar composition of the mixture is [Polymer] : [Oxide] = 2:3 for ZnO and 2:1 for other systems.

The addition of ZnO and $Fe_2O_3$ changes significantly the TG curves. Obviously, starting temperatures of the initial weight reduction are about 40

K lower for the ZnO and $Fe_2O_3$ systems than that of pure PVDCcp. In the ZnO system this phenomenon is probably related to the formation of water according to the following apparent reaction:

$$ZnO\,(s) + 2\,HCl\,(\text{from PVDCcp}) = ZnCl_2\,(s) + H_2O\,(g).$$

The precipitation of water was clearly observed at lower temperature of the quartz reaction tube. According to our previous simultaneous TG-MS analysis for PVC-ZnO mixture, the weight reduction of the system starts ca. 20 K below that of pure PVC and only the mass spectra of water is observed at the initial weight reduction stage /1/. It is considered that the contact between PVC melt and ZnO particles induces the dechlorination from PVC chain at temperature lower than that of de-HCl reaction of pure PVC. A similar mechanism works presumably for the dechlorination of PVDCcp by the addition of zinc oxide. On the other hand, the weight reduction in TG curve cannot be explained only by the evaporation of $H_2O$, since the maximum formation of water would result in the weight reduction of ca. 9 %. Therefore, the present result indicates the simultaneous formation of volatile hydrocarbons and/or evaporation of HCl, that is not reacted with ZnO, at the early stage of the decomposition. It should be noted that the kinetics of the de-HCl reaction is faster than that of pure PVC as well as PVDCcp, as observed in pyrolysis experiments at constant temperature /5/.

In the case of PVDCcp – $Fe_2O_3$ mixture, the formation of volatile iron chloride is responsible for the weight reduction starting at about 433 K, whereby precipitation of white hygroscopic compound is observed at the cold part of the quartz reaction tube at the initial stage of the decomposition. This compound is easily dissolved in water after pyrolysis run, and the existence of iron was confirmed by an ICP measurement. It is of interest that the weight reduction for the above two systems starts at nearly the same temperature. From the present result we speculate that, in molecular scale, the oxygen in the oxide is responsible for the oxygen – chlorine exchange reaction at the initial stage of thermal decomposition of PVDCcp, presumably lowering the decomposition temperature. It is here noted that our previous study of the pyrolysis of PET on single crystalline ZnO indicated that the unique morphology of the carbonaceous compound formed by the reaction was due to the oxygen- terminated surface of the metal oxide /6/.

The abrupt weight reduction above 673 K for the PVDCcp - ZnO system associates with the evaporation of $ZnCl_2$ as well as the degradation products. It should be noted that the similar TG behavior was observed in the PVC-ZnO system /1/.

Contrary to the PVDCcp – ZnO and $Fe_2O_3$ systems, the addition of rare earth oxides and CaO does not apparently change the TG curve, though their different dechlorination behavior is discussed in the following sections.

## 3.2 Influence of metal oxide on the formation of hydrogen chloride

As reported in literature /4,7,8/, chlorine in polymer is released as hydrogen chloride as well as chlorinated organic compounds in thermal degradation of PVC and PVDC. Table 1 shows the amount of HCl in the water trap for various PVDCcp – metal oxide mixtures in the present experiments. The composition is [polymer unit]:[oxide] = 2:1. The amount of chlorine is normalized by that of the initial chlorine in the sample mixture. Within the experimental error, i.e. ~10%, almost all chlorine is converted to HCl in the case of pure PVDCcp. It should be noted here that chlorinated organic compounds are also formed with the amount of the order of milligrams of compounds per 1g PVDCcp as discussed later. The table shows that the addition of oxide leads to the suppression of HCl, and that the apparent ability of HCl suppression is clearly different among oxides examined in the present study. The mixture with zinc oxide is particularly effective for the reduction of HCl emission. This is owing to the formation of $ZnCl_2$ as mentioned above. On the other hand, the degree of chlorination of iron oxide is considerably smaller than that of zinc oxide. This result has also been observed in our previous study for PVC – oxide mixtures /3/ and is comparable to the work by Kasaoka *et al.* of the chlorination of oxides by HCl gas /9/. In the case of rare earth oxide, the formation of oxychloride (LaOCl or NdOCl) was confirmed by XRD measurements for the pyrolysis residues, as discussed later.

**Table 1**

Ratio of Cl captured at water trap and the initial chlorine for the pyrolysis of PVDCcp - oxide mixtures at 1073 K, together with result of PVC systems /3/. The molar composition of the mixture is [polymer] : [oxide] = 2: 1.

| Oxide | None | ZnO | $Fe_2O_3$ | CaO | $La_2O_3$ | $Nd_2O_3$ |
|---|---|---|---|---|---|---|
| PVDCcp | ~100 | 59 | 71 | 66 | 61 | 60 |
| PVC | 92 | 36 | 69 | 51 | 3 | 25 |

### 3.3 Pyrolysis residue

Fig. 2 shows the XRD pattern of pyrolysis residues of PVDCcp – metal oxide mixtures. It is clearly seen that the pyrolysis residue does not contain chlorinated compounds for $Fe_2O_3$ and ZnO added samples. The results are due to the evaporation of the corresponding chlorides, in accordance with that of TG as presented in Fig. 1. The pyrolysis of $2PVC - 1Fe_2O_3$ mixture gives rise to the complete reduction of the oxide /3/, while in the case of the $2PVDCcp - 3Fe_2O_3$ mixture the oxide is not fully reduced, so that the apparent partial pressure of oxygen is higher for the latter system than that of the former.

In the cases of rare earth oxides and CaO, the pyrolysis residues contain chlorinated compounds in the form of oxychloride and complex chlorinated compounds, respectively. In the case of rare earth oxide the results is the same as that observed in our previous study on the pyrolysis of PVC systems, where only the stable oxychloride is found in XRD pattern for the pyrolysis residue. For the calcium system, the interpretation of XRD data is extremely complicated, since the hygroscopic nature of the pyrolysis residue, probably due to the calcium oxide and related compounds, is also responsible for the XRD result.

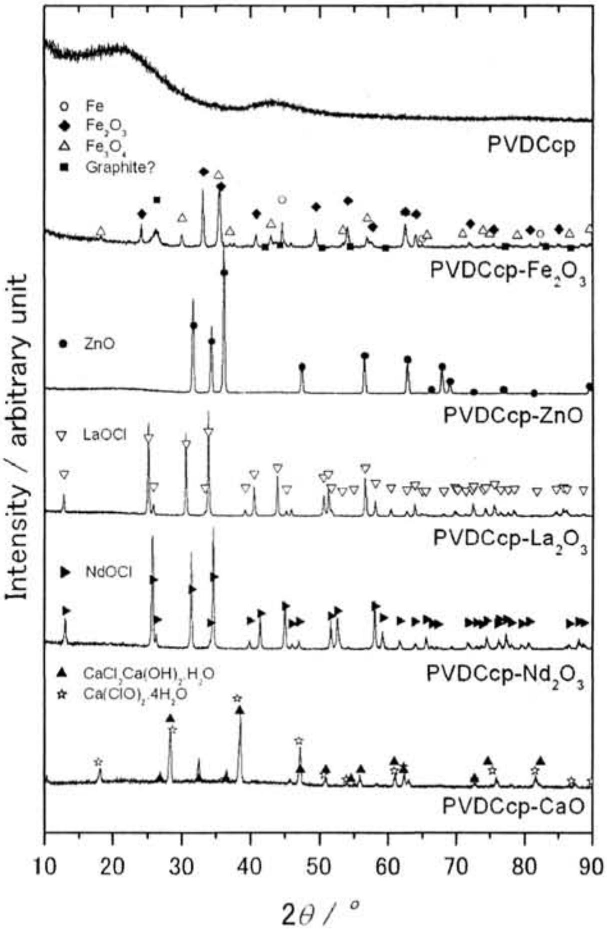

**Fig. 2:** XRD patterns of the pyrolysis residues of PVDCcp – metal oxide mixtures. Pyrolysis temperature is 1073 K. The composition of the mixture is [Polymer] : [Oxide] = 2:3 for ZnO and 2:1 for other systems in molar ratio.

### 3.4 Product analysis of chlorinated organic compounds

It is known that thermal degradation products of PVDC include mono-, di-, and tri-chlorobenzene (CB) /7/, though quantitative information has not been, so far, provided. In the present study we have performed the quantitative analysis of these compounds which have been captured at a hexane trap. The analytical results are summarized in Fig. 3. Obviously, the addition of oxide results in the suppression of the CB group compounds. The formation of these compounds is related with the cyclization of polyene containing chlorine that is produced at the early stage of dehydrochlorination. The present result accordingly indicates that the oxide prevent the cyclization. It should be, however, noted that the suppression of CB is not observed for the PVC system, and the addition of some oxides, e.g. $Fe_2O_3$ and $CeO_2$, leads to the enhancement of the formation of mono CB /3/. As for the influence of the amount of oxide, the formation of CBs decreases, in general, with increasing the oxide concentration. This tendency can be understood by the increase of the reaction sites of the chlorination of oxide. The reason of an opposite tendency for the zinc oxide system is unclear yet. A substantial decrease of the CBs was observed for the $La_2O_3$ system, that is strongly related with the formation of a stable lanthanum oxychloride, as discussed in section 3.5.

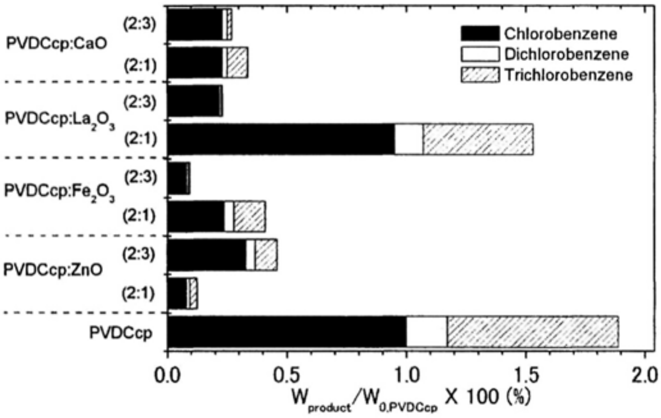

**Fig. 3:** Product yields (100×weight of product /weight of initial polymer) of mono-, di-, and tri-chlorobenzenes at 1073 K. The molar composition of polymer unit and oxide is shown in parenthesis.

In addition to the formation of CB compounds, a series of chloronaphathalenes (di-, tri-, and tetra-chloronaphthalene), CNs, has been collected from the quartz reaction tube by THF in the present study. The results of the quantitative analysis for these products are summarized in Fig. 4. In this case, we have carried out quantitative analysis of 1,8-dichloronaphthalene (1,8-diCN), and the total abundance of chromatograph for other CNs was calculated based on the result of 1,8-diCN to give the product yield. Because of the limitation of the analysis accuracy a precise interpretation of the result is currently not possible. However, it is clearly seen that the addition of $Fe_2O_3$ reduces the emission of these chlorinated organic compounds: the reduction of ca. 90 % was observed in comparison with the case of pure PVDCcp. Taking into account the experimental fact that the formation of iron chloride, strong Lewis acid, from the PVDCcp – $Fe_2O_3$ mixture is observed, we anticipate that the cyclization of polyene, which is formed after the de-hydrochlorination process, is inhibited by the chloride. The electron pair in polyene is attracted to compounds which have high acidity. It should be noted that the addition of $FeCl_3$ enhances the cross-linking of polyenes formed in thermal decomposition of PVC /10/. Further investigation is needed to clarify the relation between the cross-linking of polyenes and the evaporation of the iron chloride at high temperature.

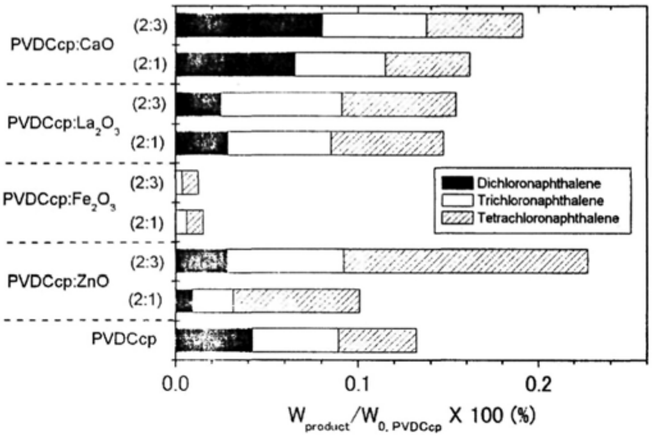

**Fig. 4:** Product yields of di-, tri-, and tetra-chloronaphthalenes (Pyrolysis temperature = 1073 K). The molar composition of polymer unit and oxide is shown in parenthesis.

### 3.5 Chlorine mass balance

Figure 5 summarizes the chlorine mass balance for some PVDCcp – oxide mixtures. For the zinc and iron systems, the amount of chloride was evaluated from the results of ICP measurements of Zn and Fe on the assumption of the stoichiometric reaction of $ZnCl_2$ and $FeCl_2$ formation. The considerably large amount of miscellaneous chlorine for the zinc system may be ascribed to the formation of water-insoluble compound on the quartz reaction tube, such as oxychloride, since zinc is not detected in the pyrolysis residues according to a SEM-EDS analysis. In the case of rare earth oxides, the oxide is converted to oxychloride according to the XRD measurements for pyrolysis residues.

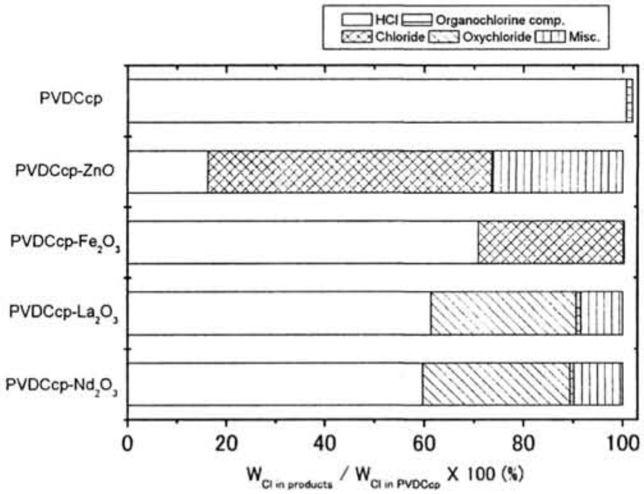

**Fig. 5:** Chlorine mass balance for the pyrolysis of PVDCcp – metal oxide at 1073 K. The composition is [Polymer] : [Oxide] = 2:3 for ZnO and 2:1 for other systems in molar ratio.

### 3.6 Chlorine fixation ability of lanthanum oxide

Here, we examine the limitation of the suppression of hydrogen chloride or the chlorine fixation ability by metal oxide. The present authors' previous study showed that the addition of $La_2O_3$ in thermal degradation of PVC resulted in the considerable suppression of HCl with the chlorine fixation of >95% as oxychloride, LaOCl /3/. In this case the high fixation ability can be achieved for sample with the composition of [Cl]:[La] = 1:1. We have, therefore, examined the chlorine fixation ability of $La_2O_3$ by varying its composition in thermal degradation of PVDCcp. The result is shown in Fig. 6. The fixation of ~78% was observed for the composition of [Cl]:[La] = 3:3 (or 1:1), and ~92 % for [Cl]:[La] = 3:4. The difference in the ability can be related to both the different physical properties, such as particle size and viscosity of decomposing polymers, and also the difference in degradation behavior of PVC and PVDCcp. The emission of HCl ends at ca. 673 K in the thermal decomposition of PVC but continues over 1073 K in the case of PVDC /4/. The high fixation ability of rare earth oxides as HCl absorber suggests their potential application to safe treatment of waste plastics including chlorine-containing polymer.

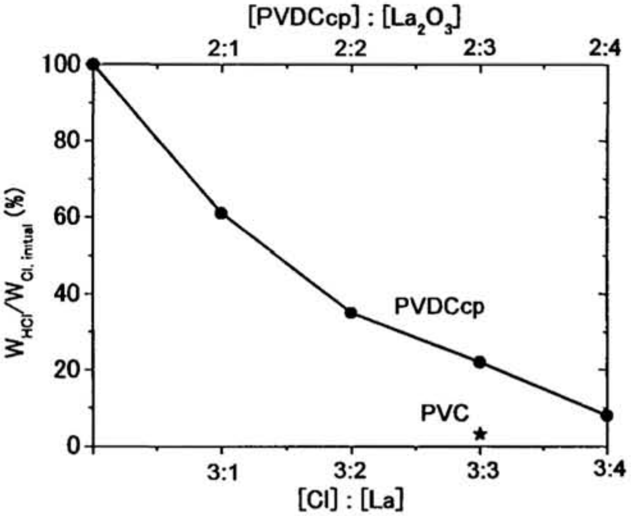

**Fig. 6:** Variation of the ratio of weight of HCl to the initial chlorine in the sample as a function of the ratio of chlorine and lanthanum for PVDCcp – $La_2O_3$ at 1073 K. ●: PVDCcp – $La_2O_3$ mixture, ★: Result of PVC-$La_2O_3$ mixture /3/.

## 4. CONCLUSION

The addition of metal oxide leads to the considerable reduction of HCl in thermal decomposition of PVDCcp. Lanthanum oxide shows the good ability to fix the chlorine up to 78% in the case of [Cl]:[La]=1:1. Moreover, it was found that the effect of iron oxide was especially remarkable for the suppression of chlorinated organic aromatic compounds. The present results are useful not only for the feedstock recycling of waste plastics including chlorinated polymers but also for environment-friendly treatment in the chlorine circulation.

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