

## THE EFFECT ON FORMATION OF PCDD/Fs AND COPLANAR PCBs DURING PVC COMBUSTION AT VARIABLE PLASTICIZER CONTENT

Kim KS, Kang WK, Ko YH, Hong KH, Cha JD, Lee JH, Yoon KD

Korea Testing Laboratory, 222-13 Guro-3Dong Guro-Gu, Seoul, Korea

### Introduction

Through combustion processes or accidental fires, organic chlorinated compounds such as dioxins are emitted from plastics. In order to form chlorinated compounds during combustion, a chlorine source is essential in the combustible. So, it is suspected that polyvinylchloride(PVC) is the main source of dioxins from plastic combustion. Chlorinated plastics such as polyvinyl chloride(PVC) release their chlorine and may be major sources of chlorine during combustion.<sup>1</sup>

To manufacture the PVC product, the addition of plasticizer is required for controlling the hardness of goods. Therefore, the emission of hazardous organic pollutants depends on the composition of PVC materials, particularly on the type and quantity of the plasticizer used.<sup>2</sup> As the content of plasticizer, PVC products are classified into three groups. The hard PVC contains about 0~3 mass% of plasticizer at 100 mass% of PVC. The semi-hard and soft PVC product contains about 15, 50 mass% of plasticizer at 100 mass% of PVC, respectively. Generally, dioctylphthalate(DOP, di-n-ethylhexylphthalate) is the major plasticizer and dibutylphthalate (DBP) or dioctyladipate(DOA) is used as a supplement.

The purpose of this study is to investigate the effect of DOP content in PVC materials and research the relationship of PCDD/Fs and coplanar PCBs(co-PCBs) from PVC combustion at variable DOP content.

### Materials and Methods

For the efficient combustion, the "3Ts" are regarded as the most important factor. The "3Ts" are high combustion temperature(over 800 °C), sufficient residence time of the combustion gas(min. 2 seconds), and adequate turbulence for mixing of the combustion gas with air. In this study, it was used downstream tubular furnace to

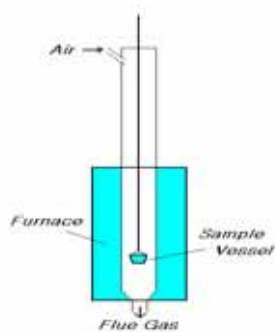


Fig. 1. Combustion apparatus.

give some turbulence and controlled to high temperature condition of 900 °C and enough residence time that is commonly used at real incineration plant.

PVC applied was free of additives and used as powders from Aldrich. DOP used was purchased from Junsei Chemical Co. Ltd.(min. 99 % purity). Samples were premixed 0, 15, 50 mass% of DOP with 100 mass% PVC, respectively. For the combustion experiment, it weighed 0.5 g as the content of the PVC in the sample. The combustion apparatus consisted of a quartz tube of 40 mm inner diameter in a 50 cm tubular furnace. A platinum sample vessel containing the PVC materials was positioned in the furnace. A high purity air (> 99.999 %) was applied and the downstream flow rate was 2 L/min. Temperature was adjusted to 900 °C at the vessel position and combustion experiment lasted 15 minutes with a total trapping of incineration products. Thermal decomposition of PVC occurred immediately after insertion and flue gas was passed through sampling device. The concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO and NO<sub>x</sub> were measured simultaneously.

Detailed measurements of air temperature revealed that the temperature was maintained about 900 °C in 30 cm behind the sample vessel. Therefore, the residence time at the flow rate of 2 L/min was 2.8 s after allowance for air expansion. It is commonly said that the longer residence time, the lower organic pollutants concentration. In this experiment, the combustion of PVC occurred in 0.5~5min after insertion. Fig. 2. shows the CO<sub>2</sub> emission at different DOP content.

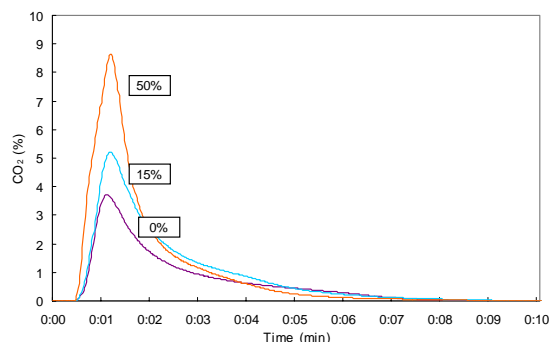


Fig. 2. CO<sub>2</sub> emission curve of PVC combustion.

The sampling device used in this experiments consisted of a silica glass microfibre filter followed by XAD-2 resin and toluene for backup solvent.

The sample extraction and clean-up procedure were mostly carried out in accordance with Korean Standard Method of Air Pollution. After cooling the furnace to room temperature, filter, adsorbent and solvent were collected and the filter and adsorbent were soxhlet extracted with toluene for 24 hours. The extract and back-up solvent were concentrated and replaced into hexane.

For PCDD/Fs and co-PCBs analysis, the sample clean-up procedures comprised sulfuric acid treatment and a mixed column with differently treated multi-layered silica. Before alumina column, the sample was divided into two parts. One was used for PCDD/Fs analysis, the other for co-PCBs. The analysis of PCDD/Fs and co-PCBs was performed on selected ion monitoring mode with a JEOL JMS-700D high resolution mass spectrometer connected with high resolution gas chromatograph.

## Results and Discussion

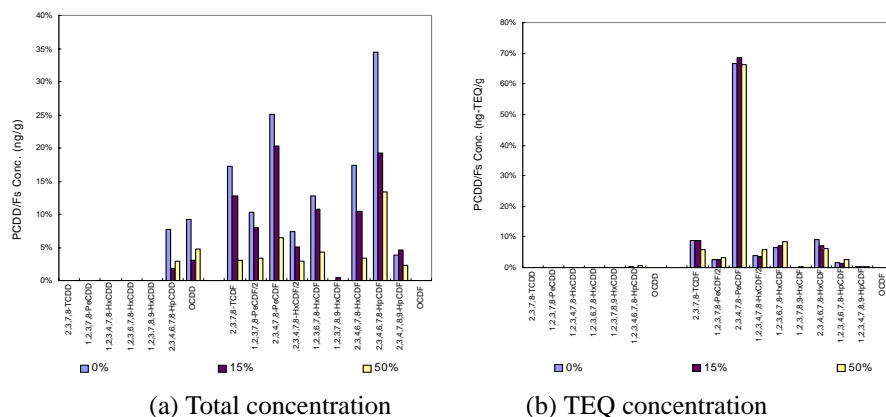
Table 1 shows the concentration of organic pollutants from PVC combustion. The concentration of PCDD/Fs and co-PCBs with DOP content was slightly decreased as the DOP content increased.

Table 1. The concentration of organic pollutants from PVC combustion.

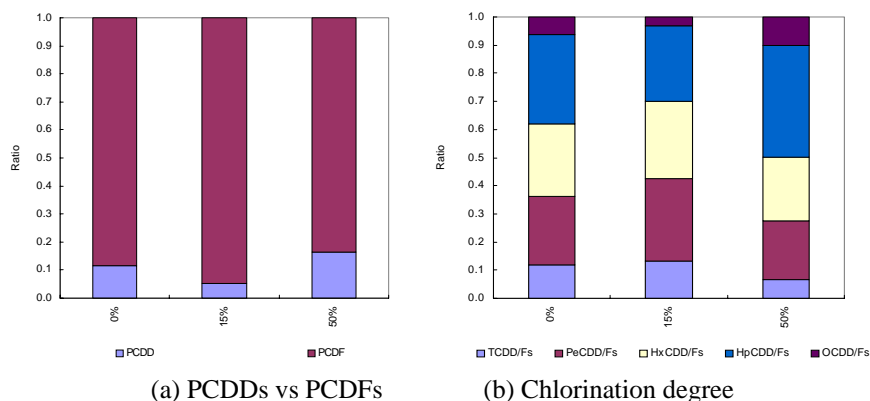
Concentration (ng/g)		DOP Content in PVC						DOP
		0%		15%		50%		
		Avg	SD	Avg	SD	Avg	SD	
PCDD/Fs	Total	1.556	0.755	0.968	0.240	0.472	0.140	N.D.
	TEQ	0.190	0.059	0.148	0.038	0.050	0.010	N.D.
co-PCBs	Total	3.523	0.400	3.658	1.012	1.526	0.342	N.D.
	TEQ	0.046	0.005	0.039	0.012	0.007	0.001	N.D.

In this experiment, 2,3,4,7,8-PeCDF and 1,2,3,4,6,7,8-HpCDF is predominant in 17 2,3,7,8-substituted toxic isomers. As the toxic equivalent(TEQ) value, 2,3,4,7,8-PeCDF which toxicity equivalency factor(TEF) is 0.5 was the majority of PCDD/Fs (Fig. 3(b)). Regardless of DOP content, PCDFs were far more than PCDDs and the portion of PCDDs is only 4.96~19.39 % (Fig. 4(a)). Low chlorinated congeners were emitted 50.7~70.0 % in whole congeners and it was different to the common emission pattern of municipal waste incinerators (MWIs) effluents, where highly chlorinated congeners are more emitted. It was a reason why the combustion condition in this study is aim to complete combustion of PVC by meeting "3Ts". Because the sampling point in this experiment was similar to the high temperature zone in the furnace outlet of MWI, it was different from the previous studies that usually carried out at the low temperature zone.

# Formation, sources and source inventories

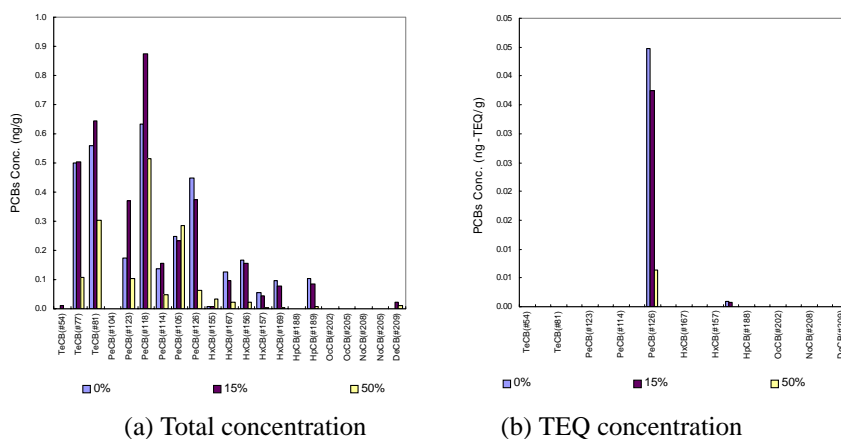


(a) Total concentration (b) TEQ concentration  
 Fig. 3. Isomer distribution of PCDD/Fs during PVC material Combustion.



(a) PCDDs vs PCDFs (b) Chlorination degree  
 Fig. 4. Relative abundance of PCDD/Fs during PVC Combustion.

For determining co-PCBs emission, 21 isomers within TeCBs~DeCBs in 209 total isomers were analyzed, where 12 isomers have TEF estimated by WHO in 1997. In the PVC combustion, low chlorinated PCBs such as TeCB and PeCB were most of co-PCBs and the portion was over 80 %. As the TEQ value, 3,3',4,4',5-PeCB (#126) whose TEF is 0.1 was the major isomer of co-PCBs.

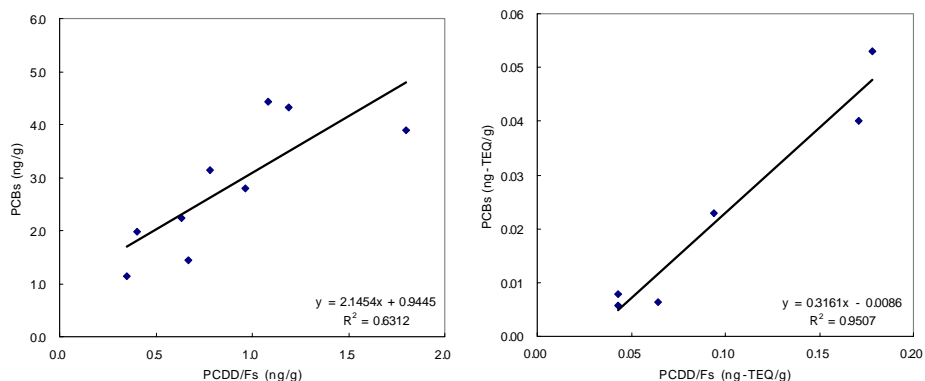


(a) Total concentration (b) TEQ concentration  
 Fig. 5. Isomer distribution of co-PCBs during PVC Combustion

## Formation, sources and source inventories

It was also investigated the relationship of PCDD/Fs and co-PCBs from PVC combustion at variable DOP content. It is generally accepted that PCBs form PCDD/Fs with some reactions furthermore.<sup>3,4,5</sup> In this study, there was found a significant correlation between PCDD/Fs and co-PCBs.

It has been shown significant correlation between PCDD/Fs and co-PCBs (Fig. 6). Because the concentration of PCDDs was too little, the interrelationship of PCDFs with co-PCBs was higher than PCDDs.



(a) PCDD/Fs vs. co-PCBs (b) PCDD/Fs vs. co-PCBs - TEQ  
Fig. 6. Correlation of PCDD/Fs & co-PCBs during PVC Combustion.

It was investigated that the effect of DOP content in PVC materials and researched the correlation of PCDD/Fs and co-PCBs from PVC combustion due to DOP content variation. From this experiments, following conclusions could be drawn:

As the DOP content in PVC material was increased, the formation of PCDD/Fs and PCBs were slightly increased.

Regardless of DOP content, the portion of low chlorinated compounds was almost larger than highly chlorinated compounds.

There was found the relationship between PCDD/Fs and co-PCBs in some extent.

### References

1. Wirts M, Lorenz W, Bahadir M. *Chemosphere* 1998;37:1489.
2. Gotlib EM, Grinberg LP, Chakirov RR. *Reactive & Functional Polymers* 2001;48:209.
3. Ballschmiter K, Swerev M. *Fresenius Z. Anal Chem* 1987;328:125.
4. Ballschmiter K, Zoller W, Buchert H, Class TH. *Fresenius Z. Anal Chem* 1985;322:587.
5. Shaub WM, Tsang W. *Environ. Sci. Tech.* 1983;17:721.