Characterization on Dioxin Emission of TiO_2 Nanoparticle-Encapsulating Poly(vinyl chloride) (TEPVC) compared to conventional PVC

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ABSTRACT

TiO_2 nanoparticle-encapsulating poly(vinyl chloride) (TEPVC) was combusted in a well-controlled laboratory-scale incinerator at a temperature of 700 °C, and then dioxins (PCDDs, PCDFs and coplanar-PCBs) formed in the exhaust gases were analyzed by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). TEPVC sample was prepared by the suspension polymerization of vinyl chloride monomer (VCM) with the 1.0wt% of surface modified amorphous TiO_2 nanoparticles based on the VCM weight reported in our previous study [1]. TEPVC shows valuable dioxin inhibition property due to the enhanced dispersibility of TiO_2 nanoparticles by encapsulation. Dioxin emission from TEPVC combustion was suppressed at the efficiencies of 39~82% by 0.926 wt% of encapsulated amorphous TiO_2 in TEPVC compared to conventional PVC.

Keywords: poly(vinyl chloride) (PVC), incineration, titanium dioxide (TiO_2), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs)

1 INTRODUCTION

Poly(vinyl chloride) (PVC) is widely used in extensive applications and more than 30 million tons of PVC are consumed annually in various commodities, so there is significant public concern about how the resulting wastes should be managed [2]. Incineration has competitive advantage in waste management and waste management depends mainly on incineration in many countries, but the incineration of PVC wastes can cause serious environmental problems because of the resulting formation of toxic chlorinated organic by-products such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), generally known as dioxin.

Titanium dioxide (TiO_2) is a material of current interest due to their wide range of applications. It has been used in catalytic combustion processes as a catalyst for suppressing the emission of dioxins and their precursors through the absorption of chlorinated aromatic compounds followed by catalytic decomposition. In our previous study, we first prepared TiO_2 nanoparticle-encapsulating poly(vinyl chloride) (TEPVC) aiming at breakthrough to enhance the dispersibility of TiO_2 nanoparticles in PVC matrix to maximize catalytic activities of TiO_2 nanoparticles [1].

The present study is aimed to measure and compare the amount of dioxin emitted from both TEPVC and PVC incineration, estimating the dioxin inhibition efficiency of TEPVC. Amorphous TiO_2 was used in the preparation of the TEPVC because amorphous TiO_2 has negligible photocatalytic activity [3], thereby TEPVC being expected to undergo no photodegradation. But during the incineration of this polymeric material, the presence of amorphous TiO_2 is expected to suppress the emission of dioxin through the absorption of toxic organic compounds followed by catalytic decomposition.

2 EXPREMENTAL

2.1 Sample Materials

Amorphous TiO_2 nanoparticles were prepared through hydrolysis of titanium tetraisopropoxide (TTIP) according to the work of Inagaki et al [2]. 20 mL of TTIP dissolved in 40 mL of absolute ethanol by injection was gradually added in distilled water of 200mL under vigorous stirring and aged for 24 h at room temperature. The colloidal suspension was then filtered out and dried in a vacuum oven to give TiO_2 nanoparticles as a white solid.

The TEPVC sample was prepared using a previously reported method [1]. The encapsulation of amorphous TiO_2 in PVC resin was achieved through the suspension polymerization of vinyl chloride monomer (VCM) with the 1.0wt% of surface modified amorphous TiO_2 nanoparticles based on the VCM weight. Conventional PVC sample was prepared through suspension polymerization, too.

2.2 Characterization of TEPVC

Wavelength dispersive X-ray fluorescence (WD-XRF) spectrometry was used to determine the amorphous TiO_2 content of the TEPVC. The WD-XRF measurements were performed on a Ti element with a Shimadzu XRF-1700 sequential X-ray fluorescence spectrometer using lithium fluoride (LiF) as an analyzing crystal with a 2*d* value of 0.4028 nm. For the calibration of the quantitative analyses, WD-XRF analysis was also carried out for several standard samples, which were prepared by the mechanical mixing of PVC with various concentrations of TiO_2 from 0 to 2.0 wt%.

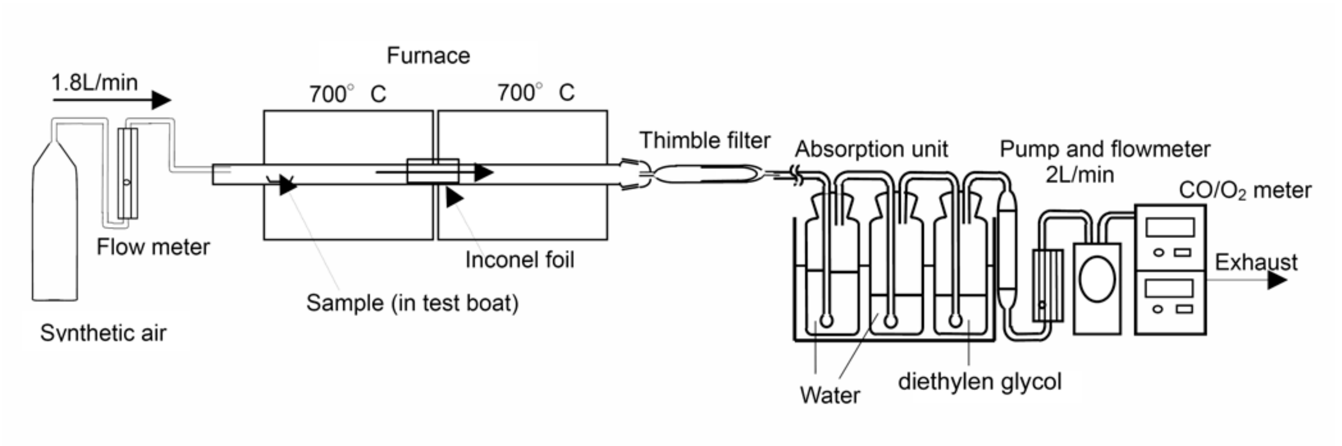

Figure 1: Schematic of the incineration test apparatus

The dispersity of amorphous TiO_2 nanoparticles in the TEPVC was investigated with transmission electron microscopy (TEM). For the TEM observations, the TEPVC grains were embedded in Gartan G-1 epoxy and cured at 60 °C for 90 min and ultra-thin cross-sections of the specimen was prepared by using a Leica Ultracut UCT ultracryomicrotome at room temperature. The TEM analyses were performed with a Jeol JEM-2000EXII at 200 kV of electron accelerating voltage.

2.3 Sample Combustion

Sample combustion, trapping of emission gas, and dioxin analysis were performed at Shimadzu Techno-Research, an official institute for dioxin measurement and analysis in Japan. TEPVC and PVC samples were first combusted in a well-controlled, laboratory-scale incinerator (Figure 1) at 700 °C. The small sample (approximately 25 mg) was placed onto a quartz boat and slid to the central position of tube furnace, then combusted. This operation was repeated for a total of 30 times, corresponding to 0.75 g of sample and 75 min of experimental period. Dioxins in exhaust gases were entrapped in an absorption unit composed of two water impingers, one diethylene glycol impinger, and the XAD-2 resin.

2.4 Dioxin Analysis

Dioxins entrapped in the absorption unit were determined by HRGC/HRMS in accordance with the Japanese standard method (Ministry of Health and Welfare of Japan, 1997). After solvent extraction with toluene for solid samples and with dichloromethane for liquid samples, a portion of the extract was spiked with $^{13}C_{12}$ labeled internal standard mixture containing one isomer each for tetra- to octa-chlorinated dibezo-*p*-dioxins and dibenzofurans and subjected to a column chromatographic clean-up procedure. This consisted of a multi-layer silica column (silica, 10% $AgNO_3$/silica, H22%- and 44% H_2SO_4/silica, silica, 2% KOH/silica, silica) and an aluminum oxide column.

HRGC/HRMS was preformed on a Waters Micromass Autospec Ultima mass spectrometer fitted with an Agilent HP6890 GC. SP-2331 (SUPELCO 60 m (length), 0.32 mm (internal diameter), 0.20 µm (film thickness)) coupled to DB-17HT (J & W 30 m, 0.32 mm, 0.15 µm) capillary column was applied to the determination of PCDD/PCDF congeners and HT8-PCB (SGE 60 m, 0.25 mm) capillary column was applied to determination of coplanar PCBs. The mass spectrometer was operated in selected ion monitoring mode (SIM) at a resolution > 10,000 and two ions were monitored for each congener group.

3 RESULTS AND DISCUSSION

3.1 Characterization of TEPVC

Figure 2 shows the dispersity of amorphous TiO_2 nanoparticles in the TEPVC. TiO_2 nanoparticles were well dispersed in PVC matrix, and the size of dispersed TiO_2 nanoparticles is in range of tens of nm.

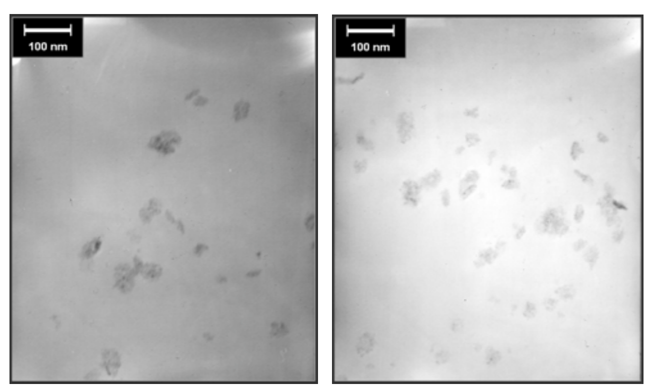

Figure 2: TEM images of the TEPVC.

WD-XRF spectrometry result indicates that amorphous TiO_2 nanoparticles were successfully incorporated within TEPVC during the encapsulation process. Amorphous TiO_2 content of TEPVC was 0.926 wt%.

	Name	TEQ factor	PVC Concentration (pg/g)	PVC Toxic equivalence (pg-TEQ/g)	TEPVC Concentration (pg/g)	TEPVC Toxic equivalence (pg-TEQ/g)
Polychlorinated dibenzo-*p*-dioxin (PCDD)	2,3,7,8-TeCDD	1	62	62	36	36
	1,2,3,7,8-PeCDD	1	130	130	70	70
	1,2,3,4,7,8-HxCDD	0.1	61	6.1	20	2.0
	1,2,3,6,7,8-HxCDD	0.1	77	7.7	22	2.2
	1,2,3,7,8,9-HxCDD	0.1	81	8.1	26	2.6
	1,2,3,4,6,7,8-HpCDD	0.01	300	3.0	66	0.66
	OCDD	0.0001	260	0.026	53	0.0053
	Total PCDDs	-	-	216.926	-	113.4653
Polychlorinated dibenzofuran (PCDF)	2,3,7,8-TeCDF	0.1	14000	1400	8100	810
	1,2,3,7,8-PeCDF	0.05	20000	1000	9400	470
	2,3,4,7,8-PeCDF	0.5	9600	4800	5000	2500
	1,2,3,4,7,8-HxCDF	0.1	18000	1800	7000	700
	1,2,3,6,7,8-HxCDF	0.1	15000	1500	6900	690
	1,2,3,7,8,9-HxCDF	0.1	4600	460	1900	190
	2,3,4,6,7,8-HxCDF	0.1	5200	520	2500	250
	1,2,3,4,6,7,8-HpCDF	0.01	37000	370	13000	130
	1,2,3,4,7,8,9-HpCDF	0.01	16000	160	5000	50
	OCDF	0.0001	49000	4.9	8600	0.86
	Total PCDFs	-	-	12014.9	-	5790.86
	Total (PCDDs+PCDFs)			12231.826		5904.3253
Coplanar polychlorinated biphenyl (Coplanar PCB)	3,4,4',5-TeCB (#81)	0.0001	1200	0.12	690	0.069
	3,3',4,4'-TeCB (#77)	0.0001	2200	0.22	1200	0.12
	3,3',4,4',5-PeCB (#126)	0.1	2000	200	1100	110
	3,3',4,4',5,5'-HxCB (#169)	0.01	710	7.1	380	3.8
	Non-ortho co-PCB		-	207.44	-	113.989
	2',3,4,4',5-PeCB (#123)	0.0001	630	0.063	360	0.036
	2,3',4,4',5-PeCB (#118)	0.0001	3700	0.37	1900	0.19
	2,3,3',4,4'-PeCB (#105)	0.0001	2200	0.22	1100	0.11
	2,3,4,4',5-PeCB (#114)	0.0005	2400	1.2	1100	0.55
	2,3',4,4',5,5'-HxCB (#167)	0.00001	1800	0.018	1100	0.011
	2,3,3',4,4',5-HxCB (#156)	0.0005	4500	2.25	2200	1.1
	2,3,3',4,4',5'-HxCB (#157)	0.0005	710	0.355	380	0.19
	2,3,3',4,4',5,5'-HpCB (#189)	0.0001	4500	0.45	2300	0.23
	Mono-ortho co-PCB	-	-	4.926	-	2.417
	Total coplanar PCBs			212.366		116.406
	Total dioxins			12444.192		6070.7313

Table 1: dioxins in the exhaust gases from conventional PVC and TEPVC combustion

3.2 Dioxin Formation from Incineration

Table 1 presents dioxins found in the exhaust gases from conventional PVC and TEPVC combustion in laboratory-scale incinerator. These results are shown on a pg/g basis, using the mass of samples consumed in the analysis. Toxic equivalence (WHO-TEQ) is calculated according to WHO-TEF (WHO/IPCS, 1998). In the case of PVC sample, PCDF congeners have been obtained in higher amounts than PCDD congeners; this is the usual trend [4]. The ratio of PCDFs to PCDDs of the combustion gas was 194, similar to the ratio of PCDFs to PCDDs of 230 in the case of TEPVC.

In the case of a blank sample, the amount of total dioxins (PCDDs, PCDFs, and co-planar PCBs) formed in the exhaust gas was 314 pg/g, which was 1/3589 of that formed from a conventional PVC sample and the TEQ was 1/100,000 of that from a conventional PVC sample, thus the dioxins from blank sample are negligible. The result of blank gas is shown on a pg/g basis assuming 1 g of sample used.

3.3 Suppression Efficiency of Dioxin Emission

The suppression efficiency of dioxin formation was calculated according to the equation

$$\text{suppression efficiency of dioxin formation (\%)} = \frac{C_{\mathrm{PVC}} - C_{\mathrm{TEPVC}}}{C_{\mathrm{PVC}}} \times 100 \qquad (1)$$

where C_{PVC} and C_{TEPVC} are the dioxin congener concentration of exhaust gases from PVC and TEPVC combustion, respectively.

Figure 4 shows the suppression efficiencies of PCDD/PCDF congeners' emission. The PCDD/PCDF congeners from TEPVC incineration are suppressed at the efficiencies of 42~82% compared to the PCDD/PCDF congeners from conventional PVC incineration. This result provides the generation of PCDDs/PCDFs from chlorinated plastics like PVC can be effectively suppressed by encapsulated amorphous TiO_2 nanoparticles. The higher chlorinated isomers of both PCDDs and PCDFs were more suppressed by amorphous TiO_2 nanoparticles encapsulated in the TEPVC.

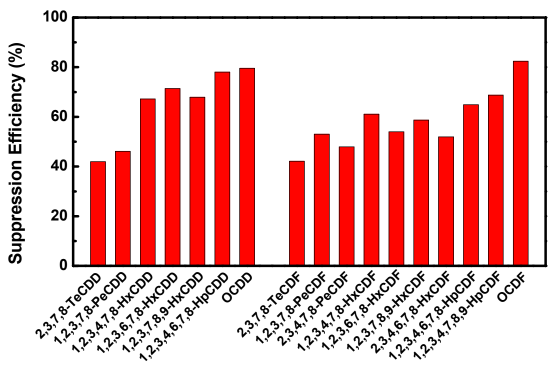

Figure 4: TEPVC's suppression efficiencies of PCDD/PCDF congeners' emission compared to the conventional PVC

Figure 5 shows the suppression efficiencies of coplanar PCB congeners' emission. The coplanar PCB congeners from TEPVC incineration are suppressed at the efficiencies of 39~54% compared to the coplanar PCB congeners from conventional PVC incineration.

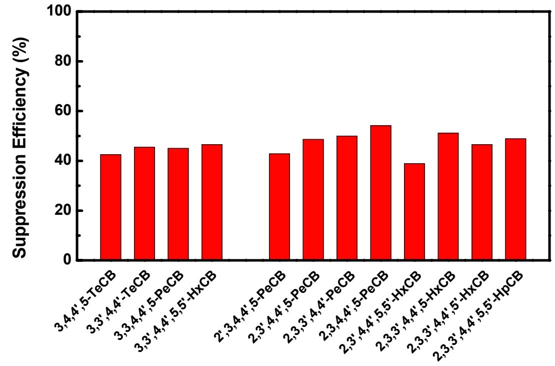

Figure 5: TEPVC's suppression efficiencies of coplanar-PCB congeners' emission compared to the conventional PVC.

4 CONCLUSIONS

TiO_2 nanoparticle-encapsulating poly(vinyl chloride) (TEPVC) shows valuable dioxin inhibition property due to the enhanced dispersibility of TiO_2 nanoparticles by encapsulation. Dioxin emission from TEPVC combustion was suppressed at the efficiencies of 39~82% by 0.926 wt% of encapsulated amorphous TiO_2 in TEPVC resin compared to conventional PVC. The results of this study show that the generation of the dioxins during combustion of PVC can be effectively suppressed by encapsulation of amorphous TiO_2 nanoparticles in the PVC resin.

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