TiO₂-encapsulating PVC capable of catalytic self-suppression of dioxin emission in waste incineration as an eco-friendly alternative to conventional PVC

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Here, we describe the preparation of TiO₂-encapsulating poly(vinyl chloride) (TEPVC), and demonstrate the potential applicability of the material as an eco-friendly alternative to conventional PVC. In particular, TEPVC shows lower emission of toxic chemicals upon waste incineration compared to PVC, owing to the catalytic oxidation and decomposition of such chemicals by the encapsulated TiO₂ nanoparticles. Surface-modified TiO₂ nanoparticles (M-TiO₂) are used for the preparation of TEPVC to facilitate the uniform dispersion of monomeric TiO₂ in the initial reaction mixture, which is the key to the preparation of a final TEPVC showing a high dispersion of functional TiO₂ nanoparticles in the PVC matrix, without significant agglomeration. The content of encapsulated M-TiO₂ in TEPVC was determined to be approximately 0.93 wt%, and the high dispersity of M-TiO₂ minimizes PVC deterioration, as determined by examinations of morphology, and thermal and mechanical properties. The emission levels of toxic chemicals upon incineration of TEPVC and unmodified PVC samples were analyzed by gas chromatography with high-resolution mass spectrometric detection, using internal standards composed of 13C-labeled congeners of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and polychlorinated biphenyls. The levels of toxic chemicals produced by incineration of TEPVC were 50% of those seen after unmodified PVC incineration; the sum of toxic equivalent values of all toxic chemicals generated from the incineration of TEPVC was thus only half that seen after incineration of unmodified PVC.

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1. Introduction

Poly(vinyl chloride) (PVC) is extensively used as a thermoplastic material because of its flame retardant properties, high chemical resistance, and low price [1,2]. More than 30 million tons of PVC are consumed annually; this will inevitably cause serious PVC waste problems within a few years [2,3]. PVC recycling is particularly problematic because of high separation and collection costs, loss of material quality after recycling, and a limited market for recyclate. Most PVC waste management has involved landfilling and incineration [4]. However, because of high population densities, limited landfill areas, high disposal costs, and contamination leaching into the soil and groundwater, waste handling policies have increasingly shifted from landfilling to incineration, especially in countries with limited land [5–7]. Although incinerating PVC offers a high degree of destruction, reduced landfill use, and the potential for energy recovery, this option can cause serious ecological and environmental problems arising from the emission of toxic dioxins and polychlorinated biphenyls (PCBs) [8–13].

The term “dioxin” is a general designation for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), which each consist of two aromatic rings covalently linked by two and one oxygen bridges, respectively. Dioxins are considered to be the most toxic chemicals ever made with toxicities over 10,000 times that of potassium cyanide, and the adverse effects of dioxins on human health, the human environment, and ecosystems have been known for many years [14–16]. Among many sources of atmospheric dioxin emission, the incineration of municipal waste is of great importance because such processes contribute significantly to overall dioxin emission [8,9]. Among municipal waste ingredients, PVC is known to be the most problematic because PVC is the single largest chlorine source, playing a significant role in the formation of dioxins and other toxic chemicals, such as PCBs, in many countries [9,17]. Therefore, finding ways to reduce the generation of such toxic chemicals has been of great interest to many researchers.

In the early stages of these efforts, researchers focused on improving PVC waste processing, mostly by maintaining an optimal combustion state during waste incineration and/or establishing new air purification facilities, some of which were reported to be successful in reducing dioxin emission [18,19]. However, upgrading all incineration facilities to optimal combustion and/or air purifica-
tion standards may take many years and a very large monetary investment. There are lots of incinerators such as home waste incinerators which are generally too small to sustain the optimal combustion condition during waste incineration [20]. The open burning of household and agricultural wastes in rural regions is another unmanageable source of dioxin, too [21]. More recently, alternative approaches have been reported to be effective in reducing dioxin emission. These include the use of secondary measures such as catalytic decomposition, photolysis, and catalytic combustion [22–28]. Combining the combustion method with a catalytic process in the treatment of toxic pollutants has several advantages, because the two-step process requires only low temperatures and is energy-efficient [26,28,29]. In one such combined approach, titania dioxide (TiO$_2$) or TiO$_2$-supported metal oxide is used to suppress dioxin emission. Various studies have examined the catalytic decomposition of chlorinated aromatic compounds on the surfaces of these catalysts [28,30–33]. In these systems, dioxin molecules are first adsorbed on the catalyst surface and are then oxidized via a redox reaction with nearby oxide or hydroxide nucleophilic species [31–35]. In post-combustion exhaust gas treatment systems, it is desirable that catalysts have a high catalytic activity to chlorinated aromatic compounds at a temperature below 300°C because large amounts of cooled flue gas pass through the equipment quickly. TiO$_2$-supported oxide of transition metal such as V and W has the favorable characteristics for this application and has been successfully applied. Nevertheless, there are still unmanageable sources remained outside the coverage of the post treatment systems [20,21]. Considering the widespread use of PVC, it is necessary to find an alternative solution which could cover these areas.

If catalyst nanoparticles with decomposition activity of chlorinated aromatic compounds are incorporated in PVC matrix, the nanoparticles can decompose chlorinated aromatic compounds during the incineration of PVC and consequently reduce dioxin emission although PVC is incinerated in the place where there is no appropriate dioxin treatment system. Previously unmanageable sources such as small waste incinerators and open burning can be managed through this approach. Moreover, catalyst nanoparticles embedded in PVC can effectively reduce dioxin generation, because catalyst nanoparticles applied as part of a post-treatment system will not have the opportunity to encounter dioxin molecules during incineration, whereas catalyst nanoparticles incorporated within PVC will be exposed to dioxins during incineration. Because catalyst nanoparticles incorporated within a PVC sample have a much higher probability of encountering dioxin molecules, the dioxin emission caused by PVC can be readily reduced to significant low-level anywhere PVC is incinerated or combusted even if the catalyst which has a relatively low activity to dioxin is applied instead of high performance catalyst commonly used in post treatment system. Among the various catalysts, TiO$_2$ has a comparatively low catalytic activity to dioxin but is colorless, odorless, biologically innoxious, and chemically resistive enough to be not dissolved in most of solvents [36]. Above all, TiO$_2$ is inexpensive and productive enough to be applied to mass production polymer PVC. However, such TiO$_2$ incorporation has unresolved problems arising mostly from the limited dispersion of TiO$_2$ nanoparticles in the polymer matrix when the conventional process is used to mix most non-polar polymers with nanoparticles. The formation of micrometer-sized agglomerates of TiO$_2$ nanoparticles can significantly decrease the area of the interface between the polymer matrix and TiO$_2$, leading to reduced efficiency of adsorption of toxic chemicals and thus to inferior suppression of dioxin emission. In a previous paper, we reported the suppression of the emission of dioxin and its precursors upon co-incineration of PVC with TiO$_2$-encapsulating polystyrene (TEPS), in which a nanoscale uniform dispersion of TiO$_2$ was obtained by encapsulation [37]. In practice, however, this approach is intrinsically limited because TEPVC shows suppression effects only when PVC and TEPVC are co-incinerated. To further increase the practical applicability of TiO$_2$ use, we investigated the direct encapsulation of TiO$_2$ in PVC, the physical properties of the material synthesized, and dioxin emission by this material when incinerated.

In this paper, we report an optimal preparation procedure for TiO$_2$-encapsulating poly(vinyl chloride) (TEPVC). The reactor used in this study mimicked industry-scale reactors producing commercial PVC, and the preparation process was not significantly different from that of a commercial PVC production process; our approach can thus be readily applied in existing PVC industries. The morphology and dispersion of TiO$_2$ nanoparticles were observed with field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM), respectively. Quantitative determination of TiO$_2$ in TEPVC was performed using X-ray fluorescence (XRF) spectrometry. We then evaluated the effects of TiO$_2$ encapsulation on the physical properties of TEPVC by comparing the thermal and tensile properties with those of unmodified PVC using differential scanning calorimetry (DSC) and a tensile test, respectively. Finally, we measured emission of PCDDs, PCDFs, and PCBs from TEPVC and unmodified PVC, with the aid of a commercial research laboratory specializing in dioxin analysis.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide, Ti(OC$_2$H$_5$)$_4$, used in the preparation of TiO$_2$, was obtained from Aldrich. 3-[(Methacryloyloxy)propyl trimethoxysilane (MPS), and anhydrous toluene (99.8%), both used for the surface modification of TiO$_2$, were also from Aldrich. All materials were used without further purification. Reagents used for suspension polymerization were obtained from the following sources: vinyl chloride (VC) from Korea Standard Gas Co. Ltd.; octyl peroxynedecanoate (BND) and diocetyl peroxydicyanate (OPP) from Chemex Co. Ltd.; poly(vinyl alcohol) (trade name K-420™) from Kuraray Co. Ltd.; octadecyl dibutyl-4-hydroxyphenylpropionate (IR), dilauryl thiodipropionate (DL), and aluminum sulfate (AS) from Hanwha Chem. Corp.; di-(2-ethylhexyl) phthalate (DEHP) from LG Chem. Ltd.; and methyl tin (trade name MT-800) from Songwon Industrial Co. Ltd. All of these chemicals were used as received. Amorphous TiO$_2$ nanoparticles used for encapsulation were prepared through hydrolysis of titanium tetraisopropoxide in ethanol solution, as described in the literature [38]. Next, MPS was grafted onto the hydroxyl groups of the TiO$_2$ nanoparticles to prepare surface-modified TiO$_2$ (M-TiO$_2$). The primary particle size of the TiO$_2$ nanoparticles was about 5 nm in diameter, as characterized by high-resolution transmission electron microscopy (HR-TEM) (Fig. S1 in Supplementary data), and the particles were determined to be amorphous based on the observation of no peaks in the X-ray diffraction (XRD) analysis (Fig. S2). The Brunauer–Emmett–Teller (BET) surface area of the prepared TiO$_2$ was 443.4 m$^2$/g. The dispersity of M-TiO$_2$ in hydrophobic liquid medium was estimated by dynamic light scattering (DLS) using an DLS-7000 spectrophotometer coupled with a GC-1000 autocorrelator (Otsuka Electronics Co., Ltd., Osaka, Japan) by utilizing an Ar laser ($\lambda = 488$ nm) at a scattering angle of 90°. From the DLS measurements, the mean ± SD diameter of the M-TiO$_2$ particles dispersed in hydrophobic solvent was determined to be 40.6 ± 11.2 nm. The grafted amount and grafting density were determined to be 1.1 mmol/g and 2.7 groups/nm, respectively.

Detailed experimental procedures and characterization methods for both TiO$_2$ and M-TiO$_2$ can be found in our previous report [37].
Table 1
Recipe for the preparation of PVC and TEPVC.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Amount (g)</th>
<th>PVC</th>
<th>TEPVC</th>
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<tbody>
<tr>
<td>Deionized water</td>
<td>396</td>
<td>396</td>
<td></td>
</tr>
<tr>
<td>Vinyl chloride (VC)</td>
<td>248</td>
<td>248</td>
<td></td>
</tr>
<tr>
<td>1,1,3,3-Tetramethylbutyl peroxynedecanate (BND)</td>
<td>0.113</td>
<td>0.113</td>
<td></td>
</tr>
<tr>
<td>Di-2-ethylhexyl peroxydicarbonate (OPP)</td>
<td>0.113</td>
<td>0.113</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>5.95</td>
<td>5.95</td>
<td></td>
</tr>
<tr>
<td>Octadecyl 3-(3,5-di-tert-butyl-4-hydroxy) phenylpropionate (IR)</td>
<td>0.025</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>Dilauryl thiodipropionate (DL)</td>
<td>0.050</td>
<td>0.050</td>
<td>2.48</td>
</tr>
<tr>
<td>Aluminum sulfate (AS)</td>
<td></td>
<td></td>
<td>2.48</td>
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</table>

2.2. Preparation of TEPVC

TEPVC was prepared by conventional suspension polymerization in a high-pressure PVC polymerization reactor equipped with a temperature controller, a high-speed mechanical agitator, and a balance-controlled vacuum VC feeder. A typical reaction recipe is summarized in Table 1, and a schematic illustration of the reaction procedure is shown in Fig. 1. The experimental procedure was as follows. First, the reactor was charged with water and cooled to approximately 4 °C. The additives used in the suspension polymerization were K-420TM (as a suspending agent), BND and OPP (as initiators), IR and DL (as antioxidants), and AS (as a scale inhibitor); these additives and M-TiO2 were combined in the reactor. VC gas was pressurized and added to the dispersion, which was then mixed with vigorous agitation at a speed of 1000 rpm for 5 h at 4 °C. After the dispersion of the initiator mixture with M-TiO2 into the monomer phase, polymerization was carried out at a temperature of 57.5 ± 0.5 °C and a pressure of approximately 9.0 ± 0.5 bar while agitation the suspension at a speed of ca. 650–700 rpm until there was a pressure drop of approximately 0.5 bar from the maximum pressure attained. At the end of the reaction, the remaining gas was vented out. The crude product was then washed several times with ethanol and water, filtered, and dried overnight under vacuum. Unmodified PVC for the comparison with TEPVC was prepared by essentially same procedure as the one for the TEPVC with the exceptions of nanoparticle addition and the stage of vigorous agitation as a means of dispersing the nanoparticle.

2.3. General characterization

The morphology of the TEPVC was determined with a JEOL JSM-6330F FE-SEM operating at 5 kV. The FE-SEM samples were coated with platinum for 5 min using a JEOL JFC-1100 ion sputter coater. The dispersion of TiO2 in TEPVC was investigated with TEM. For TEM, the PVC grains were embedded in Gartan G-1 epoxy and cured at 60 °C for 90 min. Ultra-thin cross-sections of the specimens were prepared using a Leica Ultracut UCT ultracytromicrotome at room temperature. The TEM analyses were performed with a JEOL JEM 200CX operating at 200 kV. XRF was used to determine the TiO2 content of TEPVC. The XRF measurements were performed on a Ti element with a Shimadzu XRF-1700 sequential XRF spectrometer using lithium fluoride (LiF) as an analyzing crystal with a 2\(\theta\) value of 0.4028 nm. The XRF spectrometer was operated at a current of 30 mA and a voltage of 40 kV in a technical vacuum. The thermal properties of TEPVC were characterized by DSC performed within the temperature range of 40–140 °C at a heating rate of 10 °C/min under a nitrogen atmosphere, employing a TA Instruments DSC 2920. The glass transition temperatures were measured as the mid-points of the transitions. A Lloyd LR10K universal testing machine was also used to evaluate the tensile properties of plasticized TEPVC with 8 parts per hundred resins of di-(2-ethylhexyl) phthalate (DEHP). The test specimens were in the form of dumbbells (ASTM D-638). Sheets with a gauge length of 50 mm and a width of 10 mm were stretched at a crosshead speed of 10 mm/min with a load cell of 1 kN.

2.4. Incineration

To investigate the suppression of dioxin emission by TiO2 in TEPVC, TEPVC and unmodified PVC were incinerated in a tubular furnace designed to reflect the incineration conditions of small
waste incinerators [20,39]. In this test, 0.75 g of the respective powder samples were used as purified and dried after polymerization, without any further sample manipulation. The incineration was performed in a temperature-controllable electric furnace at 700 °C with synthetic air (21%, v/v, oxygen) as the carrier gas with a flow rate of approximately 1.8 L/min. The dioxins and PCBs emitted as a result of incineration were collected using a method based on US EPA method 23 for sampling dioxins and dioxin-like compounds. A schematic diagram of the incineration apparatus and the toxic chemical collectors is shown in Fig. S3. A small sample (approximately 25 mg) was placed onto a quartz boat with a micro-spatalus and slid to the central position, and then the sample was combusted in the tube furnace. After the sample was consumed, the operation was repeated 29 times, corresponding to combustion of 0.75 g of sample over a 75 min experimental period. The sample residues and soot generated by combustion were trapped in a thimble filter. The exhaust gases produced were trapped using a thimble filter, two water impingers and a diethylene glycol impinger in an ice-bath, and an absorption tube filled with Amberlite XAD-2 resin, sequentially along the stream. A vacuum pump was located at the exit port. The vacuum pump was in operation over the entire time course of the experiment. The pumping rate was 2 L/min, to accommodate the thermal expansion of gas supplied from the cylinder. The volume of sample for each test was chosen to prevent flow-back of combustion gases and to maintain incineration temperature during combustion. After testing, the test rig from the quartz tube (including areas where attached combustion residue was confirmed) to the absorption unit was rinsed with water, acetone, and dichloromethane, and these solutions were also recovered. After a series of pretreatments (as illustrated in a flow diagram in Fig. S4), the concentrated solutions of produced toxicants were subjected to quantitative analysis.

2.5. Analyses of dioxins and PCBs

Pretreated concentrated samples of produced toxic chemicals were analyzed by gas chromatography with high resolution mass spectrometric detection (GC/HRMS), using a Waters Micromass Autospec Ultima magnetic sector high resolution mass spectrometer equipped with a Hewlett-Packard 6890 gas chromatograph. Two separate analyses were conducted according to US EPA protocols. PCDDs/PCDFs were measured following the protocol of EPA Method 1613B; PCBs were quantified by the protocol of EPA Method 1668A. Quantification of target analytes was achieved by isotope dilution using 13C-labeled surrogate standards. More detailed procedures including operating conditions for both GC and MS, as well as lists of native and internal standards, can be found in Supplementary data.

3. Results and discussion

3.1. Preparation and general characterization

Because PVC production processes have evolved in diverse directions to impart better properties to final products in a time- and energy-efficient manner, industrial production processes are often very different from simple laboratory-scale syntheses. For example, commercial processes may use multiple and complex initiator mixtures, antioxidants, and scale inhibitors. To make our approach more practically applicable to the existing PVC industry, we used a home-made 1L high-pressure pilot reactor designed to mimic industry-scale reactors, and chose a general TEPVC recipe and preparation procedure typical of a process used to synthesize commercial-grade PVC, as summarized in Table 1. Prior to the preparation of TEPVC, unmodified PVC without TiO2 nanoparticles was prepared, and the general properties of this PVC were compared with those of commercial PVC, to verify the validity of our approach to the production of PVC with properties equivalent to those of commercial-grade PVC.

Fig. 2 shows FE-SEM images of the prepared unmodified PVC and commercial-grade suspension PVC (Hanwha Chem. Corp., P-1000™), with degree of polymerization of approximately 1000 ± 50; comparison of the images demonstrates that the size, shape, and size distribution did not differ significantly between the samples. The diameter of the prepared unmodified PVC was determined to be in the range 100–160 μm by particle size analysis, which was identical to that of the commercial PVC. Other physical properties of the prepared unmodified PVC such as the bulk density and cold plasticizer absorption were found to meet the standard requirements for commercial-grade materials (Table 2).

The encapsulation of TiO2 via PVC suspension polymerization requires an additional process step to disperse M-TiO2 in the monomer phase. The grafting of MPS onto inorganic particles has been reported to render the particles hydrophobic [40]. Thus, it was expected that M-TiO2 could be readily dispersed in liquefied droplets of vinyl chloride (VC). Droplets containing the M-TiO2 particles were subsequently polymerized to form TEPVC. As shown in

<table>
<thead>
<tr>
<th>Table 2 Physical properties of the PVC resins.※</th>
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<tr>
<td>Properties</td>
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<tr>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
</tr>
<tr>
<td>Cold plasticizer absorption (%)</td>
</tr>
<tr>
<td>Particle size (μm)</td>
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</table>

※ These properties of the PVC resins were determined with the aid of the PVC manufacturing company.
Table 1, a proportion of 1 wt% of M-TiO$_2$ (compared to VC weight) was used for encapsulation. Fig. 3 shows FE-SEM images of TEPVC at various magnifications. The diameter of the TEPVC grains was in the range 100–160 μm, and was thus similar to the grain size range of commercial-grade suspension PVC. As can be clearly seen in Fig. 3, there were no significant TiO$_2$ agglomerates on the surface of the TEPVC sample. The dispersion of TiO$_2$ nanoparticles in TEPVC particles was examined by TEM, as shown in Fig. 4. The TiO$_2$ nanoparticles were well dispersed on a scale of ~20–60 nm without significant agglomeration. When it is considered that large agglomerates of nanoparticles, with sizes ranging from hundreds of nanometers to a few micrometers, are commonly observed in conventional polymer/inorganic nanoparticle composites prepared by mechanical mixing, the degree of dispersion of nanoparticles in the polymer matrix was found to be significantly enhanced by the encapsulation approach.

Quantitative analysis of the encapsulated TiO$_2$ nanoparticles in TEPVC was performed by wavelength-dispersive XRF (WD-XRF). WD-XRF is regarded as a valuable technique for characterizing the contents of specific components in samples, based on the detection of characteristic fluorescence X-rays. In addition, we have reported that WD-XRF is effective in both qualitative and quantitative characterization of TiO$_2$ encapsulation into a polymeric matrix, and details of our analysis method have been published [37]. Prior to quantitative analysis of the TiO$_2$ content of TEPVC, a calibration curve was established using a series of standard samples made by mechanical mixing of unmodified PVC with various concentrations of M-TiO$_2$ from 0 to 2.0 wt%. From the intensity of Ti K$_\alpha$ measured in the TEPVC sample, the M-TiO$_2$ content in TEPVC was determined to be approximately 0.93 wt%, after reference to calibration data. When it is considered that unencapsulated free TiO$_2$ was completely removed by the successive washing treatments (Fig. 3), it is clear that the measured M-TiO$_2$ content directly reflects the amount of M-TiO$_2$ encapsulated in TEPVC.

The glass transition temperature, $T_g$, as measured using DSC, is an important indicator of the thermal properties of a polymer. Fig. S5 shows DSC thermograms of TEPVC and unmodified PVC. The unmodified PVC sample had a $T_g$ of approximately 85.2 °C, in good agreement with that of the commercial product. A similar $T_g$ value was obtained for TEPVC, although TiO$_2$ encapsulation resulted in a little difference (ca. 0.5 °C) in $T_g$. Fig. S6 shows the stress–strain curves of plasticized samples of various forms of PVC. Here, TEPVC/DEHP is a plasticized material derived from TEPVC, and PVC/DEHP is the plasticized sample of unmodified PVC; both were prepared using DEHP as a plasticizer. In particular, PVC/M-TiO$_2$/DEHP was prepared (for comparison purposes) by mechanical addition of M-TiO$_2$ to unmodified PVC. As can be seen in Fig. S6, the ultimate maximum stress and the elongation of the specimen at maximum stress were markedly lower for PVC/M-TiO$_2$/DEHP than for PVC/DEHP, indicating that the addition of a small amount of M-TiO$_2$ by mechanical mixing seriously degraded the mechanical properties of PVC. By contrast, the TEPVC/DEHP sample showed substantially increased mechanical properties compared with the PVC/M-TiO$_2$/DEHP sample, and showed almost the same or slightly...
better mechanical properties than did PVC/DEHP. These findings imply that M-TiO₂ is well dispersed in the polymer matrix after encapsulation, and that encapsulation of M-TiO₂ does not result in any serious deterioration in the ductility or toughness of the PVC. The data show that the encapsulation of TiO₂ nanoparticles in PVC was successfully accomplished without causing any significant changes to the morphology or physical properties of PVC. This is essential if the new technology is to be readily applied in existing PVC industries, to offer the advantage of lower dioxin emission upon incineration, as described below.

3.2. Incineration, analyses of dioxins and PCBs

Incineration experiments were performed using the unmodified PVC and TEPVC prepared in this study, and the weights of produced toxic chemicals including dioxins (PCDDs and PCDFs) and PCBs were determined by GC/HRMS with the aid of Shimadzu Techno-Research Inc., a commercial research laboratory specializing in dioxin analysis. The overall weights of dioxins and PCBs were estimated by using ¹³C-labeled internal standards consisting of over 30 congeners of PCDDs, PCDFs, and PCBs. Fig. 5 shows the weights of selected congeners of (a) PCDDs, (b) PCDFs, and (c) PCBs, with respect to the weight of sample used for the incineration. The suppression efficiencies of TEPVC for dioxin and PCB emission can be calculated with the following equation:

$$E_{\text{suppression}}(\%) = \left( 1 - \frac{C_{\text{TEPVC}}}{C_{\text{PVC}}} \right) \times 100$$

where $E_{\text{suppression}}$ is the suppression efficiency of TEPVC, with respect to PVC, for the selected PCDDs, PCDFs, and PCBs, and $C_{\text{PVC}}$ and $C_{\text{TEPVC}}$ are the weights of the toxic substances of interest with respect to the weights of samples used for the incineration of PVC and TEPVC. In Fig. 5, the weights of dioxins and PCBs from the TEPVC sample are shown to be reduced compared with PVC, with suppression efficiencies in the range 40–80%. According to our literature survey, the catalytic activity of catalyst nanoparticle incorporated within polymeric material to individual dioxin congener is not reported. The catalytic activities of the pure TiO₂ to chlorinated aromatic compounds diluted in gas phase were reported in several literatures. Khaleel et al. reported that 0.15 g of TiO₂ has ~30% of removal efficiency to 1 µL pulse introduction of chlorobenzene at 325 °C [41]. Liu et al. also reported that 1.0 mL of TiO₂ show ~70% of removal efficiency to 1300 ppm of chlorobenzene at 400 °C [29]. Choi et al. reported TiO₂ has 20% of removal efficiency to 1000 ppm of 1,2-dichlorobenzene at 300 °C and the removal efficiency increased with increasing temperature [42]. TiO₂-supported transition metal oxide catalysts applied municipal waste incinerator have higher efficiency than pure TiO₂. According to the review of catalytic combustion by Everaert et al., commoencatalytic flue gas management systems attached to municipal waste incinerators have 80–99.5% of removal efficiencies at temperature range of 180–240 °C when they operate separate dioxin abatement [43]. Comparing efficiency data with each other, however, it should be considered that all dioxins contained fly ash as well as flue gas are included in self-suppression efficiency of TEPVC. Recently, Choi et al. reported a similar approach with our presented study [42]. They embedded 5–10 wt% of oxide particles including TiO₂, Fe₂O₃ and TiO₂-masked Fe₂O₃ inside polyethylene and polystyrene, and then showed CO₂ conversion rate increased from ~10% to 20–60% by embedded oxide during the incineration of them. This result reveals the emission of volatile organic compounds (VOCs) during the incineration of polymeric materials could be reduced by embedded catalyst nanoparticles. This study is, however, limited by lacks of individual VOC substances observation and data on chlorine-contained polymers such as PVC, considering the importance of halogenated and more especially chlorinated VOCs due to their toxicity and high stability. The suppression efficiency data in Fig. 5 show a clear trend: higher suppression efficiency is observed for higher chlorinated dioxins. Recent results of in situ FT-IR studies suggest that the catalytic oxidation of chlorinated aromatic compounds on TiO₂ or TiO₂-supported metal oxide occurs via a concerted mechanism [31,32,35]. In this mechanism, the aromatic
compound is first adsorbed on the catalyst, and then the remaining aromatic ring is oxidized via a nucleophilic attack on the chlorine position in the aromatic ring. Hetrick et al. observed the surface intermediates during the oxidation of the different chlorophenols and chlorobenzenes over these catalysts, and suggest that a similar reaction pathway is operating in the oxidation of chlorinated aromatic compounds [35]. In the first step of the oxidation, chlorinated aromatic compounds are dissociatively adsorbed on Lewis acid sites via Cl abstraction [31,34]. In the adsorbed aromatic molecule, moreover, chlorine plays an important role in activating the aromatic ring towards nucleophilic attacks [31,34]. Consequently, a higher number of chlorine atoms in a dioxin molecule offers more chances for oxidation, which would explain our observation of higher suppression efficiencies in highly chlorinated dioxins.

Because toxicities vary among the congeners of PCDDs, PCDFs, and PCBs, the representation of combined toxicity as one simple measure can provide intuitive and direct information on the toxicities of all emitted chemicals. The toxic equivalent (TEQ) measure is one such example: TEQ is calculated by comparing the toxicity of each individual PCDD, PCDF, and PCB congener to that of the most toxic form of dioxin, 2,3,7,8-TeCDD. This means that some dioxins/furans/biphenyls might count as only half a TEQ if the corresponding congener examined. The overall reduction in toxin emission upon incineration of TEPVC was estimated by comparing the sum of TEQ values of all toxic chemicals generated from the incineration of TEPVC with that from the incineration of unmodified PVC. This analysis showed that the emission of dioxins and other toxic chemicals during PVC incineration can be halved using TEPVC, indicating the potential applicability of TEPVC as an eco-friendly alternative to conventional PVC. It is obvious that subsequent studies on the detailed mechanisms of dioxin decomposition on the surface of incorporated TiO$_2$ nanoparticles and the improvements of physical properties of TEPVC remain to be performed for the commercial application of this polymer–catalyst nanocomposite. It is hoped that this study will stimulate further investigations in the field of catalytic elimination of environmental pollutants.

**Acknowledgments**

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**Appendix A. Supplementary data**


**References**


**Fig. 6.** Toxic equivalent (TEQ) values for various toxic chemicals generated from incineration of unmodified PVC (unfilled bars, left axis), total TEQ values for unmodified PVC (striped bar), and for TEPVC, with estimated suppression efficiencies shown by TEPVC (solid bar, right axis).