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TiO_2-encapsulating PVC capable of catalytic self-suppression of dioxin emission in waste incineration as an eco-friendly alternative to conventional PVC

Hyonggoo Yoo, Seung-Yeop Kwak*

Department of Materials Science and Engineering, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151–744, Republic of Korea

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ABSTRACT

Here, we describe the preparation of TiO_2-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 TiO_2 nanoparticles. Surface-modified TiO_2 nanoparticles (M-TiO_2) are used for the preparation of TEPVC to facilitate the uniform dispersion of monomeric TiO_2 in the initial reaction mixture, which is the key to the preparation of a final TEPVC showing a high dispersion of functional TiO_2 nanoparticles in the PVC matrix, without significant agglomeration. The content of encapsulated M-TiO_2 in TEPVC was determined to be approximately 0.93 wt%, and the high dispersity of M-TiO_2 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 ^{13}C-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.

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-

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* Corresponding author. Tel.: +82 2 880 4301, fax: +82 2 885 9671.
E-mail address: sykwak@snu.ac.kr (S.-Y. Kwak).

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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 unmanagable 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, titanium 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 TEPS shows suppression effects only when PVC and TEPS 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, $Ti(OCH(CH_3)_2)_4$, used in the preparation of TiO_2, was obtained from Aldrich. 3-(Methacryloxy)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 peroxyneodecanoate (BND) and dioctyl peroxydicarbonate (OPP) from Chemex Co. Ltd.; poly(vinyl alcohol) (trade name K-420^{TM}) 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].