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**Synthesis of nano-flame retardant and its use as
a promising substitute of antimony trioxide in
flame retardant flexible poly(vinyl chloride)**

THESIS DOCTORAL

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RESUMEN

Poli (cloruro de vinilo) (PVC), un material termoplástico versátil, se ha estado usando en diferentes campos de aplicación tales como alambre y cable, materiales de construcción y tapicería debido a su excelente resistencia mecánica, estabilidad térmica, retardante de llama y por sus características aislantes. Debido al alto contenido de cloro que contiene el PVC, que actúa en la fase de vapor mediante un mecanismo radicalario para interrumpir los procesos exotérmicos y suprimir la combustión, el PVC posee una alta retardancia de llama intrínsecamente. Sin embargo, la adición de una gran cantidad de plastificantes inflamables en PVC para preparar PVC flexible resta valor a las propiedades ignifugas del PVC en sí. El retardante de llama tradicional para PVC flexible es el trióxido de antimonio, pero está demostrado que tiene una toxicidad potencial debido a las impurezas en los productos comerciales como el arsénico. Por otro lado, la reserva limitada de elementos de antimonio en la corteza terrestre da como resultado un aumento en el precio de dicho retardante de llama. Por lo tanto, deben desarrollarse sustitutos del trióxido de antimonio (Sb_2O_3) para fabricar PVC flexible retardante de llama respetuoso con el medio ambiente y de alto rendimiento.

Basándose en el estado del arte en la última década, los compuestos con base metálica exhiben una alta eficiencia como retardantes de llama para PVC flexible y tienen un gran potencial para reemplazar el Sb_2O_3 nocivo. Además, los nanocompuestos poliméricos han despertado un gran interés entre los investigadores debido a las propiedades únicas que poseen los aditivos de relleno con la dimensión en nanoescala. Inspirados en esto, los compuestos a base de zinc o estaño con nanoestructuras se diseñaron y sintetizaron sutilmente en esta tesis, utilizando como retardantes de llama en PVC flexible para reemplazar parcial o totalmente a Sb_2O_3 .

En primer lugar, las nanopartículas de carbonato de zinc (ZC) se sintetizaron a través de un método hidrotermal de un solo paso como un trabajo exploratorio. El producto industrial correspondiente a ZC tiene una baja temperatura de descomposición térmica, no disponible en el procedimiento de procesamiento de PVC. Por nuestro método, la estabilidad térmica del carbonato de zinc se mejoró y su tamaño de partícula se ubicó en el rango nanométrico. Se encontró que al sustituir hasta 75% de Sb_2O_3 por ZC en PVC flexible, el nanocompuesto mostró el mejor rendimiento en comparación con otras muestras. Alcanzó la calificación V-0 en la prueba UL-94 y

su valor de LOI aumentó a 36.7%. El pico de la tasa de liberación de calor (PHRR) y la liberación total de calor (THR) del nanocompuesto se redujeron obviamente.

Posteriormente, para realizar la sustitución total de Sb_2O_3 , se empleó un elemento más efectivo como el estaño. Mientras tanto, se fabricaron retardantes de llama con nanoestructura jerárquica a medida. La sílice porosa jerárquica (TOS) dopada con estaño se preparó mediante un método fácil sol-gel in situ. Los resultados mostraron que el índice limitante de oxígeno (LOI) del compuesto flexible de PVC aumentó en presencia de TOS y alcanzó casi el mismo nivel que el compuesto mezclado con Sb_2O_3 , acompañado con clasificación UL-94 V-0 sin goteo. Mientras tanto, TOS también mejoró las propiedades de tracción del compuesto. Sin embargo, los resultados obtenidos de la calorimetría de cono no fueron satisfactorios. En otras palabras, TOS no pudo disminuir la liberación de calor del compuesto durante la combustión de manera efectiva.

Para mejorar el rendimiento del compuesto de PVC flexible en la prueba de calorímetro de cono sin comprometer otras propiedades, se sintetizó mediante un método simple un material híbrido de óxido de estaño/óxido de hierro con estructura nanoporosa. El valor de LOI del material compuesto en presencia del material híbrido era más alto que el del material compuesto mezclado con Sb_2O_3 , mientras que el PHRR y el THR para el material compuesto que contenía el material híbrido eran más bajos que los del material compuesto mezclado con Sb_2O_3 . Los beneficios extra impartidos por $\alpha\text{-Fe}_2\text{O}_3$ en el híbrido mejoraron la retardancia a la llama del compuesto fPVC con una cantidad reducida de gas HCl corrosivo y la con supresión de la producción de humo, sin deterioro de las propiedades mecánicas, mostrando un rendimiento mucho mejor que los compuestos de fPVC basados en Sb_2O_3 . El mecanismo ign fugo correspondiente se estudió mediante mediciones de todos los lados y se discutió en profundidad. La serie de trabajos en esta tesis propuso la gran manera potencial de preparar composites flexibles de PVC ign fugos sin Sb_2O_3 .

ABSTRACT

Poly(vinyl chloride) (PVC), a versatile thermoplastic material, has been widely used in various aspects, such as wire and cable, building materials, and upholstery because of their excellent mechanical strength, thermal stability, flame retardancy and insulation characteristics. Due to the high content of chlorine containing in PVC, which acts in the vapour phase by a radical mechanism to interrupt the exothermic processes and to suppress combustion, PVC has high flame retardancy intrinsically. However, the addition of large amount of flammable plasticizers into PVC to prepare flexible PVC detracts from flame retardant properties of pristine PVC. The traditional flame retardant for flexible PVC is antimony trioxide, but it is proved to hold potential toxicity because of the impurities in the commercial products such as arsenic. Meanwhile, the limited reserve of antimony element in earth crust results in increasing price of such flame retardant. Therefore, substitutes for antimony trioxide (Sb_2O_3) should be developed in order to fabricate eco-benign flame retardant flexible PVC with high performance.

Based on the state of art over the last decade, metal-based compounds exhibit high efficiency as flame retardants for flexible PVC and hold great potential to replace harmful Sb_2O_3 . Besides, polymer nanocomposites have attracted extensive interest among researchers because of the unique properties endowed by the fillers with the dimension in nanoscale. Inspired by this, zinc- or tin-based compounds with nanostructures were subtly designed and synthesized in this thesis, utilizing as flame retardants in flexible PVC to partially or totally replace Sb_2O_3 .

First, zinc carbonate nanoparticles (ZC) were synthesized via a facile one-step hydrothermal method as an exploratory work. The industrial product corresponding to ZC has low thermal decomposition temperature, not available in PVC processing procedure. By our method, thermal stability of zinc carbonate was improved, and its particle size was located in the nanometric range. It is found that substituting up to 75% Sb_2O_3 by ZC in flexible PVC, the nanocomposite showed best performance compared with other samples. It reached V-0 rating in UL-94 test and its LOI value increased to 36.7%. The peak of heat release rate (PHRR) and total heat release (THR) of the nanocomposite reduced obviously.

Afterwards, to realize total substitution of Sb_2O_3 , more effective element such as tin was employed. Meanwhile, flame retardants with tailor made hierarchical nanostructure were fabricated. Tin-doped hierarchical porous silica (TOS) was prepared by a facile in situ sol-gel

method. Results showed limiting oxygen index (LOI) of flexible PVC composite increased in presence of TOS and attained nearly the same level as that of Sb_2O_3 -blended composite, accompanied with UL-94 V-0 rating without dripping. Meanwhile, TOS also enhanced the tensile properties of the composite. However, the results obtained from cone calorimetry were not satisfactory. In other words, TOS was unable to decrease heat release from the composite during combustion effectively.

To improve the performance of the flexible PVC composite in cone calorimeter test without compromising other properties, a tin oxide/iron oxide hybrid material with nanoporous structure was synthesized by a simple method. The LOI value of the composite in presence of the hybrid material was higher than that of Sb_2O_3 -blended composite, while the PHRR and THR for the composite containing the hybrid material were lower than those of Sb_2O_3 -blended composite. The extra benefits imparted by $\alpha\text{-Fe}_2\text{O}_3$ in the hybrid improved the flame retardancy of fPVC composite with reduced amount of corrosive HCl gas and suppressed smoke production, without deterioration of the mechanical property, showing much better performance than those of Sb_2O_3 -based fPVC composite. The corresponding flame retardant mechanism was studied by all-sided measurements and discussed in depth. The series of work in this thesis proposed the great potential way to prepare Sb_2O_3 -free flame retardant flexible PVC composites.

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ABBREVIATIONS

av-SEA	Average specific extinction area
CY	Char yield
DOP	Diethyl phthalate
EDX	Energy dispersive X-ray detector
FEGSEM	Field emission gun scanning electron microscope
FT-IR	Fourier transform infrared spectroscopy
HRR	Heat release rate
ICP	Inductively coupled plasma
LOI	Limiting oxygen index
MCC	Microscale combustion calorimeter
PHRR	Peak of heat release rate
PVC	Poly(vinyl chloride)
SDR	Smoke density rating
SEM	Scanning electron microscope
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis
TG-FTIR	Thermogravimetric analysis-Fourier transform infrared spectroscopy
THR	Total heat release
TOTM	Triethyl trimellitate
TSP	Total smoke production
TTI	Time to ignition
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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CHAPTER 1

INTRODUCTION

“Scientists believe in things, not in person.”

-Marie Curie

1.1 Background: Flammability of flexible PVC composite

Poly(vinyl chloride), well known by its abbreviation PVC, is among the most extensively used commodity thermoplastic materials. It ranks the second largest manufactured resin around the world because of its easy processing, good mechanical properties, and low production cost. It is widely applied in construction materials, children toys, food packing, medical tubing, blood bags, credit cards, wall papers, wire and cables, bottles and so forth. Since 2010 the production of PVC resin has been over 31 million tons every year [1]. Among the major types of plastics, the consumption of PVC contributes to 10.1% of total demand around Europe in 2015 (Figure 1-1).

Figure 1-1: European plastic demand by category in 2015 [2].

The PVC application fields globally in 2015 at a total consumption of 41.9 million t are shown in Figure 1-2. Among these applications, flexible products occupy a relatively high proportion. In order to obtain PVC materials with requirements in flexibility, a large amount of plasticizers were cooperated to make PVC easy process. The plasticizers increase the elasticity and cold resistance of the PVC material and also decrease its processing temperature. PVC formulations including plasticizers are termed as plasticized PVC. They are also called flexible PVC or soft PVC. The other ones without plasticizers are generally denoted as unplasticized PVC (uPVC) or sometimes rigid PVC. Semi-rigid PVC are referred to those plasticized PVC whose plasticizer amounts- whilst commonly low- do decrease the modulus compared with unplasticized PVC but still higher than values for flexible ones. The structure of uPVC features a chlorine atom located on each alternative carbon in the polymer chain resulting in a quite rigid and relatively stiff plastic. Unfortunately, pristine PVC is too brittle to be readily processed by extrusion molding to harvest various products in diverse applications [3]. Therefore, in most cases PVC is usually blended with a large amount of plasticizers, up to 70 wt.% [4]. In the presence of plasticizers, the dipole bonding between polymer chains is greatly diminished, thus freedom of chain movement is increased to obtain flexible materials [5].

Figure 1-2: PVC application fields globally in 2015 (source: IHS Chemical).

Neat PVC features a relatively high chlorine content of 56.7 mass%, which makes it more resistant to ignition and burning than most organic polymers [6]. The release of the HCl by the decomposition of PVC prohibits flame combustion as the halogen entering into the gas phase contributes to a ‘flame poisoning effect’, namely the slowing down of the free radical chain reactions in the flame. Unlike carbon monoxide, HCl concentration rapidly dropped down as it is

absorbed on surfaces, and it often does not travel far [7]. HCl as a gas-phase inhibitor can effectively inhibit the burning. In addition to the generation of an HCl gas-phase inhibitor, the generation of a large amount of stable char residue in the condensed phases may be even more important in terms of flame-retarding and smoke-suppressing properties [8]. Pyrolysis of PVC yields an isotropic carbon char residue [9] which contributes to the mechanism of flame-retardant action. PVC will cease burning as soon as the source of heat or flame is removed. Even in dry powder form, PVC is hardly ignited, relatively safe to air-convey without serious risk of dust explosions unless blended with more flammable substances. The minimum radiant flux for ignition is about 21 kW/m^2 and the self-ignition temperature is 507°C [10]. However, the conventional plasticizers used in the manufacture of flexible PVC detract from this outstanding fire resistance. These plasticizers also promote a particular combustion mechanism that ends up generating a significant amount of dense and dark smoke [11]. The limiting oxygen index (LOI) is the minimum concentration of oxygen in the mixture with nitrogen that will support combustion of a polymer. When the PVC products contain 45 parts dioctyl phthalate (DOP) plasticizer, the LOI value would decrease to about 24% and the PVC would thus become a high-flammability material [12]. Therefore, flame retardants are usually imperative in flexible PVC in order to reduce its fire hazard.

1.2 Motivation for the development of Sb_2O_3 -free flame retardant flexible PVC composites

Due to the flammable property of flexible PVC, a large number of chemical compounds have been reported to be flame retardants for PVC. These compounds include alloys, inorganic compounds, coordination compounds, and organic compounds [13]. Antimony compounds, especially antimony trioxide (Sb_2O_3) and antimony pentoxide (Sb_2O_5), render excellent flame retardancy to halogen containing polymeric materials such as PVC because of the synergistic flame retardant effect between antimony trioxide and halogenated compounds [14]. Sb_2O_3 itself is relatively inert in the early stage of fire situations because the temperature at which it sublimates is 1550°C . Reactions of Sb_2O_3 and chlorinated polymers and additives have been studied very carefully and several antimony oxychlorides have been detected [15]. Although some oxychlorides can volatilize into the flame, it is believed that antimony trichloride (SbCl_3 , boiling point 223°C) is the main contributor in the inhibition of the flame reactions via scavenging of free radicals, so the flame retardant mechanism of Sb_2O_3 remains in gas phase [16]. Though Sb_2O_3 holds good

performance in improving the flame retardance of PVC, along with the use of Sb_2O_3 in large doses and the increasing environmental concern in the society, the drawbacks of Sb_2O_3 have also come out visibly. The main widely accepted problems of Sb_2O_3 are summarized below:

1. The impurities in commercial available Sb_2O_3 product such as arsenic and lead are harmful to human being and environment. Even high-quality commercial grades of antimony trioxide contain between 99.2% and 99.5% antimony trioxide with varying amounts of impurities among which the arsenic is the main component [17]. Arsenic causes acute and chronic adverse health effects, including cancer [18]. In one experimental study, female rats were exposed to 1.6 or 4.3 mg/m^3 of commercial grade antimony trioxide (containing 0.02% of arsenic) resulting in an increase in lung tumors, including carcinomas, especially in the high-dose group [19]. In addition, the purification for commercial Sb_2O_3 is difficult and causes extra energy penalty. As a result, the severe hazard caused by the arsenic in commercial product of Sb_2O_3 cannot be ignored.
2. On the other hand, the content of antimony in the earth's crust is limited. Until recently, the price of antimony is still raising. It has risen by more than 400% over the past 10 years [20]. The resource dependent feature of Sb_2O_3 also restricts its application in the future market.
3. Sb_2O_3 itself is also proved to be potentially toxic and carcinogenic, and can cause diseases of the liver, skin, and respiratory and cardiovascular systems; excessive amounts of antimony may cause acute cardiac diseases [21, 22]. The toxicity of antimony depends on its chemical form: the toxicity of organic antimony compounds is lower than that of inorganic antimony compounds, and the toxicity of Sb (V) is lower than that of Sb (III); SbH_3 and Sb_2O_3 have the highest toxicities [23].

Considering the potential hazard and scanty source of Sb_2O_3 , it is urgent to seek the harmless, high-efficiency and cost-effective replacements.

1.3 Motivation for the reduction of corrosive HCl release amount during the burning of flexible PVC composites

As mentioned above, a large amount of HCl gas escapes in the course of the degradation of PVC composite during the combustion. The evolution of corrosive HCl gas is harmful to humanity asset and human beings.

1. This inorganic irritant exacerbates the irritating and choking effects of the smoke released

during the combustion of PVC. HCl readily combines with water to produce a dense white smoke capable of reducing visibility to zero before much heat. Furthermore, it is known to be immediate corrosive agents of the surface of the respiratory tract and will also contribute to delayed and long-lasting pulmonary effects. All of above hazards of HCl improve the risks and difficulties of fire rescue when fire accident happens.

2. HCl gas is highly corrosive and an acid rain contributor. Moreover, HCl either directly, or indirectly through production of chlorine, may contribute to subsequent formation of highly toxic dioxins and furans in the combustion products. As these pollutants are released into the atmosphere, they will be harmful to the environment and human health.
3. During the complete combustion of virgin PVC, nearly all the Cl element in the polymer is released in the form of corrosive HCl gas. The HCl gas combines with the vapour in the atmosphere resulting in the HCl acid which corrodes the furniture, electronic devices and facilities. The ruined things are unable to be restored, leading to serious financial loss to the owners.

HCl was identified as one of primary toxicants depending on the chemical composition of burning PVC [24]. The immediate threats of HCl are zero visibility during fire rescue, the highly irritating to human beings, formation of environment toxins and corrosive action to property, thus the capture of hydrogen chloride is significantly important [25]. However, no study has reported about the reduction of the quantity of HCl emitted during the burning of PVC due to the inability of existing technologies to calculate or measure the amounts of this corrosive gas, though the monitor of HCl gas releasing during the thermal degradation of PVC by several analytical methods has been realized.

1.4 Objective of the study

In order to substitute Sb_2O_3 in flame retardant flexible PVC system and with an attempt to reduce the HCl release, suitable compounds should be selected. The systematic study in the thesis proceeds step by step to achieve the final target. The components of as-synthesized novel flame retardants in this study are inspired by the current literature while the unique nanostructures of the synthetic products are firstly designed by our group. The objective of the study is divided into several points and will be realized:

1. Design and fabrication of novel flame retardants to partially until totally substitute Sb_2O_3 in

flexible PVC composite.

2. The HCl gas released during the combustion of flexible PVC composites were collected from cone calorimeter test and compared the content between each sample by a facility designed by our group firstly. And the tailor made flame retardant is utilized to reduce the amount of HCl gas released from PVC.
3. The flame retardant mechanism is studied and proposed by means of all-sided measurements.
4. Study the thermal stability and mechanical properties of flame retardant flexible PVC composites.

1.5 Outline of the thesis

The dissertation is divided into seven core chapters regarding the preparation of zinc and tin compounds and utilization of them as flame retardants to replace Sb_2O_3 in flexible PVC composites. Chapter 2 provides a brief review about the state of art of flame retardants and substituents for Sb_2O_3 emerged in the last decade for PVC, stimulating us to design the flame retardants to replace Sb_2O_3 . Chapter 3 describes the materials and techniques employed in this systematic research. Chapter 4 illustrates the synthesis of zinc carbonate nanoparticles and partial replacement of Sb_2O_3 as flame retardant in flexible PVC. Chapter 5 and 6 focus on the preparation of tin compound-based Sb_2O_3 -free flame retardant flexible PVC composites. In the end, the conclusions for this research and prospect for the future work are presented in Chapter 7. In addition, the publications are listed in Chapter 8.

CHAPTER 2

STATE OF ART

“Genius only means hard-working all one's life.”

-Mendeleev

2.1 Thermal degradation of PVC

PVC combustion is a thermal degradation process. Investigation on the thermal degradation mechanism offer insight to the effect of flame retardants on the PVC system [26]. It is reported that the activation energy based on Arrhenius-type relationship for thermal degradation of PVC and some other polymers in the same units: PVC around 20, polystyrene 55, polyethylene 46 and polypropylene 65, indicating the relatively low thermal stability of PVC. As we know, PVC is notorious for its instability namely extensive degradation, particularly during the processing and application under critical temperature. The thermal decomposition of PVC is initiated by autocatalytic dehydrochlorination reaction followed by the formation of conjugated double bonds or polyenes sequences $[-(\text{CH}=\text{CH})_n-]$. As a result, undesirable color change of PVC occurs and deterioration of its physical and mechanical performances along with a change of molecular weight due to chain-scission or cross-linking of the polymer molecules [27]. A variety of defect sites in the polymer chains are responsible for the instability of PVC. Potential defect structures are branching, chloroallyl groups, end groups, oxygen containing groups, head-to-head structures and the stereo order of the monomer units [28]. The obvious outward manifestations of thermal degradation of PVC are the generation of hydrogen chloride, color variation and deleterious effect

of physical, chemical and electrical properties. The liberation of HCl begins at the glass transition temperature around 70 °C, accounting for the main volatiles with small amounts of benzene, toluene and other hydrocarbons. This stage happens evidently at the temperature about 250-350 °C resulting in a predominant weight loss of 65% [27]. It is widely accepted that the pyrolysis of PVC proceeds with elimination of HCl by means of chain mechanism termed as “zipper elimination” or “unzipping” [29]: carbon-carbon double bonds are generated and compose the allyl chloride fabric with the next chlorine along the chain that is thus strikingly activated. During this process, chlorine is nearly completely removed. The second stage is the degradation of the hydrocarbon backbone, which inherently results in a color change [30]. Due to the catalytic action of HCl in the production of double bond linkages, the unsaturated hydrocarbons formed splits up further into small unsaturated linkages, yielding volatile saturated and unsaturated, aliphatic and aromatic hydrocarbons, in which benzene and toluene are the major products in high yield [31]. The two-stage thermal degradation process of PVC was shown in Scheme 2-1. Based on this scheme, it can be seen that a high-efficiency flame retardant for PVC promotes the dehydrochlorination process to produce HCl earlier and then enhances the crosslinking of polymer to facilitate the char formation. The HCl acts as flame inhibitor while char isolates the underlying polymer from flame zone, resulting in the flame retardant behavior.

Scheme 2-1: Two-stage thermal decomposition process of PVC. (Adapted from Wypych, 1985).

2.2 Flame retardancy of PVC

To optimize the performances of PVC to meet industry application, it must be modified with highly inflammable components (plasticizers, stabilizers), which will reduce the flame resistance of PVC. In order to improve the flame retardancy of PVC composites, from the technological point of view, the most convenient and cost-effective method is to introduce flame retardants into the polymer melt upon molding. The flame retardants used for this purpose must be thermally stable under conditions of PVC treatment (215-225 °C), easily measured in doses and dispersed in the polymeric matrix, characterized by high efficiency of flame-retarding action, and must not release the toxic substances in the course of the combustion of the obtained compositions. According to the thermal decomposition process of PVC, the suitable flame retardants for PVC perhaps act as catalysts to accelerate the dehydrochlorination process, producing more HCl as flame poison. Meanwhile, the dehydrochlorination facilitates early crosslinking and char formation of PVC conducive to improve the flame retardancy.

In PVC composites, as the most important concern and attention, smoke production is generally directed toward smoke suppression in PVC, rather than flame retardancy. A key point to confine the smoke formation of PVC is to minimize the production of volatile fuels through crosslinking, which fabricates nonvolatile char [32]. Generally, the combustion process of PVC materials can be divided into three steps: (1) non-flaming mode appearing before ignition, (2) flaming mode, and (3) after-glowing mode. The smoke emission happens in both the non-flaming step and the flaming step, while there is no smoke evolved in the after-glowing step [33]. The first step in the smoke emission process is the fog of elimination of HCl without heat release, while the second step is mainly the black particles generated from the aromatic organics. The mechanism of smoke suppressants for PVC is based on interference in Diels-Alder condensation reactions and in the formation of benzene and other aromatic compounds [34, 35].

2.3 Flame retardants for PVC

The typical flame retardants for PVC emerged in the last decade are summarized as follows.

2.3.1 Metal-based flame retardants for PVC

Metal-based flame retardants are extensively applied in PVC including metal (hydr)oxides, inorganic metal salts and organometallic compounds, mainly because these specified metals feature particular effect on the thermal decomposition process of PVC. The metal-based flame

retardants mainly included tin, zinc, copper, iron, aluminum, magnesium, molybdenum, and other elements.

Metal (hydr)oxides

Tin oxide (SnO_2) has been used in many polymers, and the flame retardant property is often adequate. The possible flame retardant mechanisms of SnO_2 comprise condensed phase and vapor phase mechanisms. One part of the SnO_2 reacted with HCl that was released from PVC when heated to form tin tetrachloride (SnCl_4), which volatilized owing to its low boiling point at 389 K, and interfered with exothermic free radical propagation reactions in the flame, reduced burn velocity and narrowed flammability limits of the substance. The other part of the SnO_2 was reduced to SnO by H_2 , and SnO reacted with HCl to form the final product SnCl_2 . SnCl_2 with boiling point at 896 K exerted its role as Lewis acid in the condensed phase. Besides SnO_2 , the flame retardancy of SnO -added PVC composite was also studied. By analogy with SnO_2 , SnO can catalyze dehydrochlorination and promote early cross-linking in the first stage of thermal degradation of PVC, and at the meantime, it can enhance the stability of the residual char [36]. The fire performance of PVC composites bearing copper (II) and molybdenum oxides were studied [37]. The results confirmed the anticipation mechanisms of the dehydrochlorination reactions, reductive coupling, and elimination of benzene with the help of metal oxides, indicated by the increasing amount of char residue and the remarkable reduction of benzene production. The flame retardancy and smoke suppression of PVC bearing zinc oxide (ZnO) was also investigated in the same report. Meanwhile, the efficiency of zinc oxide was lower than that of tin compounds, such as zinc hydroxystannate, tin oxide, and tin monoxide [36], but higher than that of iron oxide (Fe_2O_3) when they both combined with aminotrimethylenephosphonic acid ammonium salt [38, 39]. Hosseini et al. exploited the char yield as a standard method for evaluating LOI of PVC sample containing ZnO nanoparticles in accordance with Van Krevelen and Hoftyzer equation: $\text{LOI} = 17.5 + 0.4Y_c$, where Y_c is char yield [40]. LOI for the PVC nanocomposite films containing 5 wt.% and 20 wt.% zinc oxide increased from 20.8% for pure PVC film to 27.9% and 28.7%, respectively. The LOI value of PVC film containing citric acid and ascorbic acid modified iron oxide (Fe_3O_4) were calculated by the equation mentioned above, and the prepared nanocomposites with LOI greater than 29% would be considered “self-extinguishing” [41]. Tang et al. also studied the flame retardancy of PVC composites treated with Fe_3O_4 nanoparticles and

graphene [42]. They concluded that the iron compounds promote early crosslinking of PVC during decomposition to increase char formation on the basis of previous report.

Apart from metal oxides, increasing attention is being paid to metal hydroxide additives, and magnesium hydroxide (MH) has been extensively used as flame retardant in PVC material. However, the high loading required to achieve the desired flame retardancy remains to be the main disadvantage. With the same adding amount, the performance of MH was worse than that of ZnO and Fe₂O₃ resulting from its relatively low efficiency [38, 39]. In order to improve the interaction between the inorganic filler and PVC matrix, surface modification by oleic acid was applied on MH to increase its hydrophobic property, leading to enhanced flame retardancy of PVC composite compared with that of the one containing the unmodified magnesium hydroxide [43]. Another flame retardant, zinc hydroxystannate (ZHS), was also exploited to coat on the surface of hydroxides in order to improve the flame retardant efficiency [44].

Inorganic metal salts

Zinc borates (ZB) are a series of effective flame retardants since they are nontoxic, smoke suppressant, afterglow suppressant, and anti-tracking agent. As one of the most cost-effective flame retardants, ZB displays synergist effect with many other kinds of flame retardants in PVC, thereby reducing cost and improving efficiency [45]. Mergen et al. firstly introduced nano ZB into PVC, and found the flame retardancy of the nanocomposite indicated by LOI value improved without affecting the mechanical properties considerably [46].

As a cheap, rich reserve and typical inert filler, calcium carbonate (CaCO₃) has been commonly selected for PVC to provide an increased thermal stability, stiffness, and toughness. Meanwhile, CaCO₃ acts as a HCl scavenger during combustion of PVC to form calcium chloride which then covers the surface of the composite material during combustion, excluding oxygen to react with the PVC molecules and leading to high LOI for combustion [47]. The addition of CaCO₃ nanoparticles obtained from *P. canaliculata* shells via hydrothermal treatment at 10 phr increased the flame resistance of PVC composite [48]. However, the flame retardant effect of CaCO₃ is limited. In another report by Xu et al., CaCO₃ showed little or no flame retardant effect on PVC, and it was deemed as inert filler only [49]. Accordingly, the authors coated CaCO₃ with SnO₂ to improve the efficiency. The same authors also studied ZHS and zinc stannate (ZS)-coated CaCO₃ as a flame-retardant agent for PVC [50]. Recently, they investigated the flame retardant properties

of PVC treated with two different morphologies of CaCO_3 coated by ZHS [51]. Sequentially, they adopted other metal hydroxystannates and stannates, including magnesium and strontium, to coat CaCO_3 [52]. The hydroxystannates-coated CaCO_3 had a better flame retardant effect than the corresponding hydroxystannates as a result of the fine dispersion of the effective hydroxystannates on the surface of substrate; furthermore, the performance of sample bearing magnesium was better than the one containing strontium. Another group compared the flame retardant effects of ZHS-coated CaCO_3 with ZHS-coated MH, and a 34% reduction in the peak of heat release rate (PHRR) for PVC sample containing 15 wt.% ZHS-coated CaCO_3 compared with that for pure PVC was found, whereas the reduction was 26% for PVC sample containing equivalent amount of ZHS-coated MH [53]. A synergistic flame retardant effect for the mixture of magnesium carbonate (MgCO_3) and $2\text{ZnCO}_3 \cdot 3\text{ZnO} \cdot 4\text{H}_2\text{O}$ (AZC) was found [54]. In presence of 20 phr MgCO_3 and 20 phr AZC, the LOI values for the composites were 28.4% and 28.0%, respectively. After adding 20 phr the mixture of MgCO_3 and AZC with the weight ratio of 10:1, the LOI value increased to 29.9%.

Inorganic metal salts involving double metals, such as stannates and ferrites, were also developed as flame retardants of PVC. The flame retardant effect of ZHS and ZS was studied in comparison with that of alumina trihydrate (ATH) and MH [55]. The results showed that ZHS and ZS greatly increased the LOI compared with the inorganic hydroxides due to the enhanced stability of the char residue reflected by the increasing activation energy of the oxidation reaction of the char. Then a series of metal hydroxystannates including Mg, Sr, Cu, Co, Ni, Mn, Fe and Zn were added into PVC to compare the flame retardant efficiency by Xu et al. [56]. Among these flame retardants, 2 phr $\text{Fe}_2\text{Sn}_3(\text{OH})_{18}$ -treated PVC composite showed highest LOI value as 37.5%, while LOI value of PVC containing 2 phr $\text{SrSn}(\text{OH})_6$ was the lowest as 33.0%. The same research group also combined ZHS with other metal hydroxystannates (metal = Mg, Sr, Mn, Fe, Co, Ni and Cu) and found that $\text{ZHS} + \text{Fe}_2\text{Sn}_3(\text{OH})_{18}$ showed best performance [57]. Furthermore, they synthesized ZS (Zn_2SnO_4) using activated carbon as template and added it into PVC [58]. The results showed that ZS with using activated carbon as template presented higher flame retardant efficiency than ZS without using activated carbon as template in PVC composites.

Recently, several organic flame retardants were modified on the surface of ZHS to improve its flame retardant properties. Melamine-dicyandiamide-formaldehyde-phosphoric acid (MDFP) was

adopted as the shell material to prepare ZHS@MDFP [59]. The decomposition of MDFP shell as the blowing agent expanded the char layer therefore improving the flame retardant capability of ZHS core and the shell improved the compatibility between ZHS and PVC matrix. Then the same group used vinyl trimethoxy silane (VTS) grafted by 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to coat onto the surface of ZHS [60]. With the incorporation of 5 phr of DOPO-VTS-ZHS, PHRR of PVC/DOPO-VTS-ZHS reduced by 39%, and total heat release (THR) decreased by 50% in comparison with those of pure PVC. Han et al. prepared ATH/ZHS microcapsule and used melamine-formaldehyde resin (MF) to encapsulate ATH/ZHS so that the compatibility between the hydrophilic microcapsule and hydrophobic PVC matrix could be improved [61, 62]. PVC/MF/ATH/ZHS microcapsule composites featured a high value of LOI, when the content of filler increased to 8.97%. Li et al. supposed that ZHS could be well combined with titanate nanotube (TNT) to obtain highly improved smoke suppressing ability in association with the synergistic effects between ZHS and TNT [63]. The LOI value of PVC/ZHS-TNT increased with filler content and reached to 29.6% when the content of the filler was 2.5 wt.%, higher than that of PVC/TNT, PVC/ZHS and PVC/ZHS+TNT. Since ZHS and its derivatives are prevailing research topic as flame retardants and smoke suppressants for PVC during the last decade, the literature and corresponding results are collected and tabulated in Table 2-1.

Table 2-1: ZHS derivatives as flame retardants and smoke suppressants for PVC.

Flame retardants	Loading amount (phr)	Highlight	Reference
ZHS	15	LOI value of 31.6%;	[36]
		15% reduction in SDR (Smoke density rating)	
ZHS-coated ATH	25	LOI value of 37%; 70% reduction in SDR	[44]
ZHS-coated MH	25	LOI value of 37.5%; 62% reduction in SDR	[44]
ZHS-SrSn(OH) ₆ -coated CaCO ₃	10	LOI value of 39.5%; 49% reduction in SDR	[52]
ZHS-coated fibrillar	30	LOI value of 35.5%	[51]

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CaCO ₃				
		LOI value of 31.6%;		
ZHS-coated MH	15	UL-94 V-0; 25%	[53]	
		reduction in PHRR		
		LOI value of 33.7%;		
ZHS-coated CaCO ₃	15	UL-94 V-0; 34%	[53]	
		reduction in PHRR		
ZHS	25	LOI value of 36%; 7%	[55]	
		reduction in SDR		
ZHS	2	LOI value of 35.5%;	[56]	
		10% reduction in SDR		
ZHS/Fe ₂ Sn ₃ (OH) ₁₈	2	LOI value of 40%;	[57]	
		47% reduction in SDR		
ZHS@MDFP	15	LOI value of 29.8%;	[59]	
		15% reduction in SDR		
		LOI value of 30.2%;		
DOPO-VTS-ZHS	5	39% and 60%	[60]	
		reduction in PHRR		
		and TSR, respectively		
		LOI value of 29.3%;		
MF/ATH/ZHS	10	~50% reduction in	[61, 62]	
		SDR; UL-94 V-0		
		LOI value of 28.5%;		
ZHS/graphene oxide	5	51% reduction in	[64]	
		PHRR		
		LOI value of 29.6%;		
ZHS/titanate nanotube	2.5	20% reduction in	[63]	
		PHRR		
<hr/>				

Besides hydroxystannates and stannates, ferrites were also under broad investigation as flame retardants and smoke suppressants for PVC. Xu's group has done a series of work to explore the

flame retardant and smoke suppressing effects of ferrites in PVC. Several ferrites including ZnFe_2O_4 , MgFe_2O_4 , NiFe_2O_4 and CuFe_2O_4 were synthesized and added into flexible PVC [65]. Subsequently, LaFeO_3 and BiFeO_3 were also synthesized and used as flame retardants and smoke suppressants for flexible PVC [11]. Afterwards, Xu and co-workers further employed thermogravimetric analysis-Fourier transform infrared spectroscopy (TG-FTIR) and X-ray photoelectron spectroscopy (XPS) to understand flame-retardant mechanism of flexible PVC filled with metallic ferrites [8]. The XPS analysis of the char residue of PVC/ BiFeO_3 showed the forms of Fe existed as FeCl_2 and FeOCl , which had strong catalytic ability for ionic dehydrochlorination of PVC. This study corroborated that BiFeO_3 not only prevented the smoke production of PVC in the course of burning, but also showed similar effect to that of Sb_2O_3 in flame retardant PVC, concurring with the results of previous report from the same research group. The synergistic effect of ZnFe_2O_4 in conjunction with MH was also studied [66]. The SDR value of composite was the lowest in presence of 19 phr MH and 1 phr ZnFe_2O_4 , and the LOI value was the highest when 10 phr MH and 10 phr ZnFe_2O_4 were added.

Organometallic compounds

Organometallic compounds as thermal stabilizers for PVC system have attracted a lot of attention, but there are only a few reports for their usage as flame retardants in the last decade. The organometallic flame retardants always function as intumescent flame retardants and smoke suppressants. The organic part is melamine (MA) or the precursor of melamine accompanied with HCl, acting as the blowing agent that promotes the intumescence of the char; the metal part reacts with HCl to form Lewis acid as the acid source in the condensed phase, catalyzing dehydrochlorination and promoting early crosslinking to the PVC compound; while PVC acts as the carbonization agent. On the other hand, the released HCl plays its role as an effective gas-phase flame inhibitor, while the metal ions can promote the stability of the char residue. Triazine derivatives containing a hydroxystannate or ZHS group were synthesized and denoted as MASN and MAZSN, respectively [67]. The LOI of pristine flexible PVC was 25.2%, and when the additive level reached 30 phr, the LOI for samples containing MASN and MAZSN reached 29.9% and 32.5%. Meanwhile, the addition of 30 phr MAZSN decreased SDR by 15 units (from 91.8 to 76.9%). Then two series of melamine salts including melamine tungstate and melamine molybdate were prepared in a simple way [68]. Compared with $(\text{MA})_2\text{WO}_4$, $(\text{MA})_2\text{MoO}_4$ had

better flame retardant and smoke suppression efficiency. With 30 phr $(MA)_2MoO_4$, the LOI of flexible PVC sample increased from 25.5 to 30.8%, and the SDR decreased from 96.30 to 62.28%. In the cone calorimeter test, the melamine salts effectively reduced the flammability parameters.

2.3.2 Clay-based flame retardants for PVC

The past decade has seen a great upsurge in research on polymer-clay nanocomposites, since clays provide enhanced fire, mechanical and barrier properties to polymer composites in comparison with traditional fillers.

Montmorillonite

Montmorillonite (MMT) is a kind of layered silicate inorganic material, the most common and extensively studied clays as nano-fillers in polymers. In 2009, Pielichowski et al. reviewed preparation and characterization of PVC-MMT nanocomposites, concerning its flammability in brief [69]. Although organoclays improve the thermal stability of PVC to a certain extent, modified MMT and another kind of clay, hectorite initiate accelerated HCl release from PVC leading to undesirable color changes of the composites [70]. In the cone calorimeter test, both organoclays reduced PHRR and smoke production compared with neat PVC. To intercalate the negatively charged anionic surfactant into the gallery spaces of MMT, a proper counter ion is indispensable during the insertion of anionic surfactants into the interlayer of MMT [71]. A dimethyl dioctadecyl ammonium chloride modified organic MMT (OMMT_{-1.44p})/PVC nanocomposite and anionic-surfactant-modified (sodium dodecanoate, sodium lauryl sulfonate and sodium monododecyl phosphate) lanthanum organic MMT (La-OMMT)/PVC nanocomposites were prepared [72]. The results from cone calorimeter test showed the flame retardancy and smoke suppression of the La-OMMT/PVC nanocomposites improved. Gao et al. modified MMT with Fe_2O_3 (MMT- Fe_2O_3) by the ion exchange methods and studied its effects on flame retardant and smoke suppression by cone calorimeter [73]. The PHRR value of PVC sample containing 6.5 phr MMT- Fe_2O_3 decreased by 56.6% compared with that of pure PVC and the THR value of PVC/MMT- Fe_2O_3 was much lower than that of PVC/MMT. Binary compounds of mixed-metal Cu (II) oxides are important flame retardants and smoke suppressants for plasticized PVC. Li et al. prepared Cu^{2+} -OMMTs by using silane agents and cupric sulfate [74]. The Cu^{2+} -OMMTs presented exfoliated dispersion in PVC due to the microcontent of Cu^{2+} in the interlayer space. They could accelerate the early crosslinking of PVC chains and increase the

amount of char residue, thereby reducing the PHRR, THR and smoke production.

Hydrotalcite (Layered double hydroxides)

Hydrotalcite has a structure similar as layered double hydroxides, which is well known as LDHs. LDHs are a series of synthetic anionic clays in which divalent cations within brucite-like layers are replaced by trivalent cations. As aforementioned, organic MMTs accelerate the degradation of PVC, limiting their practical application [75]. On the contrary, hydrotalcite can act as HCl scavengers to stabilize PVC [76]. To reduce the smoke release of rigid PVC during burning, LDHs and ZnO were used together to modify the polymer [77]. The LOI was highest and the SDR was lowest when the contents of LDHs and ZnO in PVC were 3 wt.% and 2 wt.%, respectively. As is mentioned above, tin-based chemicals, such as ZS, ZHS and SnO₂ are effective, non-toxic flame retardants and smoke suppressants for PVC [78]. With the properties of LDH and tin chemistries combined, Sn-LDH materials are anticipated to exhibit improved fire behaviors in PVC. Zheng et al. synthesized Sn-LDH hybrid flame retardants using a facile co-precipitation method and compounded into highly filled flexible PVC cable formulations [79]. In the LOI test, the value of the sample containing 90 phr ATH and 10 phr LDH (without Sn) was the same as that of the sample containing 100 phr ATH. After loading tin into LDH, the addition of 10 phr Sn-LDH at highest tin amount with 90 phr ATH into the PVC reduced PHRR by 64%, significantly improving the fire performance of PVC. Focke et al. investigated whether LDH can impart flame retardant properties comparable to those supplied by MH and hydromagnesite [80]. Hydromagnesite (HM) with the formula $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ is a basic magnesium hydroxycarbonate mineral that also features a layered structure. In their research, HM and LDH with the formula $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3) \cdot 4\text{H}_2\text{O}$ were all synthesized according to the literature. Considering the data from cone calorimeter test, the LDH filler performed better than MH and HM in terms of most fire-retardant parameters. Recently, Yang prepared an organo-modified CuAl-LDH intercalated by sodium dodecylbenzene sulfate and mixed it with PVC by melt blending [81]. With the addition of 3 wt.% organo-modified LDH, LOI of PVC nanocomposite increased from 27.4 to 31.1% and the nanocomposite achieved V-0 rating in UL-94 test.

Others

Tallow-triethanol-ammonium modified hectorite- and bentonite-based clays were prepared and incorporated into PVC to form nanocomposites [82]. The thermal stability of the nanocomposites

was lowered as compared to uncompounded PVC, while smoke production was significantly decreased with the addition of well-dispersed nanoclays. The authors proposed that this finding was not in line with the classic measurement of thermal stability, and thus they suggested that the assumed mechanism of smoke generation during burning, of HCl evolution resulting in the formation of aromatic species might need revision. Along with this, a reduction in the PHRR of the nanocomposites was observed. Halloysite nanotubes (HNTs) are a type of natural aluminosilicate nanotube and can be used as fillers for polymers [83, 84]. When HNTs were added into PVC, the smoke production rate and the total volume of smoke measured by cone calorimetry were reduced, implying the obvious effect on smoke suppression for PVC [85].

2.3.3 Carbon-based flame retardants for PVC

Expandable graphite

Expandable graphite (EG) is a partially oxidized form of graphite containing intercalated guest species like sulfuric acid anions in or between the stacked graphene layers [86]. Focke et al. studied the fire behavior of PVC/EG composite using cone calorimeter [87]. The addition of EG improved the flame retardancy of plasticized PVC. In presence of only 5 wt.% EG, the PHRR lowered from 325 to 63 kW/m² and the THR reduced from 55 to 10.7 MJ/m². All the composites treated with EG ignited and burned very briefly before flame out. But after the flame out, they sequently released smoke and low amount of combustion gases CO₂ and CO, due to the pyrolysis and glowing combustion of the exposed surface during the latter part of the cone calorimeter tests.

Graphene

Although a myriad of studies about the graphene as flame retardant in different polymer composites were reported continually since its discovery, the report related to graphene flame retarded PVC composites was extremely rare. Until recently, Hu and co-workers hybridized graphene with titanium dioxide (TiO₂) to investigate the synergistic effects in the properties improvements of PVC composites [88]. The incorporation of 2 wt.% hybrid material into PVC reduced PHRR by 21% in microscale combustion calorimeter (MCC) while the addition of graphene and TiO₂ separately caused a 10% and 11% reduction, respectively. Thereafter, Li and co-workers prepared ZHS-decorated graphene oxide (ZHS/GO) nanohybrid and studied their synergistic flame retardant effect [64]. The results demonstrated better dispersion of ZHS/GO than ZHS or GO alone in the PVC matrix because of the oxygen-containing groups acting as anchoring

sites for ZHS on the surface of GO. Then titanate nanotubes (TNTs) were adopted to decorate graphene oxide to afford TNTs/GO nanocomposites by the same group [89]. The LOI value of PVC nanocomposite containing 2.5 wt.% of TNTs/GO increased from 25.8% to 27.4% in comparison with that of pure one. Likewise, the PHRR and THR of the nanocomposite were reduced by 20 and 29% in presence of TNTs/GO. All the results showed that TNTs/GO effectually improved the flame retardancy than TNTs and GO alone. The decoration of TNTs suppressed the restacking of GO and promoted the uniform dispersion of TNTs/GO in the PVC matrix. Qu et al. designed and synthesized zinc borate ($4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O}$)/reduction graphene oxide (RGO) hybrid material [90]. The addition of 7.71wt.% ZB/RGO enhanced the synergistic effect with MH as flame retardants in PVC composites. The PVC/ZB/RGO/MH formulation achieved an LOI value of 29.5%, 24% higher than neat PVC. Meanwhile, the PHRR and TSP for PVC/ZB/RGO/MH blends were reduced to 35% and 34%, respectively. Tang et al. demonstrated that the addition of Fe_3O_4 nanoparticles improved the dispersion state of graphene in PVC matrix [42]. The PVC composites containing Fe_3O_4 nanoparticles and graphene alone featured a slight reduction in PHRR, PSPR and TSP compared with those of neat PVC. However, when the combination of Fe_3O_4 nanoparticles and graphene was applied, these parameters of the ternary PVC composite showed an obvious reduction. The positive effect of uniform filler dispersion on the quality of protective layers of residue was reported by Kashiwagi et al. [91]. The integrated residual surface is indispensable at the macroscopic and microscopic scale to achieve high flame retardancy by nanocomposites. The mixture of Fe_3O_4 /graphene promoted the carbonization of the degradation products of PVC into closed char with high resistance to oxidation.

2.3.4 Waste reutilization as flame retardants

Just in the past decade, people are becoming unprecedented awareness of waste pollution and seeking solutions for a cleaner planet. Waste reutilization as flame retardants for PVC not only reduces the manufacturing cost of PVC composites, but also tackles the environment problem and achieves complete recycling of renewable resources, approaching a win-win result.

Fly ash (FA) is a fine powder material recovered as a by-product during the combustion of coal at thermal power stations. Anandhan et al. converted FA into a nanostructured material (MCA-FA) by mechano-chemical activation (MCA) using a high energy planetary ball mill and prepared PVC composites with MCA-FA by a solution casting method [92]. The addition of 1, 3, 5 wt.% of

MCA-FA resulted in LOI of 26, 28 and 29%, respectively. It showed that the flammable PVC could be turned into a 'self-extinguishing' material by adding just 3 wt.% of MCA-FA. When compared with FA without modification, the MCA-FA improved flame retardancy of PVC at a much lower loading, signifying the advantage of its higher surface area.

Carbide slag is a byproduct of the PVC manufacturing industry and an industrial waste produced by calcium carbide hydrolysis to prepare C_2H_2 gas. He et al. chose 2% KH570 to modify carbide slag (MCS) and added it into wood flour/PVC composites [93]. The LOI values increased with the raise of filler content, and the value achieved to the maximum which increased from 39.6 to 42.6% with the addition of 30 phr MCS. On the other hand, MCS was effective smoke suppressants for composites. As the addition of MCS was 30 phr, it decreased the SDR by 28 units (from 73.9 to 46%) and diminished the maximum smoke density by 22 units (from 93 to 71.1%).

Waste printed circuit boards (PCBs) contains metals and nonmetal portions such as copper, tin, lead, gold, silver, and brominated resin [94]. Xiu and coworkers dealt waste PCBs with supercritical water oxidation treatment (SCWO) and used SCWO-treated waste PCBs directly as flame retardants for PVC [95]. In this research, three groups of experiments with different SCWO treatment conditions were performed and designated as FR1, FR2 and FR3, respectively. The main crystalline phases in FR1 were Cu, SnO_2 and CuSn alloy, and the flame retardant property of FR1 might mainly ascribe to SnO_2 contained in FR1. Oxides of copper could react with HCl and promote the removal reaction of HCl from PVC. The HCl and generated water vapor could dilute the oxygen around and exerted flame-retardation effects in gas phase. The existence of copper oxides was regarded as a key factor for the flame retardant property of PVC samples containing FR2 or FR3. It seemed that the flame retardant property of the mixture of Cu_2O and CuO were superior to that of CuO alone thanks to the synergistic effect of flame retardancy between Cu_2O and CuO.

2.3.5 Alternatives of antimonial flame retardants for PVC

In view of the underlying toxicity and decreasing reserve of antimony, substitutes have to be developed to partially or totally replace harmful Sb_2O_3 in PVC composites. The potential alternatives of Sb_2O_3 emerged over the last decade are introduced as follows.

Zinc borate

Zinc borate has been under research for many years and it is considered to be a suitable substitute

for Sb_2O_3 . ZB ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) displayed synergistic effect with Sb_2O_3 on flame retardancy as illustrated by LOI [45]. Although ZB alone was only slightly effective, it did display a strong synergistic effect with Sb_2O_3 at a total loading of more than 10 phr. In the cone calorimeter test, partial replacement of Sb_2O_3 with ZB resulted in a drastic reduction in HRR. The replacement also realized significant carbon monoxide reduction. The formulations with high ratios of ZB to Sb_2O_3 yielded greatest smoke production in the smoke chamber test. Depending on the fire standard to be achieved and co-additives used, ZB can either partially or completely replace Sb_2O_3 , thereby reducing cost and weight.

Tin oxide

SnO_2 is always accompanied by Sb_2O_3 to synergistically flame retard PVC. The mechanism of SnO_2 is different from Sb_2O_3 : Sb_2O_3 acts in the gas phase and SnO_2 exerts its flame retardant role in the solid phase. The role of SnO_2 is the enhancement of the CY and improvement of the char morphology. The char of pure PVC features dense structure with some pores, while the char of PVC treated with SnO_2 displays a porous honeycomb-like structure. The honeycomb-like char can prevent the entrance of oxygen and heat into the PVC bulk and escape of combustible volatiles into the interface. SnO_2 also makes the char stable in the second stage of PVC decomposition, indicated by the higher activation energy and decomposition temperature than those of pure PVC. Therefore, there is a good synergistic effect between Sb_2O_3 and SnO_2 in flexible PVC [96]. Based on the results, Wang et al. concluded that SnO_2 could replace Sb_2O_3 in flexible PVC, at least partly.

Zinc stannate/hydroxystannate

Qu's group carried out the research to study the synergistic effects of ZHS and Sb_2O_3 in flexible PVC [36]. As mentioned in the preceding text, ZHS played its role in the condensed phase. Zn^{2+} forming a Lewis acid catalyzed dehydrochlorination of PVC and promoted early cross-linking, leading to rapid charring. Sn^{4+} might react with the char and increase the char stability. These dual functions cooperated with the gas-phase action of Sb_2O_3 , thus ZHS and Sb_2O_3 presented significant synergistic effects on the flame retardancy of flexible PVC. The incorporation of 5 phr Sb_2O_3 /ZHS (1:1, weight ratio) increased LOI to 31.7%, while the LOI for samples containing 5 phr Sb_2O_3 and 5 phr ZHS alone were 30.8% and 29.3%, respectively. The authors also treated PVC samples with ZnO, SnO_2 and SnO combining with Sb_2O_3 to compare and study their

synergistic flame retardant effects in the PVC samples since ZHS comprised of Zn^{2+} and Sn^{4+} . The SDR values of the samples containing ZHS, SnO_2 and SnO were lower than that of pure flexible PVC, especially for 15 phr ZHS- or SnO -treated samples. Neither ZnO nor Sb_2O_3 showed any smoke suppressing ability, and even increased smoke production. Considering the flame retardant and smoke suppression properties, ZHS had the potential to replace part of Sb_2O_3 to improve the overall effect and reduce the harm brought forth by Sb_2O_3 .

Phosphate ester

Phosphate esters are always exploited as flame retardant plasticizers for PVC. It is found that PVC has to be blended with 20% phosphate type plasticizer along with non-flame-retardant plasticizer in order to be self-extinguishing [29]. Zhang et al. chose a kind of organophosphorus flame retardant plasticizer, tris(1-chloropropan-2-yl) phosphate (TCPP) to compare the flame retardancy property of plasticized PVC with the combination of Sb_2O_3 and polyester plasticizer (PEP). The LOI of PVC with PEP and PEP/3 phr Sb_2O_3 were 26 and 32%, respectively. The LOI increased to 35% when the TCPP was used as the flame retardant plasticizer, higher than Sb_2O_3 flame-retarded PVC composite, indicating that TCPP was effective in prompting flame-retardance.

Montmorillonite

MMT was also employed to partially replace Sb_2O_3 and studied their synergism as flame retardants for flexible PVC, but the results were not so satisfactory [12]. Though the addition of $\text{MMT/Sb}_2\text{O}_3$ increased LOI significantly compared with pure flexible PVC, all the values were lower than the case where in presence of Sb_2O_3 alone. It indicated that there was no synergism between MMT and Sb_2O_3 on flame retardant effect for flexible PVC. But the incorporation of MMT into Sb_2O_3 decreased the SDR of the PVC composites compared with Sb_2O_3 -treated one since the addition of Sb_2O_3 alone increased the smoke production of PVC. Therefore, MMT is not an ideal candidate to replace Sb_2O_3 as flame retardant for PVC.

2.4 Summary

From the research emerged during the last decade, it can be concluded that among various flame retardants for flexible PVC composites, those that containing metals especially which can form Lewis acid catalysts with Cl during the combustion of PVC are the most effective ones. This is because according to the thermal degradation process of PVC introduced at the beginning of this chapter, Lewis acid is able to catalyze the dehydrochlorination process to release HCl earlier

which retards the flame as “poison”. Meanwhile, it can promote the early crosslinking of the polymer benefiting to the char formation. The compact and robust char residue prevents combustible volatiles escaping to the flame zone to fuel the flame, thereby avoid further burning. Among a variety of metals, zinc, tin and iron perform most effectively due to the strong Lewis acidity of their corresponding chlorine salt. These metal-based flame retardants have the great potential to substitute Sb_2O_3 under suitable modification in flexible PVC composite, at least partly.

However, only a few research groups focus on the related area, and the study of the replacement for Sb_2O_3 is far from enough. In addition, to my best knowledge, the monitor and reduction of HCl released during the combustion (instead of pyrolysis) of PVC has never been reported. Recently, the preparation of polymer nanocomposites by the addition of nanofillers with special nanostructures provides new solution towards high-performance flame retardant polymeric materials. Inspired by the previous report, metal-based flame retardants with unique nanostructures are designed and synthesized in this thesis. The thus-obtained flame retardants are blended into flexible PVC composites to compare the fire behaviors with those of Sb_2O_3 -treated ones. Moreover, the relative amount of HCl released during the combustion of PVC composites are monitored by a method designed firstly in our group. The novel nano-flame retardants are anticipated to totally replace Sb_2O_3 and at the same time reduce the HCl releasing amount during the combustion of flexible PVC composites.

In the next chapter, the materials and techniques used in the study will be introduced briefly. And then the study will be carried out as following three steps in successive chapters (Chapter 4-6):

1. In the initial stage, a facile one-step synthesis method is adopted to prepare single-component flame retardant to partially replace Sb_2O_3 . This study acts as exploratory work to help us get familiar with the property of PVC composite including the thermal stability, flammability and mechanical properties, and provide enlightenment for the further research.
2. Next, metal element with high activity is in-situ doped into a carrier fabricated via a simple sol-gel method. The thus-obtained flame retardant is anticipated to totally replace Sb_2O_3 in flexible PVC composite, at least achieving the similar level as Sb_2O_3 in several fire tests, such as LOI and UL-94.
3. Subsequently, on the basis of previous work, more efficient components are selected and

more complex nanostructures are designed. A hybrid composed of binary metal oxides is manufactured in a large scale by a rapid precipitation method. The tailor made flame retardant is promising to totally substitute Sb_2O_3 in flexible PVC composite, and even surpass Sb_2O_3 to show better performance in fire tests.

CHAPTER 3

MATERIALS AND CHARACTERIZATION METHODS

“Will, work and wait are the pyramidal cornerstones for success.”

-Louis Pasteur

3.1 Materials

The materials involved in this thesis are listed below: zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], urea [$\text{CO}(\text{NH}_2)_2$], ethanol (EtOH), hexadecyltrimethylammonium bromide (CTAB), ammonium hydroxide solution (ACS reagent, 28.0-30.0% NH_3 basis), tetraethoxysilane (TEOS), tin (IV) oxide (nanopowder, < 100 nm particle size), tin (IV) chloride, commercial tin oxide (-325 mesh, 99.9% trace metals basis, denoted as c- SnO_2), tin (II) chloride dehydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, reagent grade, 98%), citric acid (ACS reagent, $\geq 99.5\%$), sodium dodecylbenzenesulfonate (SDBS), sodium hydroxide (reagent grade, $\geq 98\%$, pellets), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ACS reagent, 97%), absolute ethanol and trioctyl trimellitate (TOTM) were purchased from Sigma Aldrich. PVC resin (K=70), Ca-Zn based heat stabilizer, epoxidized soy oil (ESBO), wax (polyethylene) and antimony trioxide (Sb_2O_3) were provided by Quimidroga, s.a. Liquid nitrogen was acquired from Linde group.

3.2 Characterization methods

3.2.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR) measurements were collected on a Nicolet iS50 spectrometer. The samples were analyzed with the transmission mode in the wavenumber range of

4000-400 cm^{-1} and the solution was set as 4 cm^{-1} . 1 mg sample and 400 mg KBr, spectrometry grade, were homogenized thoroughly in an agate mortar and pellets of 1 cm diameter and about 1 mm thickness were obtained by pressing, under vacuum, about 100 mg of mixture with precaution taken to avoid moisture uptake. Samples were dried at 80 $^{\circ}\text{C}$ in an oven before the FT-IR scan.

3.2.2 X-ray diffraction measurement

Powder X-ray diffraction (XRD) was performed with a Philip X' Pert PRO diffractometer equipped with a Cu $K\alpha$ tube and Ni filter ($\lambda = 0.15405 \text{ nm}$), operating at 45 kV voltage and 40 mA current.

3.2.3 Field emission gun scanning electron microscope

Field emission gun scanning electron microscope (FEGSEM) dual-beam microscope images of as-synthesized sample were observed by Helios NanoLab 600i, FEI.

3.2.4 Particle size distribution measurement

For the particle size Malvern laser diffraction equipment Mastersizer 2000 was used, which makes use of the theory of Fraunhofer.

3.2.5 Scanning electron microscope

Scanning electron microscope (SEM) images of cross section of composite and the char layer after burning were observed by EVO MA15 Zeiss equipped with energy dispersive X-ray detector (EDX). All the samples were coated with a conductive gold layer.

3.2.6 Transmission electron microscope

Transmission electron microscope (TEM) gave high magnification and detailed vision of the morphology and microstructures of the composites. Samples were prepared with a Leica ultramicrotome at room temperature. Ultramicrotomy ultrathin sections had a thickness of 50 nm. 1% uranyl acetate was added as a contrast agent. TEM analysis was carried out on a Tecnai T20 (FEI company) at 200 kV in Bright Field imaging mode.

3.2.7 Nitrogen adsorption-desorption measurement

N_2 adsorption and desorption isotherms at -196 $^{\circ}\text{C}$ were measured on a Micromeritics instrument (ASAP 2010). The specific surface area and the pore size distribution were calculated by the Brauner–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) model, respectively.

3.2.8 X-ray photoelectron spectroscopy

The second UHV chamber was equipped with an Organic Molecular Beam Epitaxy (OMBE) system, a monochromatized X-ray source, an ultraviolet He discharge lamp, a hemispherical energy analyzer (SPHERA-U7), and low energy electron diffraction (LEED) optics. The unpolarized He I ($h\nu = 21.2$ eV) and He II ($h\nu = 40.8$ eV) lines of the UV lamp were used for Ultraviolet Photoelectron Spectroscopy (UPS), and the Al K α line ($h\nu = 1486.7$ eV) was used from an Al anode for X-ray Photoelectron Spectroscopy (XPS). The analyzer pass energy was set to 20 eV for the XPS measurements to have a resolution of 0.6 eV, whereas for the UPS the pass energy was set to 5 eV corresponding to a resolution of 0.1 eV. The angular acceptance for the used aperture size is defined solely by the magnification mode, i.e. $1750 \times 2750 \mu\text{m}^2$.

3.2.9 Raman spectroscopy

The Raman spectra for the char residues were recorded at ambient temperature on a LeicaDM 2700 microscope with YAG laser (50 mW at 532 nm) and a diffraction grating of 1800 l/mm.

3.2.10 Inductively coupled plasma/optical emission spectrometry

The element ratio was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES: Perkin Elmer Optima 3300DV and Spectro Arcos). The auxiliary gas (Ar) flow rate, carrier gas (Ar) flow rate and plasma gas (Ar) flow rate were 1.0, 1.0 and 12 L/min, respectively, and the wavelengths used were Cr (II) 267.716 nm; Cu (I) 324.754 nm and Pb (II) 220.353 nm. The solution uptake rate was 2.0 mL min^{-1} and the integration time was 12 s.

3.2.11 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was determined from room temperature to 800°C , with a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 atmosphere with flow speed 90 ml min^{-1} using a TA Q50 thermogravimetric analyzer.

3.2.12 Limiting oxygen index

The LOI test is an indicator of the ease of combustion in an oxygen-nitrogen atmosphere through downward burning of a vertically mounted sample (Scheme 3-1). It is a technique for measuring the minimum oxygen concentration to support candle-like combustion of plastics over 3 min or until the testing sample is consumed for more than 5 cm from the top. It is a simple, convenient, fast, and effective method for the study of flame retardancy of PVC materials. A higher LOI value indicates a greater efficiency for the flame retardant. The oxygen index was described as follows

and oxygen index of the air is 21 [97].

$$\text{LOI}\% = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100\%$$

where $[\text{O}_2]$ and $[\text{N}_2]$ are the concentration of oxygen and nitrogen in a mixture of two gases. The sheet dimensions of the samples were $130 \times 6.5 \times 3.2$ mm. The test method is generally reproducible to an accuracy of $\pm 0.1\%$, providing a useful comparison of the relative flammability of different materials, but the correlation with large scale fires is highly questionable [98]. The LOI of neat PVC is 45 ~ 49%, compared to most non-halogen polymers, which have LOI ranging from 17.4% (polypropylene or polymethyl methacrylate) to 26% (polycarbonate). However, after adding a large amount of flammable plasticizers, the LOI value of plasticized PVC drops down into the range of flammable materials, commonly below 25%. Therefore, LOI test is the most direct and fast way to determine the fire hazard of PVC materials both in the lab and in industry.

Scheme 3-1: The LOI test apparatus [99].

3.2.13 UL-94

The UL-94 tests were developed by Underwriters Laboratories as combustion tests of polymeric materials for parts in devices and appliances. In terms of all the UL-94 tests, vertical burning test is the most widely used measurement for examining the ignitability and flame spread of polymeric materials [100]. A UL-94 test measures the ability of a sample to self-sustain ignition and propagation in an upward flame spread configuration. The tests were carried out in a UL-94 Horizontal/Vertical Flame Chamber (FTT, UK) in accordance with ASTM D3801. The sheet dimensions of the samples were $130 \times 13 \times 0.6$ mm. The Bunsen burner generates blue flame by consuming methane with a length of 20 mm and a power of 50 W. As shown in Scheme 3-2, the distance between the top of the burner and the bottom of the sample is maintained at around 10

mm.

Scheme 3-2: Schematic view of the UL-94 vertical burning test [99].

The ratings of UL-94 tests are determined by calculating the time required for the flame to extinguish after ignition twice. The flame was applied centrally to the bottom of the specimen for 10 s. The afterflame time was recorded twice, when the flame was removed and after 10 s each time. The afterglow time was recorded if the specimen shows afterglow phenomenon after the second flame application. A piece of cotton (approximately $50 \times 50 \times 6$ mm) was positioned 300 ± 10 mm below the end of the specimen in order to record whether any dripping induced ignition of the cotton. The specific burning characteristics required for each classification are summarized in Table 3-1. The unplasticized PVC can pass V-0 rating in the UL-94 easily because of its inherent flame retardancy. With increasing the adding amount of flammable plasticizers, the ratings alter from V-1, V-2 until no rating. Another method to examine the differences clearly between pure plasticized PVC sample and flame retardant-treated plasticized PVC sample is to decrease the thickness of sample sheets when the addition of plasticizer is fixed.

Table 3-1: Classification for UL-94 vertical burning test [99].

	V-0	V-1	V-2
Total flaming combustion for each specimen	≤ 10 s	≤ 30 s	≤ 30 s
Total flaming combustion for all 5 specimens of any set	≤ 50 s	≤ 250 s	≤ 250 s
Flaming and glowing combustion for each specimen after 2nd burner flame application	≤ 30 s	≤ 60 s	≤ 60 s
Cotton ignited by flaming drips from any specimen	No	No	Yes
Glowing or flaming combustion of any specimen to holding clamp	No	No	No

3.2.14 Cone calorimeter test

The schematic view of cone calorimeter was shown in Scheme 3-3. The measuring principle of this test, standardized as ASTM E 1354 or ISO 5660, is that of oxygen consumption in the combustion gases of a specimen subjected to a defined heat flux. The produced gases are collected in an exhaust duct system with centrifugal fan and a hood and the heat release rate (HRR) is calculated based on the fact that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released throughout polymer combustion. The equation is shown as follows: $HRR = E \times (Q - q)$, where E is average value of the net heat release per unit mass of oxygen consumed $E = 13.1 \text{ kJ/g}$, Q is mass flow rate of oxygen in the incoming air and q is mass flow rate of oxygen in the exhaust gases [101]. The main parameter that determined during combustion in the cone calorimeter test is the heat release rate, which is the basic parameter for fire modeling and evaluating fire behavior of materials. HRR denotes the rate at which heat energy is released per unit area of the sample. It is recognized to be the most important parameter to quantify the size of fire and an effective flame-retardant system generally shows a lower HRR value. Other parameters such as time to ignition (TTI), mass loss and smoke release can also be measured. Cone calorimetry tests were carried out using a Cone Calorimeter (FTT, UK) in accordance with the ISO 5660-1 standard. Specimens with sheet dimensions of $100 \times 100 \times 3.2 \text{ mm}$ were irradiated at a heat flux of 50 kW/m^2 . A specimen was placed under a cone shaped radiant heater. The specimen was ignited once the pyrolysis products were ignited in the atmosphere. The combustion products went through an instrument exhausted pipe and were filtered prior to detection.

Scheme 3-3: Schematic view of the cone calorimeter [102].

3.2.15 Detection of HCl release amount during combustion

During the cone calorimeter test, the emission of HCl gas in the gases released from the cone calorimeter from each sample was collected using the apparatus shown in Scheme 3-4. The Cl^- concentration in the aqueous solution was measured using a DIONEX ion chromatograph DX-500 equipped with conductimetric and amperometric detectors.

Scheme 3-4: Schematic diagram depicting the collection of HCl gas during cone calorimetry.

3.2.16 Tensile test

The tensile test samples were dumbbell-shaped with dimensions of 75 mm × 10 mm × 2 mm, complying with ISO 527-2 (1996) standard. An Instron 5966 (USA), universal tensile testing machine equipped with a digital image correlation (DIC) system was utilized to carry out the tensile tests at a 1mm/min test speed. Minimum 3 specimens were tested for each sample to obtain a reliable average value and standard deviations.

CHAPTER 4

SYNTHESIS OF NANO ZINC CARBONATE AND ITS USE AS A PARTIAL SUBSTITUTE OF ANTIMONY TRIOXIDE IN FLAME RETARDANT FLEXIBLE POLY(VINYL CHLORIDE)

“Chemistry is necessarily an experimental science: its conclusions are drawn from data, and its principles supported by evidence from facts.”

-Michael Faraday

4.1 Introduction

Nowadays, more and more researchers focus on the synergism between inorganic zinc compounds and Sb_2O_3 , aiming to partly replace Sb_2O_3 and maintain the flame retardancy at the same time. In a cone calorimeter study investigated by Shen, in flexible PVC, partial replacement of antimony oxide with the zinc borate reduced not only the peak of heat release rate, but also the carbon monoxide production drastically at a heat flux of 35 kW/m^2 [45]. Another synergism was observed by Scharrel et al. for the combination of zinc sulfide (ZnS) and Sb_2O_3 as flame retardant for flexible PVC in cone calorimetry in terms of time to ignition, heat release rate, smoke production, mass loss and CO production [103]. It was also found that a cooperative action of gas-phase (Sb_2O_3) and condensed phase (ZnS) mechanism was achieved. It is proved that the synergism of ZnS and Sb_2O_3 allows the possibility of replacing half of Sb_2O_3 by ZnS to reach equivalent flame retardancy. Qu et al. proved that Sb_2O_3 and ZHS had a synergistic effect on the flame retardancy of flexible PVC [36]. The LOI value for 5 phr Sb_2O_3 /ZHS (weight ratio = 1:1) as flame retardant

was 31.7% while the LOI value for 5 phr Sb_2O_3 was 30.8%. They presumed that ZHS acted as a flame retardant in the condensed phase, cooperating with the vapor-phase action of Sb_2O_3 , so ZHS and Sb_2O_3 generated synergistic effects on the flame retardancy of flexible PVC.

Since zinc element shows certain flame retardancy in flexible PVC, moreover, the synergistic effects of zinc compounds with Sb_2O_3 in PVC composites investigated before are not so obvious, thus the research on zinc compounds as flame retardant in flexible PVC is far from enough. Zinc carbonate (ZnCO_3 , denoted as ZC) is predicted to have great potential to make contribution to flame retarding PVC by an integration of Zn^{2+} and CO_2 (dilute agent for combustible gases) released during decomposition. However, the synthesis of corresponding product in industry, zinc carbonate hydroxide [$\text{Zn}(\text{OH})_2 \cdot x\text{ZnCO}_3$], consists of multiple steps. Meanwhile, its decomposition temperature due to the existed hydroxyl started at about 150 °C which is lower than the processing temperature for flexible PVC (170 °C) [104]. Therefore, the commercial product may be not suitable to be used as flame retardant in flexible PVC. Zinc carbonate without hydroxyl needs to be synthesized for the sake of enhancing thermal stability in terms of PVC processing. To our best knowledge, there is no relevant report on one-step synthesis of ZnCO_3 in hydrothermal condition and addition into flexible PVC as flame retardant. Consequently, an attempt to replace part of harmful Sb_2O_3 in flame retardant flexible PVC composite by using ZC nanoparticles as exploratory work was carried out in this chapter. The synergistic effect between ZC and Sb_2O_3 on the flame retardancy of flexible PVC composites was discussed. Thermal stability, flame retardancy and mechanical property of flexible PVC composites were investigated. Also the mechanism of synergistic effect of nano ZC and Sb_2O_3 flame retarding flexible PVC was proposed.

4.2 Synthesis of ZC nanoparticles and preparation of flexible PVC composites

The facile synthesis of ZC nanoparticles utilized hydrothermal method. At first, a certain amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea with molar ratio 1 to 1 were solved in 100 ml distilled water and the mixed solution was stirred vigorously for 30 min at room temperature. After a clear solution was obtained, it was transferred into 200 ml autoclave reactor. Then the autoclave reactor was put into the oven for 12 h at 140 °C. The obtained precipitate was filtered, washed several times by distilled water and dried in oven at 70 °C overnight.

The flexible PVC composites were formulated with 35 phr TOTM, 7.5 phr heat stabilizer, 5 phr

ESBO, 0.2 phr wax and 5 phr (3.2 wt%) flame retardant. The designated formulation of the PVC compound was summarized in Table 4-1. Phr means parts per hundred parts of base resin.

Table 4-1: Formulation of flexible PVC composites.

Component	Content/phr
PVC resin	100
TOTM	35
Ca-Zn based heat stabilizer	7.5
Epoxidized soy oil	5
Wax	0.2
Flame retardant	5

The pristine PVC resin and additives were dry blended well and then plasticized by a twin-screw extruder system (KETSE 20/40 EC, Brabender) with the processing temperature around 170 °C and the speed 80 rpm. The products of extrusion were pelletized and dried. Then the pellets were put into injection molding machine (Arburg 320 C) with the processing temperature around 180 °C in order to shape into the sample sheets with suitable dimensions applied on LOI, cone calorimeter and tensile tests. UL-94 sample sheets were compression molded by hot-plate press (LabPro 400, Fontijne Presses) at 180 °C and then cut into suitable size. The details of flame retardants containing in the tested samples are tabulated in Table 4-2.

Table 4-2: Details of flame retardants containing in the tested samples.

Sample	Flame retardant	Ratio ^a	Content/phr
PVC-0	-	-	-
PVC-1	Sb ₂ O ₃	-	5
PVC-2	Sb ₂ O ₃ /ZC	3:1	5
PVC-3	Sb ₂ O ₃ /ZC	1:1	5
PVC-4	Sb ₂ O ₃ /ZC	1:3	5
PVC-5	ZC	-	5

^a Weight ratio between the constituents of flame retardants.

4.3 Structure characterization of flame retardant

The XRD pattern of as-synthesized sample is shown in Figure 4-1. The lines observed in the XRD

spectrum corresponded well with those of smithsonite (JCPDS file 008-0449) whose chemical formula is ZnCO_3 . There was no heterogeneous peak detected in the XRD spectra which proved the as-synthesized sample a pure substance.

Figure 4-1: XRD pattern of as-synthesized sample.

The grain size of the sample can be seen from the FEGSEM images (Figure 4-2) that the material is composed of nanoparticles. The tendency to aggregation might be explained due to the high Gibbs free energy in the system caused by the high specific surface area of each particle. By well dispersed in ethanol solution via ultrasonic, the achieved particle size distribution stated the dimension of ay-synthesized sample ranged around 91.3 nm in a nanoscale.

Figure 4-2: FEGSEM images of synthesized ZC: (a) 20000x; (b) 50000x and its particle size distribution (c).

The precipitation process of zinc nitrite and urea under normal pressure and temperature formed $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ (JCPDS file 005-0664) [105, 106]. In comparison, the hydrothermal method provided sufficient conditions to impel urea to hydrolyze thoroughly in order to generate CO_3^{2-} and react with Zn^{2+} via replacement reaction without any OH^- existing in the final product. It could be elucidated by following process:

Figure 4-3 exhibited the cross section of PVC-4 composite containing $\text{Sb}_2\text{O}_3/\text{ZC}$ at weight ratio 1:3. The compositions of the spread particles on the surface were evidenced by EDS point detection. It can be seen that micrometric Sb_2O_3 with 1-2 μm particle size possessed random distribution while nanometric ZC with much less than 1 μm particle size evenly dispersed in the composite. It illuminated the fine size of ZC is beneficial to the uniform distribution in the composite system.

Figure 4-3: SEM image with EDS point detection of the cross section of PVC-4.

4.4 Thermal stability of flexible PVC composites

Figure 4-4 presents the TGA and DTG curves for flexible PVC and corresponding composites containing 5 phr each flame retardant and TGA curve for as-synthesized ZC. The TGA analysis of as-synthesized sample indicated that the decomposition temperature was in agreement with ZnCO_3 and approximately 3 wt% of weight loss was observed up to about 300 $^{\circ}\text{C}$ due to the evaporation of water adsorbed onto the surface of powder. Thereafter, a decrease in weight occurred owing to the release of CO_2 with the weight loss of around 34.1 wt% which was very close to the theoretical weight loss (35.2 wt%) and the residue was zinc oxide. This result confirmed the XRD results, suggesting that the appropriate chemical was obtained.

The thermal decomposition of flexible PVC composites is divided into two stages. The first stage is ascribed to the dehydrochlorination of the polymer chain and plasticizer degradation [107]. And the second stage mainly involves cyclization of conjugated polyene sequences to form aromatic compounds [103]. As shown in Figure 4-4 and Table 4-3, the onset decomposition temperatures ($T_{5\%}$, temperature at 5% weight loss) of PVC-4 and PVC-5 were obviously lower than PVC-0, while on the contrary, the $T_{5\%}$ of PVC-1 was slightly higher than PVC-0. This finding is illustrated with the assumption that ZC might react with the HCl released from PVC to form $ZnCl_2$ which is a strong Lewis acid and it might catalyze the dehydrochlorination and promote the early crosslinking to the PVC compound. Whereas for PVC-1, AT did not decompose and melt at the low temperature, therefore the onset decomposition temperature of PVC-1 was increased.

Figure 4-4: TGA curves of flexible PVC composites and as-synthesized ZC and DTG curves of flexible PVC composites.

The temperatures at the maximum rate of weight loss at the first stage of decomposition (T_{max1}) of PVC-4 and PVC-5 decreased by about 25 °C than those of PVC-0 and PVC-1, while the temperatures at the maximum rate of weight loss at the second stage of decomposition (T_{max2}) of PVC-4 and PVC-5 were nearly the same with those of PVC-0 and PVC-1. These results revealed that the stability of the residue was enhanced, although the enhancement was not so marked due to the low adding amount of ZC (2.4 wt% and 3.2 wt% respectively). The residue of PVC-1 kept similar with that of PVC-0, caused by that AT played its role in the gas phase as flame retardant

for PVC. When ZC was added, both residues of PVC-4 and PVC-5 increased significantly by around 33 wt% in comparison to the sample without treating with ZC. The results showed that the main role of ZC in PVC degradation was to catalyze dehydrochlorination, promote early cross-linking in the first stage, and enhance the char stability in the second stage. To the aspect of the formation of residues, ZC improved the thermal stability of the composite.

Table 4-3: TGA and DTG results of flexible PVC composites.

Sample	T _{5%} (°C)	T _{max1} (°C)	T _{max2} (°C)	Residue at 750 °C (wt%)
PVC-0	271	289	465	15.4
PVC-1	277	291	463	15.5
PVC-4	252	264	462	20.9
PVC-5	251	261	466	21.7

(T_{5%} , temperature at 5% weight loss; T_{max1}, temperature at the maximum rate of weight loss at the first stage of decomposition; T_{max2}, temperature at the maximum rate of weight loss at the second stage of decomposition.)

4.5 Fire behavior of flexible PVC composites

LOI and UL-94

LOI results of flexible PVC composites are shown in Figure 4-5. Addition of 5 phr flame retardants significantly improved the flame retardant properties of flexible PVC composites. The addition of ZC itself increased the LOI value from 25 to 32.2%. Nevertheless, the sample containing Sb₂O₃ still showed 2.3% higher than the sample treated with ZC, which meant Sb₂O₃ presented relatively high efficiency in flame retarding PVC by using it alone. However, when added Sb₂O₃ compounded with ZC into PVC composite, the anti-ignition property had a further improvement. By controlling the ratio of Sb₂O₃ to ZC in flexible PVC composites from 3:1, 1:1 to 1:3, respectively, the LOI values increased gradually; PVC-4 in which Sb₂O₃/ZC is at 1:3 presented the highest value up to 36.7% among all the composites. Thereby, synergistic flame retardancy as a result existed in the combination of Sb₂O₃ and ZC for flexible PVC composites.

Figure 4-5: LOI and UL-94 results of flexible PVC composites.

Vertical burning test (UL-94) was also taken into account to test the flammability of flexible PVC composites. The sample sheets in the typical run and in this work differ in the thickness. In terms of the inherent flame retardancy of PVC, the UL-94 test was always ignored and deemed to be meaningless by most reports. Unlike the typical run, the sample sheets adopted in this work were thin films with the thickness of only 0.6 mm instead of conventional 3.2 mm. By this way, the difference could be observed readily during combustion of the samples. The results are labeled in Figure 4-5. During the test, PVC-0 burnt very fast with dripping happened and was not self-extinguished after the removal of burner. Things changed better in the presence of Sb_2O_3 : the sample reached a V-0 rating but dripping emerged again (not ignite the cotton). The same thing occurred on PVC-2 as well. With the increasing amount of ZC in PVC composites, all the samples (PVC-3, 4, 5) passed UL-94 test with a V-0 rating accompanied with no dripping phenomenon happened. The dripping of PVC-0, PVC-1 and PVC-2 in vertical burning test might be due to the fragile char layer formed during the combustion, which was not tough enough to make it as an integrated part throughout. The improvement of PVC-3 and PVC-4 in UL-94 test along with LOI test was attributed distinctly to the synergistic effect of Sb_2O_3 and ZC in flexible PVC. The ZC promoted char forming to block the release of combustible gases to protect the polymer underneath and CO_2 emitting might dilute the fuel gases to inhibit the combustion, while Sb_2O_3 acted as a scavenger to capture free radicals in order to stop the flame reaction. As a summary, the flame retardant $\text{Sb}_2\text{O}_3/\text{ZC}$ (weight ratio at 1:3) performed highest efficiency on flexible PVC in the LOI and UL-94 tests.

Cone calorimeter

Cone calorimeter was carried out to investigate the fire behavior of flexible PVC composites in forced-flaming situation and provided a wealth of information on combustion behavior [108]. Compared with LOI and UL-94 tests, the cone calorimeter test plays an important role in the quantitative analysis of the flammability [109]. Therefore the cone calorimeter was utilized to evaluate the burning behavior of flexible PVC composites by measuring the heat release rate, peak of heat release rate, time to ignition, total heat release, and mass loss. The details of data are listed in Table 4-4.

Flexible PVC's HRR curve (Figure 4-6a) showed that the composite burnt very violently after ignition, indicating its tinder property. PHRR is an important parameter to evaluate the intensity of fires [110]. The sharp HRR peak of PVC-0 appeared with PHRR of $218 \pm 9 \text{ kW/m}^2$, and then the value decreased slightly in the case of Sb_2O_3 , while with the addition of ZC, the composites showed different degrees of PHRR reduction mainly ascribing to probable effect caused by fine size ZC. This phenomenon pointed out that the presence of ZC weakened the intensity of fires in flexible PVC system. Among all the samples, the PHRR of PVC-4 significantly reduced to $149 \pm 4 \text{ kW/m}^2$ which was a reduction of 31.7% compared with that of PVC-0. Also, PVC-4's HRR curve described a much milder burning procedure. Furthermore, PVC-4 released less heat than all the other samples and reduced THR strikingly from 81 ± 4 to $53 \pm 3 \text{ MJ/m}^2$. As shown in Figure 4-6b, no matter in any time period PVC-4 had the lowest THR value which meant the burning rate of heat release of PVC-4 was relatively slow. It is assumed that specific surface area might play a key role in cone calorimeter test. Nanoscale additive with larger surface area may make the path length longer that the transfer of oxygen and combustible gases was inhibited, leading to retard heat release [111]. In addition, it seemed Sb_2O_3 produced little efficiency in reducing heat release of burning flexible PVC.

The most noteworthy results from the cone calorimeter came from the difference of prolonged TTI of PVC-2, PVC-3 and PVC-4 as compared with those of PVC-1 and PVC-5. The result is so interesting that it's worthy to have a further discussion. The sole flame retardant flexible PVC composites extended the TTI from 20 ± 0 to $26 \pm 2 \text{ s}$. In contrast, the compounded flame retardants delayed the ignition time markedly (from 36 ± 1 to $38 \pm 1 \text{ s}$) while the flame retardants

used separately had no such effect. A proposed mechanism is as follows: ZC might have a capability to catalyze dehydrochlorination of PVC to generate HCl and synchronously Sb_2O_3 melted at high temperature to react with HCl to form SbCl_3 (gas phase) which is an effective vapor-phase flame inhibitor in order to stop the flame reaction, hence contribute to the flame retardancy thereby postpone the time to ignition.

Figure 4-6c showed the mass loss as a function of combustion time. The decrease of residue of PVC-1 compared with that of PVC-0 proved that Sb_2O_3 did not contribute to the char forming. The increases of char residue of PVC-4 and PVC-5 were consistent with the results in the LOI test that demonstrated ZC might promote early cross-linking of PVC to form char layer which limited the heat and mass exchange between gaseous and condensed phases, as a result, contributed to the flame retardancy.

Figure 4-6: Cone calorimeter data of flexible PVC composites: (a) heat release rate curves; (b) total heat release curves; (c) weight loss curves.

Table 4-4: Cone calorimeter data summary of flexible PVC composites.

Sample	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	Char residue (wt.%)
PVC-0	20 ±0	218 ±9	81 ±4	11.9 ±0.4
PVC-1	25 ±1	192 ±3	84 ±2	9.6 ±0.7
PVC-2	38 ±1	161 ±6	67 ±3	14.6 ±0.3
PVC-3	36 ±1	170 ±5	57 ±4	15.6 ±0.3
PVC-4	37 ±1	149 ±4	53 ±3	17.1 ±0.5
PVC-5	26 ±2	159 ±4	57 ±2	16.6 ±0.4

(TTI, time to ignition; PHRR, peak of heat release rate; THR, total heat release.)

Char residue analysis

The surface morphology of the char residues collected after cone calorimeter test was investigated with SEM to analyze the flame retardant mechanism of ZC. The digital photographs and SEM images of char residues are shown in Figure 4-7. The morphology of the char formed in PVC-0 had honeycomb structure with many tiny pores, and the char formed in AT-treated PVC-1 was porous also. However, the morphology of the char for PVC composite containing ZC is quite different from aforementioned two samples. A large quantity of small flakes was detected evenly distributed on the surface of the char residue. These recognized flakes might be zinc chloride generated during the combustion reaction. The uniform distribution of the flakes implied the nanometric ZC dispersed well in PVC polymer system correlated with the SEM image of cross section belong to PVC-4 shown before. Moreover, the char residues of PVC-4 and PVC-5 were dense, continuous and tough. These dense structures were presumed to form barriers to inhibit combustible gases and transfer of heat energy to the PVC bulk which is beneficial in improving flame retardancy.

Figure 4-7: Digital photographs of the residues collected after cone calorimeter test and corresponding SEM micrographs.

4.6 Tensile property of flexible PVC composites

Tensile property of flame retardant flexible PVC composites is one of the most important properties that are used to evaluate the quality of the product in practical application. The experimental tensile test curves are shown in Figure 4-8. The tensile properties of the flexible PVC composites were measured and the results are listed in Table 4-5. The plasticized PVC showed flexible property, presenting a relatively high elongation at break ($75 \pm 4\%$) due to the plasticization. With adding Sb_2O_3 , the tensile strength at yield of PVC-1 improved slightly from

11.8 $\pm$ 1 MPa to 13.8 $\pm$ 1 MPa. As an inorganic commercial product, Sb₂O₃ was not compatible well with PVC matrix, therefore the elongation at break of PVC-1 decreased to 56 $\pm$ 3%, while in the presence of ZC, the tensile property showed better performance than the addition of AT alone. The tensile strength of PVC-4 and PVC-5 improved to 15.9 $\pm$ 1 MPa and 16.6 $\pm$ 1 MPa, increasing by 35% and 41% respectively compared with that of PVC-0, accompanying with significant enhancement in elongation at break (124 $\pm$ 5% and 124 $\pm$ 7%, respectively).

Figure 4-8: Tensile stress-strain curves of flexible PVC composites.

It is assumed that the fine dispersion of as-synthesized ZC in flexible PVC because of its nanometric size, enhanced the interaction between the flame retardant and PVC matrix, therefore the mechanical property increased to some extent. Additionally, the increase in tensile modulus from 138 $\pm$ 4 MPa (PVC-0) to more than 230 MPa (PVC-4 and PVC-5) was expected due to the high Young's modulus of the ceramic counterpart. The flexible PVC composite exhibited relatively lower modulus, so the incorporation should increase the modulus of the composite [112].

Table 4-5: Tensile properties of flexible PVC composites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
PVC-0	11.8 $\pm$ 1	75 $\pm$ 4	138 $\pm$ 4
PVC-1	13.8 $\pm$ 1	56 $\pm$ 3	216 $\pm$ 4
PVC-4	15.9 $\pm$ 1	124 $\pm$ 5	247 $\pm$ 6
PVC-5	16.6 $\pm$ 1	124 $\pm$ 7	236 $\pm$ 3

4.7 Summary

Zinc carbonate nanoparticles were synthesized by a novel hydrothermal method with zinc nitrite and urea as starting materials. XRD, FEGSEM, particle size distribution and TGA confirmed the structure, morphology and thermal stability of the synthesized material. The results obtained from LOI, UL-94 and cone calorimeter tests indicated nano ZnCO_3 was a good flame retardant for flexible PVC. Importantly, by combining with Sb_2O_3 , the flame retardant efficiency on flexible PVC was improved significantly. The flame retardant $\text{Sb}_2\text{O}_3/\text{ZnCO}_3$ with weight ratio 1:3 exhibited highest efficiency in fire tests: LOI value increased from 25 to 36.7%; passed V-0 rating without dripping; PHRR decreased from 218 ± 9 to $149 \pm 4 \text{ kW/m}^2$ and THR reduced from 81 ± 4 to $53 \pm 3 \text{ MJ/m}^2$. Moreover, nano ZnCO_3 was also beneficial to improve tensile property of flexible PVC composites. Owing to the synergistic effect, using nano ZnCO_3 replaced 75% Sb_2O_3 in the flame retardant PVC system and reduced the harm caused by Sb_2O_3 . These results displayed the potential to partially replace Sb_2O_3 by the as-synthesized flame retardant in the exploratory work. In the following chapters, the efforts will be focused on total substitute of Sb_2O_3 by the hierarchical structural tin-based compounds.

CHAPTER 5

SYNTHESIS OF NANOPOROUS SILICA DOPED WITH TIN AND ITS USE AS A SUBSTITUTE OF ANTIMONY TRIOXIDE IN FLAME RETARDANT FLEXIBLE POLY(VINYL CHLORIDE)

“A fact acquires its true and full value only through the idea which is developed from it.”

-Justus Von Liebig

5.1 Introduction

Silicon derivatives as flame retardants are attractive because of their excellent thermal-resistance, non-toxicity and non-generation of toxic gases during combustion [113]. They have shown prominent effectiveness in improving flame retardancy and thermal stability properties of polymers. Recently, Li et al. had proved that mesoporous silica had excellent synergism with intumescent flame retardants in polypropylene [114]. Qian et al. doped aluminum on mesoporous silica and used it to flame retard polylactide effectively [111]. And Zhang et al. also ascertained mesoporous silica had benefits in enhancing thermal stability of polymethyl methacrylate matrixes [115]. Therefore, porous silica has drawn immense attention among researchers. Nevertheless, to our best knowledge, porous silica as flame retardant in PVC system has never been reported. It is probably because without suitable modification, the efficiency in flame retarding PVC seems not to be so obvious by adopting the porous silica alone. Nowadays, a wealth of reports as mentioned in Chapter 2 have come out to put forward that tin element is one of the most proper candidates to replace antimony owing to its compounds exhibiting superactive performance as flame retardant in PVC. Qu et al. partially substituted Sb_2O_3 with different tin compounds and found the LOI of all the composites improved and smoke density rating decreased [4]. Wang et al. reported that

SnO₂ showed synergistic effect to Sb₂O₃ enhancing the LOI greatly in fPVC and concluded that SnO₂ had the probability to replace Sb₂O₃, at least partly [21]. Since porous silica is a good support and can be doped kinds of metals in its matrix, in view of the porous structure and fire retardant element, the integration of porous silica and tin is predicted to show high efficiency as flame retardant for flexible PVC.

In this chapter, hierarchical porous silica (HPS) was synthesized by template method and tin was introduced into HPS system directly by in-situ synthetic method. As Sn-O-Si bond existed in the as-synthesized product, thus it was named after TOS (Tin-Oxygen-Silicon). For reference, the thermal stability and fire behavior of flexible PVC composites containing 5 phr Sb₂O₃, SnO₂, HPS, or TOS were all investigated. Meanwhile, the tensile properties of the composites were also taken into consider. Based on the results obtained in the exploratory work, TOS was synthesized with an attempt to totally substitute Sb₂O₃.

5.2 Synthesis of HPS, TOS and preparation of flexible PVC composites

The synthesis of hierarchical porous silica adopted a promoted template method. In a typical run, EtOH and deionized water were mixed and the pH of solution was adjusted to 10.0 with the addition of ammonium hydroxide solution. Then CTAB was added with rapid stirring at room temperature. After a clear solution appeared, TEOS was added drop by drop slowly. The total system was kept stirring for 4 h at 50 °C. The molar ratio of EtOH: H₂O: CTAB: TEOS is 225: 675: 1: 0.225. Sediment was collected by pressure filtration and was dried at 80 °C overnight. The surfactant CTAB was removed by calcination in air at 540 °C for 6 h.

The grafting of tin on hierarchical porous silica adopted in-situ synthetic method. The initial step was similar as the preparation of HPS. After adding TEOS 5 min, a certain amount of tin (IV) chloride was added into the solution drop wise. Then the turbid solution continued to be stirred at 50 °C for 4 h. The obtained material was washed three times with deionized water and ethanol, and then the filtered product was dried overnight at 80 °C. Finally, the surfactant was eliminated by calcination in air at 540 °C for 6 h. Scheme 5-1 presents the schematic program of the proposed synthesis procedure of TOS.

Scheme 5-1: Illustration of preparation of cell-like mesoporous TOS.

The processing procedure of flexible PVC composites was similar as Chapter 4 mentioned previously. The flame retardants employed in this research comprised of 5 phr Sb_2O_3 , SnO_2 , HPS and TOS. Other components in flexible PVC composites were the same as before.

5.3 Structural characterization of flame retardant

In FT-IR spectra of synthesized sample (Figure 5-1), the bands at 1090 and 806 cm^{-1} for HPS, arising from the symmetric and asymmetric stretching vibration of the tetrahedral SiO_4 units, shifted to lower wave numbers as heteroatom Sn was introduced, while the bands at 1630 cm^{-1} corresponding to the surface Si-OH vibration [116, 117], and the bands at 460 cm^{-1} ascribing to the Si-O- bending vibration were unchangeable [118]. The same phenomena were observed for silica doped with Cu and Ti [119, 120], indicated a strong interaction between heteroatoms and silicon, e.g., Si-O-M bonds were formed. The reason was explained as follows:

The greater bond length of M-O than that of Si-O led to the decrease of the force constant (k) and the bigger atomic weight of tin caused the increase of the reduced mass (μ), hence the vibration frequencies calculated from the formula:

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

decreased [116]. Meanwhile, the emerged broad peak at 620 cm^{-1} of TOS was assigned to the vibration of Sn-O-Si structure [121, 122]. All the results suggested from FT-IR spectra that Sn atom successfully incorporated in the framework to form the structure of Si-O-Sn instead of depositing on the surface of HPS only.

Figure 5-1: FT-IR spectra of HPS and TOS.

To further verify the existence of Si-O-Sn bond in the as-synthesized sample, XPS analysis was performed and the resulting spectra are depicted in Figure 5-2. The Sn 3d XPS spectrum consisted of a doublet peak with binding energies of 496.6 eV for Sn 3d_{3/2} and 488.2 eV for Sn 3d_{5/2}, which are remarkably higher with respect to pure SnO₂, that are present at 495.1 eV and 486.7 eV, respectively [123]. This shift could be explained by the strong effect of Sn-O bond polarization in the Si-O-Sn bond [124, 125]. Meanwhile, three peaks observed in the O 1s XPS spectrum, one of low-intensity at 530.4 eV and another at 532.5 eV, are referred to SnO₂ and SiO₂, respectively. The rest peak at 533.1 eV resulted from the Si-O-Sn bond formed on the surface of product, in line with the previous reports [126-128].

Figure 5-2: Sn 3d and O 1s XPS spectra of TOS.

The XRD pattern of as-synthesized TOS was shown in Figure 5-3. The peaks located at $2\theta = 34^\circ$, 38° , 51° and 58° were ascribed to stannosilicate (SnSiO₄) with JCPDS file 00-020-1295,

implying the reaction happened between tin and HPS. The probable reaction equation was presented as follows:

The molecular formula of SnSiO_4 was:

Meanwhile, the peaks appeared at $2\theta = 27^\circ$, 39° and 54° were belonged to HPS (SiO_2) framework with JCPDS file 01-085-0798. And the peaks of oxidized tin (SnO_2) adsorbing on the surface of HPS were observed at $2\theta = 43^\circ$, 62° , 65° and 66° . It can be seen that the amount of adsorbed tin was lower than interacted tin based on the peak area. The result obtained from XRD pattern was in agreement with FT-IR that tin element has been successfully introduced into HPS system.

Figure 5-3: XRD pattern of as-synthesized TOS.

The morphology detection, microstructure identification and elemental analysis were carried out by FEGSEM and TEM coupled with EDX. The images and EDX spectrum were recorded in Figure 5-4 and Figure 5-5. The shape of HPS (Figure 5-4a) was regular spherical with the diameter less than 500 nm. After doping with tin element, the figure (Figure 5-4b) of TOS changed slightly. Due to the interaction between tin and silica backbone, the surface energy of the sample varied thereby adherence among individuals occurred. The outlines of the spheres became

cell-like but the diameter kept nearly the same. The EDX spectrum derived from FEGSEM clearly indicated that the product was composed of Si, Sn and O elements.

Figure 5-4: FEGSEM images of (a) HPS and (b) TOS, inset: EDX spectrum of TOS.

The morphology discerned in the low magnification TEM images (Figure 5-5a, c) was consistent with the results obtained from SEM images. The high magnification TEM images (Figure 5-5b, e) disclosed the disordered porous structure existing in both products with the pore diameter less than 10 nm. The ambiguity of pores seen from the center section was probably ascribed to high thickness of the samples and overlap of disordered pores while the porous structure was able to be observed more clearly from the broken part of TOS shown in Figure 5-5e. The elemental analysis affiliated to both SEM and TEM illustrated TOS consisted of silicon, tin and oxygen elements.

Figure 5-5: Low magnification TEM images of HPS (a) and TOS (d); High magnification TEM images of HPS (b) and TOS (e); Elemental analysis of HPS (c) and TOS (f).

The exact molar ratio of Sn to Si in the TOS was detected by several means including the quantitative analysis of XPS, EDX analysis of FEGSEM and TEM, and ICP-OES. The results were summarized in Table 5-1. The values of the ratio are very close and the molar ratio of Sn to Si in the sample is around 0.049 inferred by ICP-OES.

Table 5-1: Molar ratio of Sn to Si in the TOS detected by different methods.

Sample	XPS	EDX		ICP-OES
		FEGSEM	TEM	
TOS	0.071	0.058	0.043	0.049

The details about pores were further studied by nitrogen adsorption-desorption isotherms and pore size distribution shown in Figure 5-6. HPS showed type-I isotherms (Figure 5-6a) defined by IUPAC that attributed to microporous structure. Besides the micropores, mesopores were also existed in the matrix in terms of the pore size distribution (Figure 5-6b). The average pore size of HPS was 1.9 nm which was consistent with the isotherms, indicative of hierarchical pores existing in the HPS. In contrast, after grafting tin in HPS the nitrogen adsorption-desorption isotherms transformed into type-IV H2 isotherms, implying the disordered mesoporous structure of TOS. Because of the formation of Sn-O-Si bond, the average pore size of TOS increased to 3.8 nm according to the pore size distribution, however, the increase of pore size was not so obvious due to the adsorption of tin oxide on the surface and inner wall of HPS. Such behaviors provided the explanation for the shape of the desorption isotherm of TOS. Furthermore, the BET surface areas of HPS and TOS were 767.6 m²/g and 369.4 m²/g, respectively. The decrease of specific surface area provided the evidence that the introduction of tin influenced the structure of HPS. Comparatively, commercially available Sb₂O₃ and SnO₂ possess much lower specific surface area of 15 m²/g and 24 m²/g correspondingly, ascribing to the lack of porosity in the structure. In summary, the as-synthesized novel flame retardant has high specific surface area and mesoporous architecture.

Figure 5-6: N₂ sorption isotherms (a) and pore size distribution (b) of HPS and TOS.

5.4 Thermal stability of flexible PVC composites

Thermal stability of flexible PVC composites was evaluated by TGA. TG and DTG curves of fPVC composites under nitrogen atmosphere were displayed in Figure 5-7 and the results were tabulated in Table 5-2. All of the samples followed a two-stage degradation process based on the TG and DTG profiles corresponding to the dehydrochlorination of the polymer, resulting in the formation of conjugated double bonds that break during the second step [44, 50]. The main degradation step in the temperature range of 200-350 °C could be attributed to the emission of hydrogen chloride [8, 52, 129].

Figure 5-7: TGA curves of flexible PVC composites.

Combining the TGA curves and onset decomposition temperature ($T_{5\%}$), the composite containing SnO₂ decomposed in advance. This finding is illustrated with the assumption that tin might react with the HCl released from PVC to form tin chloride which is a strong Lewis acid and it might catalyze the dehydrochlorination and promote the early crosslinking to the PVC compound. This tin-based catalyst was considered to relate its solid acid nature as non-transition

metal showing a tendency to accept an electron pair by the expanded d orbital. The things changed better when HPS was chosen as the carrier for the tin element. The $T_{5\%}$ increased slightly from 251 °C to 258 °C. Additionally from DTG profiles and data, the temperature at the maximum rate of weight loss at the first stage of decomposition (T_{max1}) of fPVC/TOS was almost the same as that of fPVC and fPVC/Sb₂O₃ while the temperatures at the maximum rate of weight loss at the second stage of decomposition (T_{max2}) of fPVC/TOS was the highest among all the composites. These results revealed that the stability of the residue was enhanced through the reaction between tin compounds and char layer [36]. Moreover, the maximum rate of the weight loss at the first stage (V_{max1}) belonged to fPVC/TOS decreased compared with fPVC and fPVC/Sb₂O₃, suggesting that TOS might form tortuous path as a physical barrier to inhibit the mass loss during the thermal degradation process. With adding Sb₂O₃ the residue at 780 °C was 15.5 wt.% which was similar as that of fPVC, caused by that Sb₂O₃ acted its role in gas phase and became SbCl₃ (g) escaping from the system. However, in the presence of HPS, the residue increased to 19.5 wt.% which was probably because silica generated a compact protective layer to block the combustible gases and heat release, meanwhile these combustible gases had the potential to be adsorbed in the porous backbone and remained in the residual. Since tin element played its role in condensed phase aforementioned, fPVC/TOS and fPVC/SnO₂ also owned relatively high amount of residue. The load of tin on the HPS endowed better thermal stability to fPVC composite compared with SnO₂ while this tin-loaded HPS retained higher residue to fPVC composite in comparison to Sb₂O₃. The lower mass loss rate and the higher char residue of fPVC/TOS composite predict better flame retardancy.

Table 5-2: TGA and DTG results of flexible PVC composites.

Sample	$T_{5\%}$ (°C)	T_{max1} (°C)	T_{max2} (°C)	V_{max1} (%/ °C)	V_{max2} (%/ °C)	Residue at 780 °C (wt.%)
fPVC	271	289	465	1.6	0.4	15.4
fPVC/Sb ₂ O ₃	277	291	463	2.0	0.3	15.5
fPVC/HPS	273	292	467	1.6	0.3	19.5
fPVC/SnO ₂	251	286	470	1.4	0.3	18.8
fPVC/TOS	258	291	477	1.4	0.3	18.7

5.5 Fire behavior of flexible PVC composites

LOI provides important information to determine the flammability of polymeric materials. LOI results of fPVC composites were shown in Figure 5-8. The LOI value of fPVC was only 25.0% due to the addition of inflammable plasticizer. When 5 phr Sb_2O_3 was added, the LOI value improved strikingly to 34.5%, approaching nearly 10 units. Sb_2O_3 indeed showed quite high efficiency in flame retarding halogen-containing polymer. SnO_2 and HPS also increased the LOI value, but they did not attain the same level as Sb_2O_3 and TOS. After assembling tin into silica system, the flame retardancy reflected by LOI value improved a lot and became extremely close to Sb_2O_3 . Such modification resulted in better performance for TOS treated composite in LOI test. The inset in Figure 5-8 revealed a crown-like continuous and robust char on the top of fPVC/TOS sample sheet after LOI test conducive to inhibit the flame propagation. It seems that SnO_2 should have higher flame retardancy than TOS because of high mass fraction of tin element in chemical formula to help form the char residue, but the results are opposite. It is probably because SnO_2 was a commercial product with a low specific surface area, therefore its dispersion in polymer matrix and interaction with polymer chain were inferior to the synthesized TOS. Relying on the high specific area and porous structure, the tin element containing in TOS interacted with the polymer sufficiently. Moreover, the LOI results also provided the evidence that synergistic effect existed between loaded tin and silica carrier so as to improve the LOI value with respect to adding them alone.

Figure 5-8: LOI results of flexible PVC composites.

Vertical burning test (UL-94) is another important test to check the fire behavior of the polymeric composites. As far as we know, the UL-94 test was always neglected for fPVC

composites since the differences between different sample sheets were not so significant because of the intrinsic flame retardancy of fPVC. Actually, based on the conventional run, even the pristine fPVC sample could pass V-0 rating without any dripping happened. Thus in this work, the thicknesses of the sample sheets were decreased from conventional 3.2 mm to 0.6 mm in order to make the difference be readily observed. Herein fPVC, fPVC/Sb₂O₃ and fPVC/TOS were chosen to implement UL-94 test. The videos of UL-94 test for each sample are presented in the supporting information. During the test, fPVC without any addition of flame retardant burnt quite fast with dripping happened and could not be self-extinguished. Only the first ignition the sample sheet was nearly exhausted which meant the level for fPVC sample was no rating. In the presence of Sb₂O₃, the sample sheet burnt much more slowly and V-0 rating was reached. However, the flame was not extinguished immediately after the removal of the burner during the second ignition. Things changed better for fPVC/TOS sample which reached a V-0 rating accompanied with no dripping happened. The SEM image of char layers after test was presented in Figure 5-9, shown that the generated char was compact with several flakes embedded in the surface rendering the char layer continuous integrity.

Figure 5-9: SEM image of char belonged to fPVC/TOS sample after UL-94 test.

The dripping of fPVC in vertical burning test might be owing to the breakable char layer formed during the combustion, which was not tough enough to make it as a whole part throughout. The synergistic effects of porous silica and tin were proposed to be the possible reason for improving the properties of PVC materials. It was believed that HPS as microcapsules are able to be obtained with a good homogeneity and dispersion in PVC matrix [130]. After loaded with tin element, tin-based Lewis acid promoted char forming to generate barriers thereby blocking the

release of combustible gases and transfer of heat energy to the PVC bulk in order to protect the polymer underneath. Most importantly, tin compounds were assumed to be able to react with the char residue and enhance its stability concluded by Qu et al. [36]. At the same time, the hierarchical porous carrier with large surface area might make the path length longer that the transfer of oxygen and combustible gases was inhibited, leading to retarded heat release. These influences resulted in the improved flame retardancy and non-dripping phenomenon for the fPVC/TOS sample. In consequence, the sample treated with TOS discerned nearly the same level as fPVC containing Sb_2O_3 in LOI test and passed UL-94 test with a satisfactory result.

5.6 Tensile property of flexible PVC composites

Due to the addition of flame retardants, mechanical property such as tensile property may be hugely deteriorated and the practical application of the flame retardants was discounted. Therefore, mechanical property is non-neglectable parameter to determine the influence caused by the additives to the polymer systems. For fPVC composites, tensile property is one of the most important mechanical property thereby the tensile tests for fPVC composites were accomplished and the experimental tensile test curves were shown in Figure 5-10. The results were listed in Table 5-3. The pristine fPVC showed relatively high elongation at break ($75 \pm 4\%$) depending on the effects of the plasticizers. After adding Sb_2O_3 , the tensile strength improved a little from 11.8 ± 1 to 13.8 ± 1 MPa, but the Young modulus possessed a remarkable increase. Since Sb_2O_3 is an inorganic commercial product, it was not able to be compatible with the polymer matrix due to the large grain size and low surface area. Hence the flexible property of the composite was ruined and the elongation at break was decreased to only 48%. The commercial SnO_2 loaded composite possessed similar performance while the parameters improved slightly. Unlike the Sb_2O_3 and SnO_2 , TOS imparted fPVC composite much better tensile property than that of untreated sample. The tensile strength was promoted from 11.8 ± 1 to 17.6 ± 1 MPa by 49% compared with the pristine one and the elongation at break reached 104%. The strong interfacial interaction between TOS and fPVC matrix caused by the large BET surface area and multitudinous porosity of TOS led to much higher tensile strength. This reinforcing effect on mechanical property imparted by the addition of little amount of inorganic nanoparticles was already confirmed by previous reports [131, 132]. Although as-synthesized HPS blended sample was conferred with the highest elongation at break, the tensile strength was much lower than that of fPVC/TOS composite.

Notably, the Young modulus was increased about 30 MPa which meant the addition of TOS did not harm the flexible attribute of the composite so much.

Figure 5-10: Tensile stress-strain curves of flexible PVC composites.

The enhancement in the mechanical property of fPVC composites endowed by TOS was also ascribed to the contribution of the silica carrier. Zhu et al. reported that silica helped enhance the mechanical properties of fPVC composites [133, 134]. In one word, the integration of tin and porous silica not only improved the flame retardancy of fPVC composite but also enhanced the tensile property in comparison to Sb_2O_3 . As a consequence, this novel synthesized TOS has been provided with the meaning of practical application in industry.

Table 5-3: Tensile properties of flexible PVC composites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
fPVC	11.8 ± 1	75 ± 4	138 ± 4
fPVC/ Sb_2O_3	13.8 ± 1	48 ± 3	216 ± 4
fPVC/HPS	14.6 ± 1	120 ± 4	124 ± 3
fPVC/ SnO_2	15.9 ± 1	74 ± 3	247 ± 4
fPVC/TOS	17.6 ± 1	104 ± 4	168 ± 3

Furthermore, during the tensile test a digital image correlation (DIC) technique was conducted to capture the state of strain distribution on the samples. The states of stain distribution for fPVC/ Sb_2O_3 and fPVC/TOS were represented in Figure 5-11. The images were captured at 22 s since the beginning of the tensile test. Figure 5-11b showed high deformation (the red part) of fPVC/TOS propagated in the center part of the sample and the distribution of deformation was

extremely uniform while fPVC/Sb₂O₃ was not which supplied the evidence that the fPVC containing TOS had higher homogeneity in strain distribution than Sb₂O₃ treated fPVC sample. The observed poorer distribution of stain for the sample containing Sb₂O₃ proved nonuniform distribution of the additive in the fPVC system. Considering the data of tensile test shown above, more homogeneous distribution of the strain field in modified fPVC sample resulted in higher mechanical property.

Figure 5-11: Digital image correlations of fPVC/Sb₂O₃ (a) and fPVC/TOS (b).

5.7 Summary

In this work, tin element was successfully incorporated into hierarchical porous silica system by a facile in-situ synthesis method. The composition and structure of as-synthesized product were investigated by all-sided characterization. This novel flame retardant TOS presented high efficiency in improving the flame retardancy and mechanical property of fPVC composite. TGA showed that TOS performed better than SnO₂ in thermal stabilizing the composite. The fPVC/TOS reached similar LOI value (34.1%) as fPVC/Sb₂O₃ and presented better fire behavior (V-0 without dripping) in UL-94 test. The mesoporous flame retardant was also beneficial for improving tensile properties of fPVC composites, especially increasing the tensile strength by 49%. Therefore, TOS has great potential to totally replace Sb₂O₃ as novel flame retardant in flexible PVC composites. However, the cone calorimeter test was further carried out and the heat release rate of fPVC treated with TOS was found to be increased compared with that of pristine fPVC. In other words, fPVC/TOS sample showed good performance in UL-94 and LOI tests, but it failed in decreasing the heat release rate upon the cone calorimeter test. Therefore, in order to develop a flame retardant for fPVC with the capability of rivaling Sb₂O₃ in UL-94, LOI and cone calorimeter tests,

more efficient components should be chosen. In the next chapter, nanoporous $\text{SnO}_2/\text{Fe}_2\text{O}_3$ hybrid was synthesized and incorporated into fPVC to totally replace Sb_2O_3 , anticipating to show better performance compared with TOS.

CHAPTER 6

SYNTHESIS OF NANOPOROUS $\text{SnO}_2\text{@Fe}_2\text{O}_3$ HYBRID AND ITS USE AS A SUBSTITUTE OF ANTIMONY TRIOXIDE IN FLAME RETARDANT FLEXIBLE POLY(VINYL CHLORIDE)

“If I have a thousand ideas and only one turns out to be good, I am satisfied.”

-Alfred Nobel

6.1 Introduction

In recent years, in view of the augmenting fire safety consideration, substantial particular flame retardants were developed to improve the fire resistance of polymers. Compared to the organic and micrometric additives, it is worth noting that polymer nanocomposite technology is demonstrated to be an effective approach because incorporating only a low loading of inorganic nanofillers into polymers may significantly improve the fire resistance, thermal property as well as mechanical property [135]. Meanwhile, nanomaterials specifically those with multicomponent functional properties have been the subject of extensive research in contrast with their single-component compounds because the synergistic interactions between each component strongly affect the properties. Therefore, deliberate tailoring of the nanostructured hybrid flame retardant and optimization of the hybrid flame retardant structure are under broad investigation. It is well known that the chemical compositions, polymorphs, and morphologies-such as crystalline sizes, shapes, orientations, and assemblies-which are related to the preparation methodology, would have a significant influence on the performances of as-prepared nanocrystals [136, 137]. In

order to develop functional flame-retardant materials with improved performance, the rational design and preparation of nanostructured materials has been continuously pursued.

Hybrid nanomaterials are constantly attracting more and more attention, since these nanoparticles have emerged at the frontier in material chemistry. In light of distinctive features of the different constituents employed together, hybrid multidimensional nanoparticles are kind of highly functional materials with modified properties [138]. However, paucity of aforesaid nanomaterials with intriguing structures as flame retardants were available, albeit myriad of other advanced hybrid nanomaterials such as carbon nanotube [139], graphene [140] and layered double hydroxide [141] were already regarded as high-efficiency flame retardant in polymer nanocomposites, namely the route toward hybrid multidimensional nanostructures deployed on flame retardant has been rarely reported to my certain knowledge. Based on this background, more efforts should be made to consummate the related area and fill this enormous vacancy.

Over the last two decades synthesis of oxide nanomaterials with fascinating shapes and sizes has been an active area of research, because of their shape- and size- dependent physical, chemical, electronic, optical and catalytic properties [142, 143]. In particular, tin oxide (SnO_2) nanomaterials have attracted considerable attention due to their wide applications in lithium-ion batteries, gas sensors, sensitized solar cells, and catalysts [144]. The versatile SnO_2 also gives rise to the interests as a novel flame retardant for polymeric materials, especially flexible poly(vinyl chloride) composite (fPVC) which is flammability caused by the addition of plasticizers, because tin chloride, a strong Lewis acid, generated from the reaction between SnO_2 and HCl leads to the early cross-linking and char formation of PVC by catalytic effect [36, 96]. Based on the previous research, tin-doped silica exhibited excellent performance in flame retardant fPVC composite [145]. Unlike the highly toxic organotin, inorganic tin compounds have already been proved to be nontoxic or quite low toxic. Yet the main problem for SnO_2 is the relatively low efficiency in flame retardant fPVC in comparison with the superior synergist effect between Sb_2O_3 and halogen. To improve this situation, modification on SnO_2 has to be carried out. The means to modify the inorganic particles with the intention of reinforcing the flame retardant of the counterpart polymer composite are divided as follows: minimization of the particle size, generation of pores or channels, or combination of other materials. In other words, the modification dedicates to enlargement of specific surface area, prolongation of path length or emergence of synergist effect.

In this work, $\alpha\text{-Fe}_2\text{O}_3$ was subtly adopted to construct a hybrid nanostructure with SnO_2 nanorod assemblies encapsulated by $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles since $\alpha\text{-Fe}_2\text{O}_3$ already showed outstanding synergistic effect with other flame retardants [146-148]. And $\alpha\text{-Fe}_2\text{O}_3$ was extremely well-known for its excellent smoke suppression effect in PVC system, while the smoke hazard of PVC during combustion was valued most [34, 149]. $\alpha\text{-Fe}_2\text{O}_3$ was also reported to be good at HCl fixation, so it might reduce the damaging and corrosive HCl gas evolved from fPVC during combustion [42, 150]. As a result, all the above-mentioned purposes are able to be achieved simultaneously with extra profits as well. For clarity, the novel flame retardant was designated as $\text{SnO}_2\text{@Fe}_2\text{O}_3$. It can be anticipated that with this exquisite structure, the thermal stability and flame retardant of fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ nanocomposite will be enhanced, resulting in a totally Sb_2O_3 -free flame retardant fPVC material.

Herein, nanoporous $\text{SnO}_2\text{@Fe}_2\text{O}_3$ hybrid multidimensional nanostructure was synthesized in a large scale via a facile and fast one-pot reaction for the first time. The composition and structure of as-synthesized product were clearly clarified through multiple characterizations. Notably, such modification on self-assembly nanoparticles is conducive to the formation of apertures in the system which might shed light on the fresh way of engineering the porous materials. The detailed and in-depth exploration about thermal property, flame retardancy and mechanical properties of $\text{SnO}_2\text{@Fe}_2\text{O}_3$ treated fPVC nanocomposite were conducted to testify the high performance of the hybrid material. Hopefully, this eventful work is committed to prepare a substitute of Sb_2O_3 in flexible PVC, not only performing well in LOI but also decreasing the heat release rate in cone calorimeter test.

6.2 Synthesis of $\text{SnO}_2\text{@Fe}_2\text{O}_3$ hybrid and preparation of flexible PVC composites

Briefly, 0.05 mol $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was firstly solved in 500 mL three-necked flask filled with 200 mL deionized water and ethanol at volume ratio 1:3 followed by adding 3.6 mmol citric acid and 1.7 mmol SDBS under vigorous stirring at 60 °C in a water bath. Soon afterwards the solution became marginally turbid indicating hydrolysis of the precursor and initial formation of nanoparticles. Subsequently, $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution (20 mL, 5M) was introduced dropwise into the solution at the speed of 2 mL/min. Then the solution with the milk white color was stirred for 1 h and sodium hydroxide solution (4 g NaOH, 20 mL H_2O) was dropped in gradually. Later, 0.02 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ dissolved in 20 mL H_2O was transferred into the flask drop by drop at the same

speed mentioned above. The khaki homogeneous solution was allowed to continue stirring for another 2 h thereafter maintained still for 1 h. The precipitate was collected by centrifugation at 5000 rpm with being rinsed by distilled water and ethanol several times. Eventually, the product was dried completely in vacuum oven at 70 °C overnight and annealed in muffle furnace at 700 °C at a rate of 2 °C min⁻¹ to oxidize and remove the organic impurities. For reference, α -Fe₂O₃ synthesized by precipitation of iron (III) chloride hexahydrate with sodium hydroxide and SnO₂ without α -Fe₂O₃ doping were also prepared.

The preparation of flexible PVC composites was the same as the previous chapters. The addition amount of flame retardants employed in this work was also 5 phr (3.2 wt.%). The flame retardants were Sb₂O₃, c-SnO₂, SnO₂, Fe₂O₃, Fe₂O₃-SnO₂ (physical mixture with the molar ratio Fe₂O₃: SnO₂ 1:5) and SnO₂@Fe₂O₃.

6.3 Structural characterization of flame retardant

The phase and composition of the final product was identified by X-ray diffraction and the pattern was shown in Figure 6-1. The broad diffraction peaks with red mark in the XRD pattern are in accordance with the tetragonal rutile SnO₂ structure (JCPDS No. 41-1445, $a=4.74$ Å, and $c=3.19$ Å), while the crystal phase of the shell marked in blue can be indexed as the hexagonal structure of α -Fe₂O₃ (JCPDS No. 33-0664, $a=5.04$ Å, and $c=13.77$ Å). A gradual shift of the diffraction maxima around 0.6° corresponding to SnO₂ standard PDF card toward larger angles with shell growth confirmed the formation of coating nanostructures [151]. This shift to higher angles in the structure is due to a smaller lattice constant caused by the compression of α -Fe₂O₃ sheath growth for SnO₂@Fe₂O₃ nanoparticles compared with bare SnO₂. Detailed analysis of the peak broadening of the (110) reflection ascribed to SnO₂ using the Scherrer equation indicates an average crystallite size ~ 10 nm, suggesting that these polycrystalline SnO₂ particles are composed of nanocrystals subunits. Correlated to the measured average particle size ~ 396.1 nm graphed in the inset, the wide difference revealed that the core was established by the self-assembly of SnO₂ nanoparticles. In addition, no other compounds of tin and iron were detected by XRD, demonstrating that the final product was assigned to a hybrid of SnO₂ and α -Fe₂O₃.

Figure 6-1: XRD pattern of as-synthesized hybrid, inset: particle size distribution.

The surface morphology and heteronanostructure were investigated by comprehensive electron microscopy. Figure 6-2a was the SEM image of SnO_2 precursor without modification. The sub-micron SnO_2 consisted of spherical- or ellipsoidal-like particles with a uniform diameter ca. 300 nm. The inset presented the digital photo of the sample for the single particle. It can be seen that the synthesized SnO_2 was faint yellow fine powder. After coating by $\alpha\text{-Fe}_2O_3$, the color of sample transformed into reddish brown according to the digital photo and the particle size enlarged to some extent. The elemental analysis conducted by EDX in the center of the particle via point detection affirmed the composition of the product involved tin, iron and oxygen without any impurities (Cr was the spinning coating). It is worth noting that the weight ratio of Sn to Fe remained at 5:1, which is consistent with the feed ratio of tin and iron sources. The result was further evidenced by ICP and the similar ratio (5.1:1) was obtained.

Figure 6-2: (a) SEM and digital photo (inset) of SnO_2 ; (b) SEM and digital photo (inset) of $\text{SnO}_2@Fe_2O_3$; (c) Elemental analysis of $\text{SnO}_2@Fe_2O_3$.

The TEM image of SnO_2 encapsulated by $\alpha\text{-Fe}_2\text{O}_3$ was manifested in Figure 6-3. It is found that SnO_2 nanorod assemblies were embedded in the $\alpha\text{-Fe}_2\text{O}_3$ sheath. The grain size of the entire particle was approximately 400 nm in agreement with the result obtained from particle size distribution. The contrast of inner nanorod ascribed to SnO_2 with average atomic number (29) is darker than the exterior Fe_2O_3 sheath whose average atomic number is much smaller (17). Epitaxial growing of the dense hematite nanocrystal on the surface of SnO_2 core to form an encapsulation architecture, which might be ascribed to the low interfacial lattice mismatch between SnO_2 and $\alpha\text{-Fe}_2\text{O}_3$ [152]. The rough surface was probably accomplished by Ostwald ripening, i. e. $\alpha\text{-Fe}_2\text{O}_3$ crystal coarsened on the surface of SnO_2 aggregates functionalized as the nuclei. In order to get deeper insight into the microstructure of the multidimensional nanocomposite, enlarged TEM observation of the red square area was further conducted. From Figure 6-3b, agglomeration of plentiful nanorods with disordered gaps in the interstice was disclosed. The diameter of monocrystal nanorod was around 10 nm, which was in agreement with the grain size calculated by XRD aforementioned. Around the nanorods, the $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles envelop endowed a loose interior texture, heralding the formation of the porosity. The high-resolution TEM (HRTEM) image (Figure 6-3b, blue square region) shown in Figure 6-3c revealed lattice fringe spacing of 0.368 nm and 0.335 nm, corresponding to the (012) and (110) lattice planes of $\alpha\text{-Fe}_2\text{O}_3$ and rutile SnO_2 , respectively, in line with XRD analysis. During the precipitation, intermediate product transformed into cassiterite nanorod which undergo anisotropic crystal growth along the [001] direction, since the (001) plane in the rutile structure has the highest surface energy [153]. Besides, the selected-area electron diffraction (SAED) pattern (Figure 6-3d) clearly indicated the polycrystalline texture of the product composed of $\alpha\text{-Fe}_2\text{O}_3$ and SnO_2 . The elemental composition characterized by EDX showed the Sn/Fe weight ratio was also close to the theoretical value 5:1. In addition, the EDX mapping images based on two individual rods encapsulated by particles obviously discerned Sn element only existing in the rods while Fe and O elements dispersing in the surroundings. The line scan across a single rod shown in Figure 6-3g firmly confirmed the core/shell structure that SnO_2 nanorod assemblies were surrounded by $\alpha\text{-Fe}_2\text{O}_3$.

Figure 6-3: (a) TEM image; (b) Enlarged TEM image; (c) HRTEM image; (d) SAED pattern; (e) EDX spectra; (f) Line scan elemental analysis of as-synthesized $\text{SnO}_2@\text{Fe}_2\text{O}_3$; (g) HAADF-STEM image and elemental mapping results (Scale bars, 30 nm).

For the sake of well understanding the existence of porous structure, nitrogen sorption measurements were performed and the results were depicted in Figure 6-4. Due to the lack of enough porogen and ultrafast collapse of framework under high temperature, SnO_2 without protective layer outside possessed non-porosity structure as shown in Figure 6-4a. Meanwhile, the BET and BJH curves demonstrated a very small specific surface area for SnO_2 of only $7.44 \text{ m}^2/\text{g}$. The similar things also happened in the prepared $\alpha\text{-Fe}_2\text{O}_3$ whose BET surface area is $8.23 \text{ m}^2/\text{g}$. Commercially available c- SnO_2 possessed even lower surface area of $5.89 \text{ m}^2/\text{g}$ because of the large particle size. Oppositely, the formation of hematite shell circumvented the crash and facilitated the development of porosity with a large BET surface. At low pressure stage the curve

of $\text{SnO}_2\text{@Fe}_2\text{O}_3$ kept adjoining with X-axis along with the tail end in a conspicuous uptrend attributed the isotherms to well-defined type-III, H_3 hysteresis loop followed IUPAC principles. The core-shell microspheres exhibited hysteresis loop at high relative pressure, which is probably due to textural porosity formed by the stacking of nanoparticles [154]. Based on BJH method and desorption branch of the nitrogen isotherm, pore size distribution was calculated and the corresponding result was portrayed in the inset of Figure 6-4b. The BJH bimodal curve exhibited that the sample had hierarchical pores with size distributions ranging from 1 to 100 nm divided into mesoporous scope and macroporous scope. Related to the peak area and TEM result, the mesopores centered at around 2.1 nm were referred to the gaps among the rod assemblies, while the larger mesopores and macropores were belong to the sheath section. This means the nanoparticles within the spongy nanostructure are not glued together but are accessible from the outside via the exterior secondary mesopore system. Furthermore, the BET surface area of the sample was measured up to a relatively high value of $77.31 \text{ m}^2/\text{g}$. And the numerous existing macropores contributed to a considerably large pore volume of $0.506 \text{ cm}^3/\text{g}$.

Figure 6-4: N_2 adsorption-desorption isotherms of (a) SnO_2 and (b) $\text{SnO}_2\text{@Fe}_2\text{O}_3$. Inset: pore size distribution based on the desorption branch.

Accordingly, a tentative mechanism for the formation of hierarchical porous $\text{SnO}_2\text{@Fe}_2\text{O}_3$ heteronanostructure was proposed in Scheme 6-1. At first, rod-like nascent nanoparticles were generated by hydrolysis-condensation process of tin precursor directed by the surfactant. Within a short time, the self-assembly nanoparticles agglomerated into bigger spherical particles with the

entrapment of in situ produced ammonium chloride (NH_4Cl) in the slits among the nanoparticles. When the iron source was introduced into the hot alkaline solution, a homogeneous $\text{Fe}(\text{OH})_3$ colloid with ultrafine nanoparticles were formed, followed by the decomposition and deposition on the surface of nuclear tin-intermediate aggregates. As the ripening process went on, the shell grew increasingly with the gradual depletion of ferric hydroxide small particles in the circumstance thereby creating a dense coating on the nuclei. During the rinse step, the internal ammonium chloride could not be removed as a result of the shielding effect of compact shell. Finally, hierarchical porous $\text{SnO}_2@\text{Fe}_2\text{O}_3$ hybrid material with preserved morphology resulted from removal of the byproduct NH_4Cl (eq 1) and degradation of hydroxides (eq 2), both supposed as the porogens, by subsequent calcination.

The tailored shell seemingly alleviated the speed of gas evolution so as to avoid the collapse of the matrix.

Scheme 6-1: Schematic illustration of a tentative mechanism for the formation of porous $\text{SnO}_2@\text{Fe}_2\text{O}_3$ heteronanostructure polycrystal.

Meantime, the microstructure of the fracture surface of fPVC/ $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocomposite was shown in Figure 6-5. The surface of the nanocomposite was extremely smooth and no obvious particles were observed on the fracture surface after the addition of the nanoparticles, which indicated a strong interaction between the nanoparticles and the PVC matrix. Additionally, the elemental analysis carried out by EDX included iron and tin elements confirming the existence of embedded hybrid product. The EDX measurements on different spots of the samples gave the same patterns, which proved the good homogeneity of the samples. Indeed it is expected that particle sizes in the nanoregime and specific crystal morphologies enhance the performance and allow a fine-tuning of the properties.

Figure 6-5: (a) SEM image of the fracture surface of fPVC/SnO₂@Fe₂O₃ nanocomposite; (b) Elemental analysis of fPVC/SnO₂@Fe₂O₃ nanocomposite.

6.4 Thermal stability of flexible PVC composites

TGA may provide the information about the thermal degradation behaviors of the nanocomposites. Thus, the TGA of fPVC blended with different additives were implemented and the results with DTG were presented in Figure 6-6. All the detailed data were tabulated in Table 6-1. The TGA curves of all the fPVC nanocomposites exhibited a two-stage thermal degradation process during raising temperature. The first degradation at about 270-320 °C was corresponding to the elimination of HCl, while the second stage at about 440-480 °C was attributed to cross-linking containing the C=C bond. The process of thermal decomposition of polyenes included cyclization and splitting of chains [155]. From the TGA curves, the temperature at 5 % mass loss ($T_{5\%}$) regarded as the onset decomposition temperature and the residual were studied. In the presence of Sb_2O_3 , the thermal stability of composite improved accompanied with the unchanged residual, indicating the role Sb_2O_3 acted in gas phase without any contribution to the char formation. In contrast, the addition of c-SnO₂ and as-synthesized SnO₂ increased residual amount significantly with the cost of the degradation of fPVC composites in advance, since tin chloride as a strong Lewis acid generated from the reaction between SnO₂ and HCl catalyzed the dehydrochlorination of fPVC promoting the HCl gas liberation, early cross linking and char formation. In addition, localized evaporation of tin chloride in terms of its low boiling point (114.1 °C) might be another reason for the rapid mass loss. The smaller size and higher surface area of prepared SnO₂ than c-SnO₂ benefited the more remarkable performance in the composite: lower onset decomposition temperature and more residual. Incorporating Fe₂O₃ realized earlier decomposition of the composite and augmented the residual due to its well-known ability of crosslinks and char

formation [146, 148, 156]. Fe_2O_3 was very effective in the fixation of evolved HCl thereby the autocatalytic effect of HCl on further dehydrochlorination was enhanced by the catalytic effect of the generated Lewis acid, improving the yield of the char. Meanwhile, FeCl_3 owned relatively high boiling point (375 °C) in favor of retaining in the system for a long time. Compared to the mixture of SnO_2 and Fe_2O_3 treated fPVC composite, the hybrid brought forward the onset decomposition temperature to 251 °C owing to the synergistic catalytic effects of the binary Lewis acids. Furthermore, the residual of fPVC/ $\text{SnO}_2@\text{Fe}_2\text{O}_3$ was the most among all the composites illustrating the synergistic char-forming effect between SnO_2 and Fe_2O_3 , while the composite containing the physical mixture had the fewer residual due to the lack of special nanostructures. From DTG curves, the maximum weight-loss temperature at first stage (T_{max1}) and second stage (T_{max2}) were investigated. At the first stage, the introduction of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ mitigated the speed of mass loss reflected from the intensity of the y axis. And at the second stage, the hybrid material added composite had the highest T_{max2} because generated metal chlorides accelerated the char formation thereafter tin chloride emerged to promote the char stability. In summary, the incorporation of porous $\text{SnO}_2@\text{Fe}_2\text{O}_3$ hybrid with large surface area and pore volume facilitated the char formation and improved the char stability of fPVC composite.

Figure 6-6: (a) TGA and (b) DTG curves of fPVC and its blends under nitrogen atmosphere.

Table 6-1: TGA and DTG data of fPVC nanocomposites.

Sample	T _{5%} (°C)	T _{max1} (°C)	T _{max2} (°C)	Residue at 700°C (wt.%)
fPVC	271	289	465	15.4
fPVC/Sb ₂ O ₃	277	291	463	15.5
fPVC/c-SnO ₂	253	286	468	18.8
fPVC/SnO ₂	240	281	471	20.1
fPVC/Fe ₂ O ₃	261	288	467	19.2
fPVC/SnO ₂ -Fe ₂ O ₃	251	286	472	19.6
fPVC/SnO ₂ @Fe ₂ O ₃	247	281	482	21.1

6.5 Flame retardancy of flexible PVC composites

LOI and cone calorimeter were carried out to evaluate the flame retardancy of fPVC composites and all the data were listed in Table 6-2. Neat fPVC was a flammable polymeric material with the LOI value as 25%. When Sb₂O₃ was loaded into the polymer, the LOI increased remarkably to 34.5%, nearly 10% higher compared to the unloaded one proving the good flame retardancy of antimony compounds in halogen contained polymer. Although the addition of c-SnO₂, SnO₂ and Fe₂O₃ raised the LOI value as well, the efficiency seemed to be lower than Sb₂O₃. The as-synthesized SnO₂ treated sample showed the highest LOI value among these three additives because of its fine size and catalytic effect of dehydrochlorination. In contrast to the individual addition, the combination of SnO₂ and Fe₂O₃ produced striking outcome that even the physical mixture imparted the similar LOI value as Sb₂O₃ incorporated sample to the composite displaying notable synergistic effect between the two oxides. Moreover, the presence of hybrid improved the LOI value to 36.5%, much better than the sample treated with Sb₂O₃. In addition to the synergistic effect of char formation, multiple hierarchical porosity and high specific surface area of SnO₂@Fe₂O₃ afforded the high efficiency of promoting the LOI value. It was noteworthy that brownish substance appeared on the top of the char layer of the iron involved samples observed during burning which ascribed to the formation of iron compounds.

In the cone calorimeter test, several primary parameters were taken into consideration, namely time to ignition, heat release rate, peak of HRR, total heat release, total smoke production and char

residue. Specifically, the HCl gas evolved from fPVC during combustion was collected by sodium bicarbonate solution and the Cl^- concentration was measured to make a comparison of the HCl amount among the composites. For the pristine fPVC composite, it cost 20 ± 1 s to be ignited, indicative of its tinder property. The effective capture of radicals in gas phase by Sb_2O_3 delayed the TTI of the composite to 25 ± 0 s, while the presence of Fe_2O_3 in consequence of HCl fastening to form acid catalyst postponed ignition time to 28 ± 0 s. The additive inherited this ability and bestowed 26 ± 1 s TTI to the composite. Figure 6-7 presented the HRR, THR and TSP plots as a function of time for all the fPVC composites. In Figure 6-7a, along with the start of the combustion a sharp peak appeared in a short time announcing that fPVC composites burned fiercely at the initial step. The Sb_2O_3 helped the composite decreased PHRR slightly from 218 ± 9 to 192 ± 3 kW/m^2 compared with that of neat fPVC composite, while the PHRR value of the composite treated with as-synthesized SnO_2 was reduced strikingly to 169 ± 3 kW/m^2 as a result of the catalytic effect that promoted early crosslinks and char formation so as to reduce the heat transfer between the heat source and polymer surface [157]. However, the c- SnO_2 behaved badly in PHRR reduction probably due to its uneven dispersion in polymer matrix caused by the large size. Besides the catalytic effect of SnO_2 to improve the char formation, tin compounds could react with the char layer to enhance the stability [96], therefore these unique properties conferred higher efficiency in relieving the PHRR value to SnO_2 than Fe_2O_3 . The incorporation of $\text{SnO}_2\text{@Fe}_2\text{O}_3$ decreased the PHRR value significantly to 148 ± 2 kW/m^2 by 32.1% compared with the neat one, because of the synergistic effect of char formation between the hybrid materials and the prolonged pathway for the transfer of oxygen and combustible volatiles caused by the porosity, leading to retarded heat release. Correspondingly, the THR values shown in Figure 6-7b possessed the similar trend as the PHRR values that the composite containing $\text{SnO}_2\text{@Fe}_2\text{O}_3$ reduced the value from 81 ± 4 to 56 ± 3 MJ/m^2 . The HRR and THR plots of fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ were much lower than the others indicating the mildest burning behavior among all the composites. The high-density black smoke is an inevitable problem for fPVC in course of burning. Thanks to the acclaimed smoke suppression ability of Fe_2O_3 accompanied with the porosity and high surface area [158], $\text{SnO}_2\text{@Fe}_2\text{O}_3$ -blended sample exhibited lower TSP value compared to the other samples, minimizing the smoke production of fPVC composite during combustion to the maximum extent. Conspicuously, the fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ remained most char residue as both of

the oxides played roles in condensed phase and contributed to char formation synergistically, reversely the fPVC/ Sb_2O_3 survived less after burning since it worked in gas phase, consistent with the results received from TGA test.

Figure 6-7: (a) HRR; (b) THR and (c) TSP plots of fPVC composites.

The Cl^- concentration fPVC/ Fe_2O_3 ($40 \pm 2 \mu\text{g/ml}$) was lower than that of fPVC/ SnO_2 ($52 \pm 3 \mu\text{g/ml}$), confirming the higher efficiency of Fe_2O_3 in decreasing the HCl release amount than SnO_2 . Meanwhile, the emerged porosity improved the adsorption of HCl thereby enhanced the effect. In

consequence, fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ presented eminent decrease in Cl^- concentration from 58 ± 6 to 33 ± 2 $\mu\text{g/ml}$, indicating that nearly half of the liberated HCl gas was removed and the relative hazard was relieved evidently.

Table 6-2: LOI and cone calorimeter results of fPVC composites.

Sample	LOI (%)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	TSP (m^2)	Char residue (wt.%)	Cl^- content ($\mu\text{g/ml}$)
fPVC	25.0	20 ± 1	218 ± 9	81 ± 4	23 ± 1.3	12 ± 1	58 ± 6
fPVC/ Sb_2O_3	34.5	25 ± 0	192 ± 3	84 ± 2	21 ± 1.2	10 ± 2	53 ± 4
fPVC/c- SnO_2	30.8	20 ± 1	204 ± 5	69 ± 3	20 ± 0.4	14 ± 2	55 ± 2
fPVC/ SnO_2	33.4	19 ± 1	169 ± 3	59 ± 2	19 ± 0.3	16 ± 1	52 ± 3
fPVC/ Fe_2O_3	32.5	28 ± 0	183 ± 4	63 ± 1	17 ± 1.1	15 ± 1	40 ± 2
fPVC/ $\text{SnO}_2\text{-Fe}_2\text{O}_3$	34.0	22 ± 1	164 ± 3	56 ± 3	18 ± 0.2	17 ± 1	48 ± 4
fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$	36.5	26 ± 1	148 ± 2	53 ± 2	16 ± 0.2	19 ± 2	33 ± 2

6.6 Flame retardant mechanism

According to literature review, metal oxides as flame retardants in PVC system play a role in the condensed phase by acting as “char reinforcers”. When a condensed phase action is the main mechanism for flame retardant additives, its efficiency strongly depends on the structure and composition of the char during combustion. Therefore, investigating the properties and the microstructure of the resultant char layers provides an insight into understanding how the flame retardant additives act in the condensed phase. As indicated in Figure 6-8a and c, the residual char of pure fPVC presented a loose char layer with a mass of holes dispersed on the surface. However, when $\text{SnO}_2\text{@Fe}_2\text{O}_3$ was added into fPVC, the porous and incompact surface changed into a more compact surface. The orange color on the surface of the char residue of fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ in the digital photo was attributed to iron species migrating to the exterior surface. More detailed information regarding the char surface was obtained in Figure 6-8d. The char layer was cohesive, compact and continuous which lowered the efficiency of heat and volatile transference because of the strong hindering effect, and provided better flame shielding for the underlying material during

combustion. Analogue to the previous work, the platelets also emerged on the surface of char residue in the presence of the inorganic hybrid. The platelets were proved to be metal chlorides in our research reported elsewhere [159]. The as-synthesized flame retardant enabled the chlorine to be fixed in the char residue.

Figure 6-8: Digital photographs and SEM images for char residue of fPVC (a,c) and fPVC/SnO₂@Fe₂O₃ (b,d).

Raman spectroscopy offers a powerful tool for characterizing carbonaceous materials. Figure 6-9 showed the Raman spectra of the residual char of fPVC and fPVC/SnO₂@Fe₂O₃ after cone calorimetry. As can be observed, the Raman spectra of the two samples exhibited a G band at around 1600 cm⁻¹ and a D band at 1357 cm⁻¹. The former was due to the first-order scattering of the E_{2g} phonon of sp² C atoms [160], while the latter arose from the activation in the first order scattering process of sp³ carbons [161]. In general, the ratio of D to G band intensity (I_D/I_G) is employed to estimate the graphitization degree of the char, where I_D and I_G are the integrated intensities of the D and G bands, respectively. A lower ratio of I_D/I_G implies the higher graphitization degree and thermal stability of char structure. The intensity ratio of the Raman spectra of fPVC/SnO₂@Fe₂O₃ was lower than that for fPVC, indicating the improvement of the graphitized carbons and higher degree of graphitization in the residual char. The lower degree of

graphitization in the char has relatively high reactivity to oxidation, leading to the char burnt out in the long time exposure to a high extent of heat flux. It can be inferred that the high content of graphitized carbons in the residual char is known to be compact and efficient in terms of thermal insulation, which can provide an effective in terms of thermal insulation, which can provide an effective shield that results in a decrease in heat and mass transfers between the flame and the material.

Figure 6-9: Raman spectra of the residual char of fPVC (a) and fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ (b).

The residual char of fPVC and fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ obtained from the cone calorimeter are further investigated by XPS analysis, and the results are summarized in Table 6-3. The characteristic C_{1s} bands at 284.6, 286.8 and 288.4 eV are ascribed to C-H and C-C in aliphatic and aromatic species, C-O (ether and/or hydroxyl group) and C=O, respectively. To study the thermal oxidative resistance, C_{ox}/C_a (C_{ox} : oxidized carbons and C_a : aliphatic and aromatic carbons) values are calculated. The C_{ox}/C_a values of the residual char of fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$ is 0.47, which is much lower than that of virgin fPVC (1.05). Therefore, the presence of this inorganic hybrid improved the thermal oxidative resistance of the protective char layer, which could effectively inhibit the oxygen permeation, heat and mass transmission, and the release of combustible gases from the matrix. It was worth noting that Cl was hardly detected in the char residue of pristine fPVC, since Cl was eliminated completely from fPVC as HCl gas form. On contrary, a certain amount of Cl remained in the char residue of fPVC/ $\text{SnO}_2\text{@Fe}_2\text{O}_3$, forming metal chloride sheets which were consistent with the SEM results. It implied that the Cl was fixed into the char residue with the help of $\text{SnO}_2\text{@Fe}_2\text{O}_3$ instead of escaping into the atmosphere, thereby reducing the amount of HCl gas evolution.

Table 6-3: XPS data of the residual char of fPVC and fPVC/ $\text{SnO}_2@ \text{Fe}_2\text{O}_3$.

System	Binding energy (eV)	Area (%)	
		Pristine fPVC char	fPVC/ $\text{SnO}_2@ \text{Fe}_2\text{O}_3$ char
C_{1s} (C-H, C-C)	284.6	41.2	56.5
C_{1s} (C-O)	286.8	37.3	24.8
C_{1s} (C=O)	288.4	6.1	2.7
O_{1s}	533.2	15.4	7.5
Cl_{2p}	198.7	0	5.4
Sn_{3d}	497.2	-	2.6
Fe_{2p}	710.8	-	0.5

In order to understand the flame retardant mechanism of $\text{SnO}_2@ \text{Fe}_2\text{O}_3$ in fPVC composite, the corresponding schematic representation was described as follows. The fabrication of 0D (Fe_2O_3 nanoparticles)/1D (SnO_2 nanorods) hybrid improved the dispersion of this filler in the composite and the formed hierarchical nanopores facilitated the strong interaction between the filler and the polymer matrix [162]. The introduction of cost-effective Fe_2O_3 into SnO_2 was conducive to the formation of nanopores in the structures, providing synergistic flame retardant effects and improving the efficacy of HCl removal. At the preliminary stage of combustion, the generated tin and iron chlorides performing as Lewis acids catalyzed the dehydrochlorination to construct more cross-linking networks in the system. Once the unsaturated carbon chain generated, iron compounds promoted the interacted crosslinks and resulted in char formation. Meanwhile, tin compounds were able to react with the char layer to improve its thermal oxidative resistance and stability. As shown in Scheme 6-3, the robust and continuous char layer separated the oxygen from penetrating into the underlying polymer and inhibited the escape of combustible volatiles as a barrier, meanwhile isolating the heat transfer, thus stopped the flame. Particularly, the high surface area benefited the interplay with the matrix while the porosity made the pathway longer for the fuels and heat transfer. Finally, the flame was efficiently retarded. By the way, due to the inhibition capability of the evolution of unsubstituted aromatics by Fe_2O_3 and more char residue was produced, the smoke was suppressed effectively. Moreover, the amount of corrosive HCl gas was also reduced since the chlorine element was preserved within the condensed phase in the form of metal chloride plates .

Scheme 6-2: Illustration for the flame-retardant mechanism for the effect of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ in fPVC.

6.7 Mechanical property of flexible PVC composites

The mechanical properties especially tensile property of fPVC composites are essential parameters to determine the influence caused by the incorporation of the additives to the polymer. In this research, tensile property of the composites treated with Sb_2O_3 , mixture of $\text{SnO}_2/\text{Fe}_2\text{O}_3$ and as-synthesized product were studied. The tensile stress-strain curves of fPVC composites were depicted in Figure 6-10 and the results were recorded in Table 6-4. The addition of Sb_2O_3 improved the tensile strength and Young modulus compared with those of pure fPVC, while the decreased elongation at break implied the ruin of the flexible property. The reason was possibly attributed to the poor dispersion of the commercial high-density Sb_2O_3 in the matrix. And the improvement in the tensile modulus and tensile strength may be presumably due to stress transfer between the matrix and the filler.

Figure 6-10: Tensile stress-strain curves of fPVC composites.

Versus the low surface area and nonporous mixture of $\text{SnO}_2\text{-Fe}_2\text{O}_3$, $\text{SnO}_2@\text{Fe}_2\text{O}_3$ treated composite increased tensile strength and elongation at break greatly to 18.6 ± 1 MPa and 91% respectively. The high specific surface area, well-developed porosity and submicron tiny size of the thus-obtained filler facilitated the uniform dispersion of the additive in the system and encouraged the interaction with polymer matrix, leading to improved tensile strength and elongation at break of the composite simultaneously [163, 164]. The chain of PVC was formed in the mesopore channels of $\text{SnO}_2@\text{Fe}_2\text{O}_3$ which restrained the agglomeration of the filler on one hand. The PVC phase in the nano-sized pores extended along the channels to the openings, which could enhance the interaction through the entanglement and inter-diffusion between the matrix and the particulate on the other hand, leading to a higher tensile strength. The large enhancement in the elongation may be due to the effect of the dispersed $\text{SnO}_2@\text{Fe}_2\text{O}_3$ particles which can act as chain extenders [165].

Table 6-4: Tensile properties of flexible PVC composites.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
fPVC	11.8 ± 1	75 ± 4	138 ± 4
fPVC/ Sb_2O_3	13.8 ± 1	48 ± 3	216 ± 4
fPVC/ $\text{SnO}_2\text{-Fe}_2\text{O}_3$	14.0 ± 1	78 ± 2	192 ± 3
fPVC/ $\text{SnO}_2@\text{Fe}_2\text{O}_3$	18.6 ± 1	91 ± 3	268 ± 4

6.8 Summary

In this work, a novel hierarchically nanoporous hybrid, named $\text{SnO}_2@Fe_2O_3$, was successfully synthesized in a large scale through a facile and fast one-pot approach for the first time. The delicate tailoring strategy has a variety of advantages: (i) The shell facilitated the generation of porosity for the hierarchical material so as to improve the specific surface area and pore volume in favor of flame retardancy efficiency; (ii) The conspicuous synergistic effect to promote char formation and stability existed between Fe_2O_3 and SnO_2 conducive to high flame retardancy; (iv) The corrosive HCl gas evolved during combustion was markedly reduced and the smoke hazard was vastly mitigated; (v) As a cheap and earth-abundant element, the introduction of iron would be beneficial to the cost control in consideration of the practical application as fire retardant. Such nanocasting strategy realized bountiful targets synchronously. In details, the LOI value of the fPVC nanocomposite treated with the as-synthesized product was increased from 25% to 36.5% and the PHRR value decreased by 32.1% compared with those of neat fPVC; the improved flame retardancy of fPVC/ $\text{SnO}_2@Fe_2O_3$ nanocomposite along with reduced HCl amount and suppressed smoke production, presented much better performance without the sacrifice of the thermal stability and mechanical property than the Sb_2O_3 loaded sample, indicating that this new nanohybrid has great potential to totally replace the toxic Sb_2O_3 and acts as a multifunctional reinforcer in fPVC composite. This research casting rallied around the high performance nanocomposite reinforced by using hierarchically nanoporous hybrid is anticipated to inspire more ideas on the design of suitable hierarchically nanostructures applied in homologous polymer system.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

“Bring forth what is true; Write it so it's clear. Defend it to your last breath.”

-Ludwig Boltzmann

7.1 Conclusions

This dissertation aims to develop a series of novel flame retardants to replace harmful Sb_2O_3 in flexible PVC composites and study the corresponding flame retardant mechanism.

1. As an exploratory work, zinc carbonate nanoparticles were synthesized by a facile one-step hydrothermal reaction. The flame retardant $\text{Sb}_2\text{O}_3/\text{ZnCO}_3$ with weight ratio 1:3 exhibited highest efficiency in fire tests: LOI value increased from 25 to 36.7%; passed V-0 rating without dripping; PHRR decreased from 218 ± 9 to $149 \pm 4 \text{ kW/m}^2$ and THR reduced from 81 ± 4 to $53 \pm 3 \text{ MJ/m}^2$. According to the results, an obvious synergistic flame retardant effect existed between Sb_2O_3 and ZnCO_3 . The flame retardant mechanism of ZC mainly existed in condensed phase. ZC reacted with HCl that released during the combustion of PVC to form zinc chloride. Zinc chloride acted as Lewis acid to catalyze the dehydrochlorination of PVC, promoting early crosslinking of polymer matrix and char formation. The compact char blocked the heat transfer and the escape of oxygen with combustible volatiles to the flame zone, protecting the underlying polymer thereby retarding the flame. It is worth to note that ZC exerted synergistic flame retardant effect with Sb_2O_3 , leading to higher flame retardant efficacy in flexible PVC. Moreover, ZnCO_3 nanoparticles were also beneficial to improve

tensile property of flexible PVC composites. The good mechanical property indicated the strong interaction between the filler and polymer matrix along with the achievement of uniform dispersion of the filler in the polymer matrix.

2. In order to realize the target about total substitution of Sb_2O_3 , other efficient metal elements with higher flame retardant efficiency such as tin were employed and hierarchical nanostructured materials were engineered. Thus, tin-doped hierarchical nanoporous silica was prepared via in situ sol-gel process. The flexible PVC composite containing 5 phr TOS reached similar LOI value (34.1%) as that of Sb_2O_3 -treated sample and achieved V-0 rating without dripping in UL-94 test. Tin chloride formed during the combustion of PVC acted as a much stronger Lewis acid catalyst than zinc chloride promoted the dehydrochlorination of PVC to form consolidated and continuous char. Meanwhile, tin chloride was proved to react with the char, enhancing the char stability. The behavior of TOS within the polymer matrix was beneficial to improve the flame retardancy of the composite. The abundant porosity conferred better interaction with polymer matrix to the filler. In addition, the mesoporous flame retardant was also beneficial for improving tensile properties of flexible PVC composites, especially increasing the tensile strength by 49%.
3. Although TOS holds huge potential to totally replace Sb_2O_3 on the basis of the results from LOI and UL-94 tests, the results from cone calorimeter tests were not so satisfactory. Therefore, tin oxide/iron oxide hybrid material with mesoporous structure was synthesized to improve the performance of corresponding composite in cone calorimeter tests without sacrificing other parameters. In details, the LOI value of the fPVC nanocomposite treated with the as-synthesized product was increased from 25 to 36.5% and the PHRR value decreased by 32.1% compared with those of neat fPVC; the improved flame retardancy of fPVC/ $\text{SnO}_2@\text{Fe}_2\text{O}_3$ nanocomposite along with reduced HCl amount and suppressed smoke production, presented much better performance without the sacrifice of the mechanical property than the Sb_2O_3 loaded sample. An in-depth discussion was carried out to study the flame retardant mechanism of $\text{SnO}_2@\text{Fe}_2\text{O}_3$: the hybrid mainly functioned in condensed phase acting as catalysts to promote dehydrochlorination process of fPVC to produce “flame poison” HCl earlier and facilitate the char formation. Both behaviors were beneficial to improve the

flame retardancy of fPVC composite. As a result, Sb_2O_3 -free flame retardant flexible PVC composite was acquired with the help of this novel hybrid.

7.2 Future work

Metal-based flame retardants, such as ZC, TOS and $\text{SnO}_2@\text{Fe}_2\text{O}_3$ synthesized in this thesis, possess one common problem that they promote the early thermal decomposition of flexible PVC composites due to their catalytic effects, resulting in the poor thermal stability which limits the practical application. How to improve the thermal stability of fPVC composites without sacrificing the flame retardancy in the presence metal-based flame retardants remains to be a challenging task. Constructing core/shell materials with metal-based flame retardants as core and inert substance which is stable at onset decomposition temperature of fPVC as protective shell might solve the problem. However, this proposal needs to be proved and the relevant research will be carried out in the future.

Although the flame retardants with hierarchical nanostructure prepared in the lab have great potential to totally replace Sb_2O_3 in flexible PVC composites, the cost of as-synthesized products cannot rival that of commercially available Sb_2O_3 . The fabrication of cost-effective alternatives for Sb_2O_3 remains to be an arduous challenge. Nowadays, due to the rapid evolution of industry, a huge amount of industrial waste is produced. It is waiting to be handled properly, and otherwise serious pollution to the environment will be caused. Actually, there are many valuable substances within the waste which can be recycled and reutilized as raw materials for preparation of flame retardants for flexible PVC. By means of this method, not only the environmental problem can be solved, but also the cost for preparation of flame retardants can be reduced. In the future, suitable industrial waste will be chosen and employed to prepare cost-effective flame retardants for flexible PVC.

Besides the cost and environmental concern, the flame retardant efficiency of Sb_2O_3 alternatives should be improved. Layered materials such as clay, layered double hydroxides and graphene have been widely used as flame retardants in various polymer systems because of the physical barrier effect and intrinsic flame retardant effect. It is a hot research spot currently, but the related report focused on layered two-dimensional flame retardants for flexible PVC are rare. On the other hand, nanoporous flame retardants possess high specific surface area, facilitating the strong interaction with the polymer matrix, thereby improving the flame retardant efficiency in the

composite. However, probably because of the difficulty in synthesizing the nanoporous materials, the related report can be hardly found. Combined with both nanostructures, nanoporous two-dimensional layered flame retardants (zinc- or tin-based) are anticipated to show high performance in flexible PVC composite. Therefore, the design and synthesis of such materials will be carried out and the fire performance of treated flexible PVC composite will be investigated in the future.

CHAPTER 8

LIST OF PUBLICATIONS AND CONFERENCES

“If I could be a piece of lab equipment, I would be a magnetic stirrer, simple but essential ...”

-Yusuke Yamauchi

a) Papers that a direct result of this doctoral thesis

The work presented in this thesis has been already published in the following papers:

1. **Y. T. Pan**, D. Y. Wang. *One-step hydrothermal synthesis of nano zinc carbonate and its use as a promising substitute for antimony trioxide in flame retardant flexible poly(vinyl chloride).* **RSC Advances**, vol. 5, pp. 27837-27843, 2015.
2. **Y. T. Pan**, C. Trempont, D. Y. Wang. *Hierarchical nanoporous silica doped with tin as novel multifunctional hybrid material to flexible poly (vinyl chloride) with greatly improved flame retardancy and mechanical properties.* **Chemical Engineering Journal**, vol. 295, pp. 451-460, 2016.
3. **Y. T. Pan**, X. Wang, Z. Li, D. Y. Wang. *A facile approach towards large-scale synthesis of hierarchically nanoporous SnO₂@Fe₂O₃ 0D/1D hybrid and its effect on flammability, thermal stability and mechanical property of flexible poly (vinyl chloride).* **Composites Part B: Engineering**, vol. 110, pp. 46-55, 2017.

b) Presentations at conferences

The work has also been presented in several interactional conferences:

1. **Y. T. Pan**, C. Trempont, D. Y. Wang. *Nanospheres silica doped with tin as high performance*

flame retardant in flexible poly(vinyl chloride). **7th Asia-Europe Symposium on Processing and Properties of Reinforced Polymers (AESPP7)**. 4th -6th February, 2015, Madrid, Spain.

2. **Y. T. Pan**, D. Y. Wang. *Synthesis and characterization of functional functionalized nanomaterials and its use as nano flame retardant in polymer materials*. **COST MP1105 SCIENTIFIC WORKSHOP**. 26th -27th March, 2015, Bucharest, Romania.
3. **Y. T. Pan**, C. Trempont, D. Y. Wang. *Hierarchical nanoporous silica doped with tin as novel multifunctional hybrid material to flexible poly(vinyl chloride)*. **COST MP1105 SCIENTIFIC WORKSHOP**. 27th-28th April, 2016, Poznan, Poland.

c) Other papers

In addition, the fabrication method of flame retardants with unique nanostructures mentioned in this thesis gave rise to other publications:

1. **Y. T. Pan**, D. Y. Wang. *Fabrication of low-fire-hazard flexible poly (vinyl chloride) via reutilization of heavy metal biosorbents*. **Journal of Hazardous Materials**, vol. 339, pp. 143-153, 2017.
2. **Y. T. Pan**, M. Castillo-Rodríguez, D. Y. Wang. *Mesoporous metal oxide/pyrophosphate hybrid originated from reutilization of water treatment resin as a novel fire hazard suppressant*. **Materials Chemistry and Physics**, vol. 203, pp. 49-57, 2017.
3. **Y. T. Pan**, L. Zhang, X. Zhao, D. Y. Wang. *Interfacial engineering of renewable metal organic framework derived honeycomb-like nanoporous aluminum hydroxide with tunable porosity*. **Chemical Science**, vol. 8, pp. 3399-3409, 2017.
4. **Y. T. Pan**, J. Wan, X. Zhao, C. Li, D. Y. Wang. *Interfacial growth of MOF-derived layered double hydroxide nanosheets on graphene slab towards fabrication of multifunctional epoxy nanocomposites*. **Chemical Engineering Journal**, vol. 330, pp. 1222-1231, 2017.
5. Y. Liu, **Y. T. Pan**, X. Wang, P. Acuña, P. Zhu, U. Wagenknecht, G. Heinrich, X. Q. Zhang, R. Wang, D. Y. Wang. *Effect of phosphorus-containing inorganic-organic hybrid coating on the flammability of cotton fabrics: Synthesis, characterization and flammability*. **Chemical Engineering Journal**, vol. 294, pp. 167-175, 2016.
6. C. Li, J. Wan, **Y. T. Pan**, P. C. Zhao, H. Fan, D. Y. Wang. *Sustainable, biobased silicone with layered double hydroxide hybrid and their application in natural-fiber reinforced phenolic composites with enhanced performance*. **ACS Sustainable Chemistry & Engineering**, vol. 4,

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7. J. Wan, J. Zhao, B. Gan, C. Li, J. Molina-Aldareguia, Y. Zhao, **Y. T. Pan**, D. Y. Wang. *Ultrastiff biobased epoxy resin with high T_g and low permittivity: From synthesis to properties.* **ACS Sustainable Chemistry & Engineering**, vol. 4, pp. 2869-2880, 2016.
 8. X. Wang, **Y. T. Pan**, J. Wan, D. Y. Wang. *An eco-friendly way to fire retardant flexible polyurethane foam: layer-by-layer assembly of fully bio-based substances.* **RSC Advances**, vol. 4, pp. 46164-46169, 2014.

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