Composites Part B 110 (2017) 46–55

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

# A facile approach towards large-scale synthesis of hierarchically nanoporous $SnO_2@Fe_2O_3$ 0D/1D hybrid and its effect on flammability, thermal stability and mechanical property of flexible poly(vinyl chloride)

Ye-Tang Pan, Xin Wang, Zhi Li, De-Yi Wang*

*IMDEA Materials Institute, C/Eric Kandel, 2, 28906 Getafe, Madrid, Spain*

A R T I C L E I N F O

*Article history:*
Received 12 July 2016
Received in revised form
27 October 2016
Accepted 5 November 2016
Available online 8 November 2016

*Keywords:*
Polymer-matrix composites (PMCs)
Hybrid
Mechanical properties
Thermal properties
Thermoplastic resin
Flammability

A B S T R A C T

Tin oxide ($SnO_2$) has versatile applications in a variety of areas. It also shows ability to improve the flame retardancy of flexible poly(vinyl chloride) (fPVC) composite and substitute the conventional toxic flame retardant-antimony trioxide ($Sb_2O_3$). However, low flame retardant efficiency and ruined thermal stability of the PVC composite in presence of $SnO_2$ remain to be the most prominent challenges. To address these issues, in this study, hematite ($\alpha$-$Fe_2O_3$) zero-dimensional nanoparticles elaborately encapsulated $SnO_2$ one-dimensional nanorod assemblies and such nanocasting facilitated the formation of hierarchical porosity in favor of high specific surface area and pore volume. The hierarchically nanoporous hybrid was synthesized via a facile and fast bottom-up method in a large scale and all-sided characterization was conducted on the investigation of its structure and fPVC compositions. The extra benefits imparted by $\alpha$-$Fe_2O_3$ in the hybrid improved the flame retardancy of fPVC composite strikingly with reduced amount of harmful HCl gas and suppressed smoke production, without deterioration of thermal stability and mechanical property, showing much better performance than those of $Sb_2O_3$-based fPVC composite. It indicated that this new eco-friendly nanohybrid had a great potential to totally replace antimonial additive. It is expected to pave the pathway about the construction of neoteric porous hybrid nanostructures and open a new avenue to develop high performance nanocomposites.



## 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 [1]. 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 [2]. 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 [3] and [4]. In order to develop functional flame-retardant materials with improved performance, the rational design and preparation of nanostructured materials has been continuously pursued.

Zero-dimensional (0D)/One-dimensional (1D) 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 [5]. However, paucity of aforesaid nanomaterials with intriguing

* Corresponding author.
*E-mail address:* deyi.wang@imdea.org (D.-Y. Wang).

http://dx.doi.org/10.1016/j.compositesb.2016.11.009
1359-8368/

structures as flame retardants were available, albeit myriad of other advanced hybrid nanomaterials such as carbon nanotube [6,7] and [8], graphene [2] and [9] and layered double hydroxide [10] and [11] were already regarded as high-efficiency flame retardant in polymer nanocomposites, namely the route toward hybrid 0D/1D 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 [12–14] and [15]. 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 [16]. 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 not only tin halide, 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 [17] and [18], but also $SnO_2$ was well known due to its large number of oxygen vacancies that are believed to promote the CO oxidation reaction with the intention of transforming the harmful fuel gas into inert $CO_2$ [19]. Based on our previous research, tin-doped silica exhibited excellent performance in flame retardant fPVC composite [20]. Nowadays, the typical flame retardant for fPVC is antimony trioxide ($Sb_2O_3$). However, despite the excellent performance in halogen contained polymer system the antimony compounds are proved to be harmful to human beings and environment on the basis of various reports that has been summarized in our previous research [21]. Therefore, a new kind of environmentally friendly flame retardant should be developed in order to totally substitute antimony compounds while $SnO_2$ presents the great potential. 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. On the other hand, addition of $SnO_2$ into fPVC brings forward the degradation of the composite accordingly deteriorates its thermal stability. 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, α-$Fe_2O_3$ was subtly adopted to construct a hybrid nanostructure with 1D $SnO_2$ nanorod assemblies as core encapsulated by 0D α-$Fe_2O_3$ nanoparticles since α-$Fe_2O_3$ already showed outstanding synergistic effect with other flame retardants [22,23] and [24]. Moreover, α-$Fe_2O_3$ is able to retard dehydrochlorination procedure thereby delay the decomposition of fPVC acting as a thermal stabilizer [25] and [26]. And α-$Fe_2O_3$ was extremely well-known for its excellent smoke suppression effect in PVC system, while the smoke hazard of PVC during combustion was valued most [27] and [28]. α-$Fe_2O_3$ was also reported to be good at HCl fixation, so it might reduce the damaging and corrosive HCl gas evolved from fPVC during combustion [29] and [30]. Last but not least, as a cost-effective and earth-abundant element, the introduction of iron benefits the control of expense in consideration of practical application of the devised additive [31]. 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 $SnO_2$@$Fe_2O_3$. It can be anticipated that with this exquisite structure, the thermal stability and flame retardant of fPVC/$SnO_2$@$Fe_2O_3$ nanocomposite will be enhanced significantly, resulting in a totally $Sb_2O_3$-free flame retardant fPVC material.

Herein, nanoporous $SnO_2$@$Fe_2O_3$ 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 $SnO_2$@$Fe_2O_3$ treated fPVC nanocomposite were conducted to testify the high performance of the hybrid material. Hopefully, this eventful work is committed to put forward the advancement of high geared nanocomposites containing nano-flame retardant with unique nanostructure.

## 2. Experimental

### *2.1. Materials*

Commercial tin oxide (−325 mesh, 99.9% trace metals basis, denoted as c-$SnO_2$), trioctyl trimellitate (TOTM, 99%), tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$, reagent grade, 98%), citric acid (ACS reagent, ≥99.5%), sodium dodecylbenzenesulfonate (SDBS), sodium hydroxide (reagent grade, ≥98%, pellets), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ACS reagent, 97%), ammonium hydroxide solution (ACS reagent, 28.0–30.0% $NH_3$ basis) and absolute ethanol were purchased from Sigma Aldrich. PVC resin (K = 70), Ca–Zn based heat stabilizer, soy oil, wax (polyethylene) and antimony trioxide ($Sb_2O_3$) were provided by Quimidroga, s.a. All the reagents were used as-received without further purification.

### *2.2. Preparation of $SnO_2$@$Fe_2O_3$ multidimensional hybrid*

The pathway employed the “bottom-up” approach leading to the $SnO_2$@$Fe_2O_3$ hybrid structure was shown as follows. Briefly, 0.05 mol $SnCl_2 \cdot 2H_2O$ 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, $NH_3 \cdot H_2O$ solution (20 mL, 5 M) 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 $FeCl_3 \cdot 6H_2O$ 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-$Fe_2O_3$ synthesized by precipitation of iron (III) chloride hexahydrate with sodium hydroxide and $SnO_2$ without α-$Fe_2O_3$ doping were also prepared.