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Hierarchical nanoporous silica doped with tin as novel multifunctional hybrid material to flexible poly(vinyl chloride) with greatly improved flame retardancy and mechanical properties

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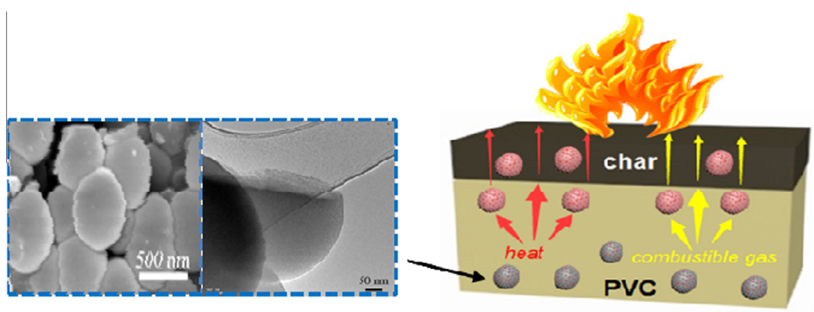
HIGHLIGHTS

- Novel mesoporous hybrid material (TOS) was synthesized via facile in-situ method.
- TOS was incorporated into flexible PVC composite to enhance its properties.
- Flammability of TOS based flexible PVC composite was decreased significantly.
- Mechanical properties of TOS based flexible PVC composite were improved greatly.
- This hybrid material has potential to totally replace antimony compounds in PVC.

GRAPHICAL ABSTRACT



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ABSTRACT

Antimony trioxide (Sb_2O_3) is a traditional widely used flame retardant in flexible poly(vinyl chloride) (fPVC). However, more and more serious drawbacks of this flame retardant, such as the underlying toxicity and decreasing reserve in the earth's crust, obligate the development of its substitutes. To address this issue, we synthesized novel mesoporous flame retardant (TOS) by grafting of tin on hierarchical nanoporous silica (HPS) via a facile in-situ synthesis method. Fourier transform infrared spectrum (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), field emission gun scanning electron microscope (FEGSEM), transmission electron microscopy (TEM) and N_2 adsorption–desorption measurement were utilized to investigate the composition and structure of the mesoporous material. TOS, HPS, commercial tin oxide (SnO_2) and Sb_2O_3 were added into fPVC composites respectively to carry out comparative study. Results showed limiting oxygen index (LOI) of fPVC composite was significantly increased in presence of TOS, accompanied with UL-94 V-0 rating without dripping. Meanwhile, TOS also enhanced the tensile properties of fPVC composite significantly. All the data illuminated that TOS greatly improved flame retardancy and mechanical property of fPVC as a novel multifunctional hybrid materials.

1. Introduction

Poly(vinyl chloride) is an extensively exploited thermoplastic material because of its valuable properties and good price/performance balance that allows penetration into various

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fields such as building construction, food packaging and electronic equipment [1,2]. Among these applications, flexible products occupy a high proportion due to their unique attributes. By means of the high adding amount of plasticizers, such as dioctyl phthalate (DOP), diisodecylphthalate (DIDP) and trioctyl trimellitate (TOTM), the flexible PVC products are produced. However, these flammable plasticizers mentioned above give rise to a challenging problem for flexible PVC, namely how to increase the flame resistance, although pristine PVC is inherently fire retardant and its performances are acceptable for certain applications because of its high chlorine content. This problem results in a crucial method which has been developed over the years among researchers: flame retardants were introduced into flexible PVC (fPVC).

A large number of chemical compounds have been reported to be flame retardants for PVC. These compounds include alloys [3], inorganic compounds [4], coordination compounds [5] and organic compounds [6]. One of the most noted flame retardants for flexible PVC in industry is antimony compounds. Antimony trioxide (Sb_2O_3) is a representative and has been used for halogen-containing polymers for many years. Nevertheless, Sb_2O_3 releases toxic or irritating vapors during combustion [7,8]. Additionally, antimony compounds are harmful to our health and cause several kinds of heavy diseases to human beings [9,10]. On the other hand, the content of antimony in the earth's crust is limited. Until recently, the antimony price was still surging. It has risen by more than 400% over the past 10 years [11]. In view of the underlying toxicity and decreasing reserve of antimony, substitutes have to be developed. However, according to recent publications in the state of the art the alternatives may require a high loading amount [12] or deteriorate the mechanical properties of the polymers [13]. In other word, the predominant position of Sb_2O_3 seems to be unshakable. Although lately a number of research related to halogen-free flame retardant with low amount of addition were emerged [14–16], more efforts have to be exerted to such field. Therefore, new flame retardants with novel structure should be developed and replace harmful Sb_2O_3 step by step.

Silicon derivatives as flame retardants are attractive because of their excellent thermal-resistance, non-toxicity and non-generation of toxic gases during combustion [17]. 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 [18]. Qian et al. doped aluminum on mesoporous silica and used it to flame retard polylactide effectively [19]. And Zhang et al. also ascertained mesoporous materials had benefits in enhancing thermal stability of polymethyl methacrylate matrixes [20]. 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 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 SnO_2 showed synergistic effect to Sb_2O_3 enhancing the LOI greatly in fPVC and concluded that SnO_2 had the probability to replace Sb_2O_3, 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 article, hierarchical porous silica (HPS) was synthesized by template method and tin was introduced into HPS system directly by in-situ synthesis manner. 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 antimony trioxide (Sb_2O_3), tin oxide (SnO_2), HPS, or TOS were all investigated. Meanwhile, the tensile properties of the composites were also taken into consider.

2. Experimental

2.1. Materials

Ethanol (EtOH), hexadecyltrimethylammonium bromide (CTAB), ammonium hydroxide solution, tetraethoxysilane (TEOS), tin (IV) oxide (nanopowder, <100 nm particle size), tin (IV) chloride and trioctyl trimellitate (TOTM) were purchased from Sigma Aldrich. Commercial PVC resin ($K = 70$), Ca–Zn based heat stabilizer, soy oil, wax (polyethylene) and antimony trioxide (primary particle size of 10–100 nm) were provided by Quimidroga, s.a. Highly pure water is prepared in the laboratory by double distillation of deionized water.

2.2. Preparation of hierarchical porous silica

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:H_2O: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.

2.3. Preparation of tin doped hierarchical porous silica

The grafting of tin on hierarchical porous silica utilized in-situ synthesis manner. The initiate 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 1 presents the schematic program of the proposed synthesis procedure of TOS.

2.4. Preparation of flexible PVC composites

The designated formulation of the PVC compound was shown as a reference and summarized in Table 1. Phr means parts per hundred parts of base resin and the flame retardants employed in this research involved Sb_2O_3, SnO_2, HPS and TOS. According to our previous report [22], neat PVC resin and additives were dry mixed sufficiently 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 with the intention of shaping into the sample sheets with suitable dimensions applied on LOI and tensile tests. And UL-94 sample sheets were compression molded by hot-plate press (LabPro 400, Fontijne Presses) at 180 °C with 10 N and then cut into suitable size.