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Preparation of zinc hydroxystannate-titanate nanotube flame retardant and evaluation its smoke suppression efficiency for flexible polyvinyl chloride matrix

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ABSTRACT

Smoke hazard is the main murderer to human life during a fire hazard of polymer-based materials. Thus zinc hydroxystannate-titanate nanotube (ZHS-TNT) flame retardant with sugar-coated haw-like microstructure was prepared by a facile in-situ solution method in order to suppress the smoke release of flexible polyvinyl chloride (PVC). Findings indicate that ZHS-TNT contributes to enhancing the flame-retardancy and smoke suppress properties of PVC and is superior to mechanically mixed ZHS and TNT. The limiting oxygen index is enhanced from 25.8 of pure PVC to 29.6 of PVC composite filled with 2.5 wt% ZHS-TNT, and the total smoke release and average specific extinction area are decreased by 40% and 34%, respectively. This is ascribed to the synergistic flame-retardant effect of ZHS and TNT.

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1. Introduction

Flexible polyvinyl chloride (PVC) is an important thermoplastic polymer in industry, but it is easily flammable, due to the high content of plasticizer. Usually, the smoke hazard mainly accounts for death in a fire accident; and Sb_2O_3, used to be a good flame retardant for flexible PVC, is toxic. Therefore, it is urgent to develop novel flame retardants with less toxicity and to suppress the smoke efficiently.

Zinc hydroxystannate (ZHS), an environmentally friendly smoke suppressant with less toxicity, is a potential candidate of novel flame retardants, because the chars formed by ZHS, one of the most important positive factors for fire prevention, can act as physical barriers to enhance the flame retardancy and smoke suppression [1]. However, ZHS usually requires a high dosage to achieve good smoke suppression, which is cost-ineffective in terms of the scarce resource of tin. This makes it imperative to combine ZHS with other components in order to enhance its flame retardancy and reduce the dosage of ZHS [2]. Titanate nanotube (TNT) is another inorganic flame retardant with several advantages, such as good ability to form network barriers, good catalytic activity for the formation of char, and good abilities to absorb flammable gases and trap radicals [3–5].

We suppose that ZHS could be well combined with TNT to achieve greatly improved smoke-suppression capability in association with the synergistic effects between ZHS and TNT. In this study, therefore, we intend to prepare a binary flame retardant consisting of sugar-coated haw-like ZHS-TNT in order to improve the flame retardancy and smoke-suppression capability of flexible PVC.

2. Experimental section

2.1. Preparation of ZHS-TNT

Firstly, 1.5 g of sodium titanate (NaTA) was added into 150 mL of H_2O under mild stirring. The pH of the solution was adjusted to 1.6 with hydrochloric acid, followed by stirring for additional 3 h. The as-generated precipitate was collected by filtration and dispersed in 20 mL of H_2O to afford a suspension. In the meantime, stannate tetrahydrate and zinc nitrate heptahydrate with a molar ratio of 1:1 were added into 150 mL of distilled water under 30 min of stirring at 0–5 °C. The resultant solution was then mixed with the as-obtained suspension and allowed to react at 0–5 °C for 3 h. At the end, the precipitate was collected by filtration and washed with distilled water, followed by drying at 60 °C in air for 18 h to afford ZHS-TNT.

2.2. Preparation of ZHS-TNT/PVC nanocomposites

ZHS-TNT/PVC nanocomposites with different contents of ZHS-TNT were prepared by the method reported in our previous research [6]. Pristine PVC and PVC composite filled with 2.5 wt%

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of the mixture of ZHS and TNT (ZHS + TNT) were also prepared under the same condition and used for comparative studies.

3. Results and discussion

3.1. Characterization of ZHS-TNT

Fig. 1 shows the XRD patterns, XPS spectra, and Raman spectra of TNT and ZHS-TNS as well as the TEM image of ZHS-TNT. The diffraction peaks of ZHS-TNT can be well indexed to those of TNT and ZHS. This indicates that the tubular structure of TNT is reserved in as-prepared ZHS-TNT. The XPS spectrum of ZHS-TNT proves the existence of Zn2p, Sn3p, Sn3d and Sn4d, which well corresponds to the composite structure and chemical composition of ZHS-TNT. Besides, the Raman absorbance bands of ZHS-TNT at 146 cm^{-1} is assigned to O-Ti-O of TNT, and they exhibit a certain degree of red shift as compared with that of TNT, which further confirms that ZHS is successfully combined with TNT to generate ZHS-TNT [7,8]. The TEM image of ZHS-TNT is shown in Fig. 1d, where the TNT nanotubes seem to penetrate through the porous ZHS nanocubes, thereby yielding ZHS-TNT with a sugar-coated haw-like structure.

The Brunauer-Emmet-Teller (BET) specific surface areas of ZHS, TNT and ZHS-TNT are 29.3, 295.4 and 137.8 m^2/g, and their total pore volumes are 0.70, 0.15 and 0.43 cm^3/g, respectively. As-prepared ZHS-TNT has a much higher specific surface area than ZHS. Besides, ZHS-TNT, mainly with a pore size of 2–4 nm, exhibits a wider size distribution than TNT and ZHS, which is attributed to the encapsulation of TNT by porous ZHS. The high specific surface area of ZHS-TNT could be helpful to absorbing flammable volatiles generated by the pyrolysis of PVC and delaying the mass transmission as well [9].

Fig. 1g schematically shows the possible controlled synthesis of ZHS-TNT by the seed-induced growth of ZHS at the defects of TNT. Briefly, in the aqueous solution of NaTA with pH = 1.6, TNT will dehydrate to generate a defective structure in the nanotubes. Thanks to the ion-exchange capacity and high surface area of the scroll-type nanotube structure with (100) facets, TNT is a very powerful adsorbent for metal ion, oxyanion and organic species. Therefore, the seeds of ZHS can easily dwell on the surface of TNT or enter into the defective structure of TNT, thereby growing into nanocubes and covering the surface of TNT.

3.2. Flame retardancy of PVC-matrix nanocomposites

The flammability of composites can be reflected by limited oxygen index (LOI), peak heat release rate (pHRR), total heat release (THR), total smoke release (TSR), and specific extinction area

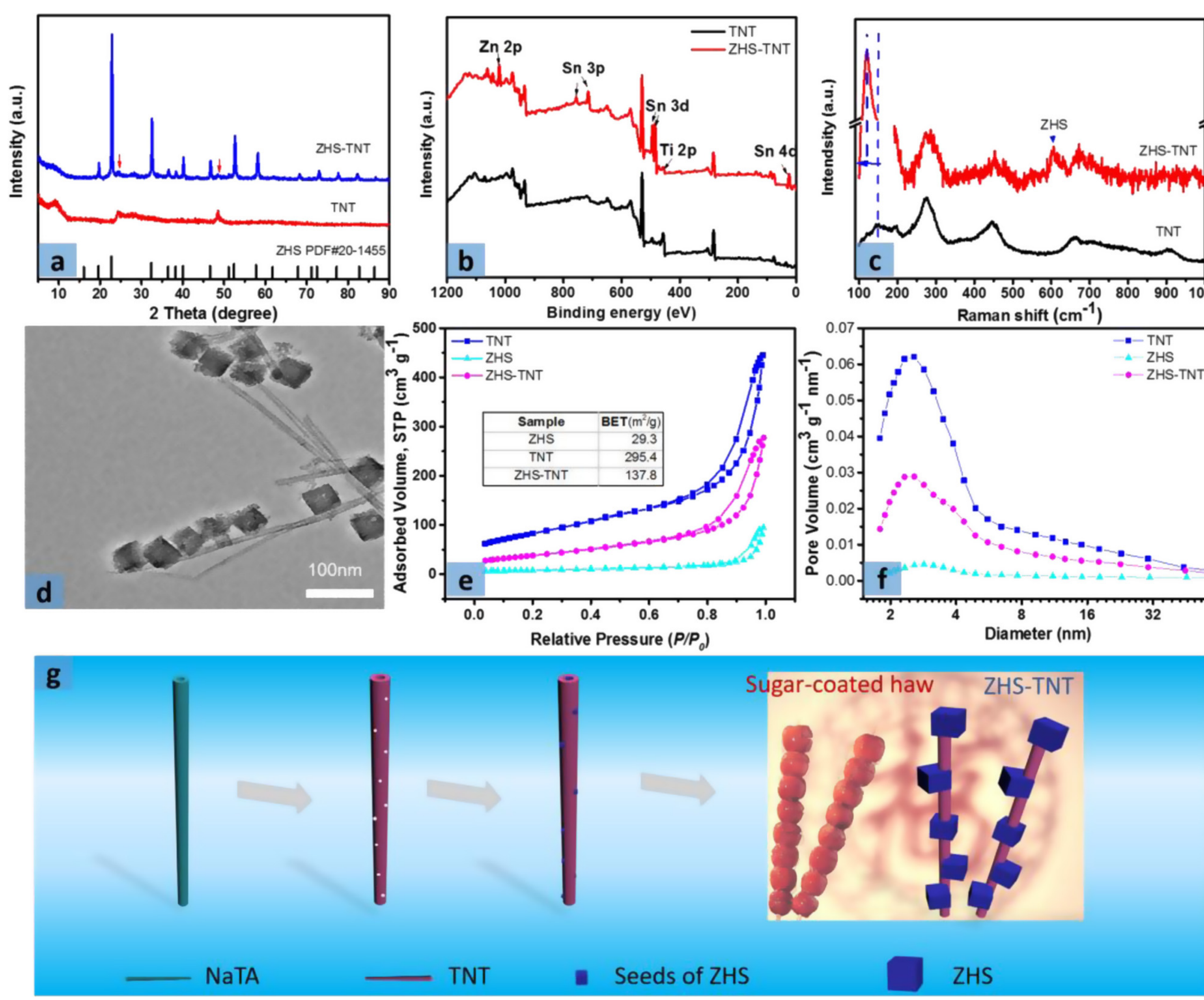

Fig. 1. XRD patterns (a), XPS spectra (b), Raman spectra (c), TEM image (d), nitrogen sorption isotherms (e), pore size distribution vs. BJH adsorption pore volume (f), and schematic diagram of preparation (g) of ZHS-TNT.

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