Journal of Hazardous Materials 314 (2016) 260–269

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

The influence of zinc hydroxystannate on reducing toxic gases (CO, NO_x and HCN) generation and fire hazards of thermoplastic polyurethane composites

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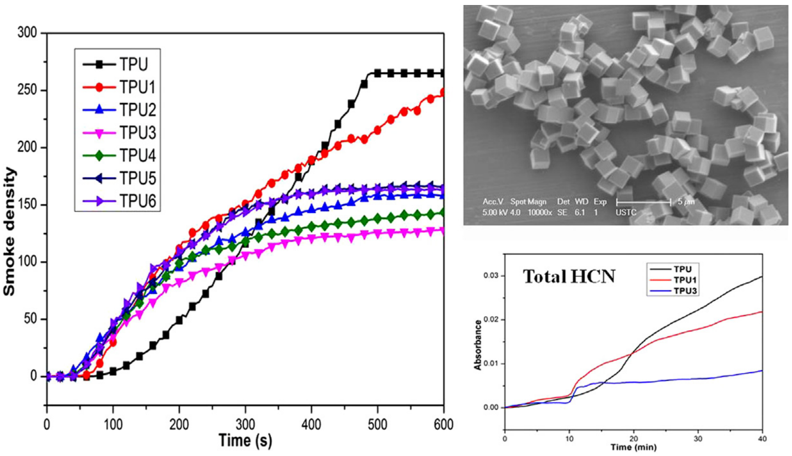
HIGHLIGHTS

- The ZnHS could significantly enhance the mechanical properties of the TPU composites.
- ZnHS has excellent smoke suppression and reduction the HRR for TPU composites.
- ZnHS shows significant decrease in CO, HCN, NO_x for TPU composites.
- These improvements are due to charring and catalytic degradation the toxic gases.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form 10 April 2016
Accepted 12 April 2016
Available online 13 April 2016

Keywords:
Toxic gases
Smoke suppression
Fire hazards
Zinc hydroxystannate
Thermoplastic polyurethane

ABSTRACT

A uniform zinc hydroxystannate (ZnHS) microcube was synthesized to reduce toxicity and fire hazards of thermoplastic polyurethane (TPU) composites using ammonium polyphosphate as a flame retardant agent. The structure, morphology and thermal properties of ZnHS were characterized by X-ray diffraction, transmission electron microscopy and thermogravimetric analysis, respectively. Smoke suppression properties and synergistic flame retardant effect of ZnHS on flame retardant TPU composites were intensively investigated by smoke density test, cone calorimeter test, and thermalgravimetric analysis. Thermogravimetric analysis/infrared spectrometry and tube furnace were employed to evaluate the toxic gases (CO, NO_x and HCN) of TPU composites. The incorporation of ZnHS into TPU matrix effectively improved the fire safety and restrained the smoke density, which is attributed to that the char residue catalyzed by ZnHS enhanced barrier effect that reduced peak heat release rate, total heat release, smoke particles and organic volatiles during combustion. Furthermore, the ZnHS synergist demonstrated high efficiency in catalytic degradation of the toxic gases, which

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http://dx.doi.org/10.1016/j.jhazmat.2016.04.029

obviously decreased total volatiled product and toxic volatiles evolved, such as the CO, HCN and NO_x, indicating suppressed toxicity of the TPU composites.

1. Introduction

Thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics and widely used in wires and cables, conveyor belts, and protective coatings, because of excellent abrasion resistance, good processability, high chemical stability and mechanical performance [1]. However, TPU is very combustible with high heat release rates after ignition. The thermal decomposition or combustion of polymer produces large amounts of toxic gas, such as CO, HCN, NO_x and so on [2–4]. Moreover, visible smoke presents challenges to people trying to escape from fires [5,6]. Heat release and inhaling toxic fire gases will lead to heavy casualties and property losses in case of fire accidents. Therefore, it is of great importance to reduce the fire hazard of TPU.

Heat is the direct hazard in fire accidents, which can cause serious molten dripping and accelerate the spread of fire. In order to decrease the peak heat release rate and the total heat release, flame retardants have been widely used in TPU [7,8]. Early flame retardants including halogenated compounds are currently being phased out because of environmental concerns. For this reason, phosphorus-[9,10], nitrogen-[11], boron-[12], and silicon-[13] based flame retardant and some nanofillers (such as layer double hydroxide [14], montmorillonite [15] and graphite [16]), have been developed to enhance the fire safety performance of TPU. The phosphorus-containing compounds render the high flame-retardant efficiency in TPU matrix compared with other flame retardants. Ammonium polyphosphate (APP) have been widely applied in TPU composites due to the high phosphorus content (31 wt%) and the formation of high quality carbon layer [17–20].

Along with the heat hazard, there is also toxic smoke in fire accidents. Toxic smoke is composed of smoke particles, organic volatiles, carbon dioxide (CO_2), carbon monoxide (CO) and hydrogen cyanide (HCN) [21–23]. Considering that majority of deaths in fires result from inhalation of toxic gases, CO and HCN are the two principal toxicants during the combustion of polymer matrix. Therefore, an enormous amount of research efforts have made into the field of fire smoke toxicity suppression in the past few years. Some literatures indicated that metal oxides and metal slats were used as synergists in TPU composites, which can significantly decrease the smoke density and heat release[24–28]. An interesting work reported the incorporated novel spinel copper cobaltate ($CuCo_2O_4$)/graphitic carbon nitride (g-C_3N_4) nanohybrids in TPU composite for enhanced flame retardancy and reduced pyrolysis toxic gas evolution of TPU. The results demonstrated that the C-$CuCo_2O_4$ could significantly decrease the pHRR, THR, CO and total gaseous products due to the high efficiency in charring and catalytic oxidation of CO [29]. The multi-metal element compounds have attracted considerable attention because of excellent properties in catalytic charring and degradation the toxic gases [30]. Meytal hydroxystannate ($MSn(OH)_6$, where M = Zn, Mg, Ca, Co, and Cu, etc.), a typical multi-metal element compound, received extensive attention for its high efficient catalysis in many fields such as photocatalyst [31–33], smoke suppression agent [34–37] and gas sensor [38]. These stannates or tin oxides could act as good catalysts for catalysis of esterification reaction and conversion of the toxic gas [39]. To the best of our knowledge, scarcely any work has been reported the synergistic effects between zinc hydroxystannate (ZnHS) and APP on achievement toxic gases (especially the CO, NO_x and HCN) suppression and flame retardant properties in TPU composites.

This work mainly aimed at the synergistic toxic gases suppression properties and reduced fire hazards between ZnHS and APP in flame retardant TPU. The ZnHS was synthesized by a typical co-precipitation method and was characterized by X-ray powder diffraction, transmission electron microscopy and thermogravimetric analysis. The toxic gases (especially the CO, NO_x and HCN) suppression was evaluated by thermogravimetric analysis/infrared spectrometry and tubular furnace. The thermal, smoke release and flame retardancy properties were investigated by thermalgravimetric analysis, smoke density test, and cone calorimeter test, respectively. Furthermore, the residual chars of TPU composites left after cone calorimeter test were dissected by Raman spectrum analysis.

2. Experimental

2.1. Materials

Thermoplastic polyester polyurethane (TPU, 85E85) was obtained from Baoding Bangtai Chemical Industry Co., Ltd. (Baoding, China). Ammonium polyphosphate (APP) (powder) was purchased from Shandong Weidong Chemical Co. LTD (Shandong, China). Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, analytical grade), tin tetrachloride ($SnCl_4{\cdot}5H_2O$) (Spectrum Pure), Sodium hydroxide (NaOH) and Ethanol (C_2H_5OH, reagent grade) were provided by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All materials were used without further purification.

2.2. Synthesis of ZnHS

ZnHS was synthesized by a typical co-precipitation method. Firstly, 0.02 mol of $Zn(NO_3)_2{\cdot}6H_2O$ and 0.02 mol of $SnCl_4{\cdot}5H_2O$ were dissolved in 300 mL water in a 500 mL three-necked flask with vigorous stirring. After that, 70 mL of 2 M NaOH aqueous solution was added dropwise to the solution with mechanical stirring at a speed of 500 rpm. After agitation for 15 min, the mixture was heated to 80 °C and kept for 4 h, and then naturally cooled to room temperature. The white solid products were collected by rinse-centrifugation cycles with three water cycles followed by one ethanol cycle. Finally, the product was dried in vacuum at 80 °C for 24 h. And the final yield of ZnHS is 94%.

2.3. Preparation of flame retardant TPU composites

TPU, APP and ZnHS were dried in vacuum drier at 80 °C for 10 h before use. Then, TPU, APP and ZnHS were melt-blended in a Brabender-like apparatus at a temperature of 175 °C for 10 min using a Rheomixer XSS-300. After mixing, the samples were hot pressed at 180 °C under 10 MPa for 5 min into sheets of suitable thickness for further analysis. The formulations are given in Table 1.

2.4. Characterization

X-ray diffraction (XRD) measurements of ZnHS microcube was performed with a Japan Rigaku D = Max-Ra rotating anode X-ray diffractometer equipped with a Cu-Ka tube and Ni filter (λ = 0.1542 nm). The SEM image of the raw materials was taken using a DXS-10 scanning electron microscope produced by the